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PHOTO-EXCITED STATES IN GERMANIUM AT
LIQUID-HELIUM TEMPERATURES*

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Ph.D. Dissertation

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EAB

I dedicate this thesis to all of the
well thought out, ingeniously clever models,
which in the course of this work
met reality and died.

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ABSTRACT

A wide variety of experimental work dealing with the basic properties of photoexcited states in Ge at liquid helium temperatures is presented. The primary emphasis is on the electron-hole liquid (EHL) and the free exciton (FE). The EHL is composed of two interpenetrating Fermi liquids, one of electrons and one of holes, each with its own Fermi level. The FE dealt with here is a mobile, loosely bound state of an electron and a hole.

We report the first absolute measurement of the density dependence of the enhancement factor $g_{eh}(0)$ for the EHL in Ge. This factor $g_{eh}(0)$ is a measure of the electron-hole spatial correlation function, and provides a valuable and sensitive test for the predictions of various many-body-theory approximations. An EHL droplet - FE gas system confined to a strain induced potential well was used. The measurement approach relied on only a few simple and verifiable assumptions. The results presented here agree quantitatively with the predictions of two

different many-body-theory approximations. A byproduct of this work was the measurement as a function of stress of: the electron and hole Fermi levels E_F^e and E_F^h , the EHL density n_L , the condensation energy ϕ of a FE relative to the EHL, and the binding energy of a FE (E_x) relative to free carriers (FC). The various measurements made are consistent with the EHL decay having a radiative component and a three body Auger component.

The decay of a FE-FC system confined to a strain induced potential well is studied. At low temperatures FE decay dominates FC decay. At high temperatures a thermally activated FC decay dominates FE decay. It is proposed that surface recombination of FC could explain the present results. Exciton lifetimes of up to 1.55 ns are reported.

The first direct measurement of the FE diffusivity D_x is reported. The evolution in time of spatial profiles of FE luminescence were measured. From these FE density profiles, $D_x(4.2K) \approx 300 \text{ cm}^2 \text{ s}^{-1}$, the surface recombination velocity $S \approx 3000 \text{ cm s}^{-1}$, and the FE lifetime $\tau_x = 27 \text{ ns}$ with surface effects excluded were determined. Evidence is presented which suggests that FE recombination at a crystal surface is not sensitive to the detailed character of that surface. It is concluded that previous measurements could have been dramatically effected by the surface recombination of FE, especially those measurements made using crystals whose dimensions are on the order of the FE diffusion length. A FE-phonon scattering time $\tau_p \approx 2 \times 10^{-10} \text{ s}$ is reported.

We have studied the hysteresis and decay of the EHL no-phonon luminescence in order to explore several hypotheses concerning nucleation sites for EHL droplets (EHD). We find evidence in one ultra-pure crystal consistent with EHD being bound on spatial concentration fluctuations

of electrically inactive impurities ($N \sim 10^{14} \text{ cm}^{-3}$). In another crystal we find evidence that the EHL are bound on shallow electrical impurities. In other crystals where no-phonon EHL luminescence is not seen, either the EHL are bound on other defects or the defects are altered such that they no longer produce EHL no-phonon luminescence.

Corrin Jeffries
Dec. 17, 1984

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CHAPTER I. INTRODUCTION

This thesis reports the results of my experimental researches into the properties of photoexcitations existing in stressed and unstressed Ge crystals at liquid helium temperatures. The specific excitations of interest are the free exciton (FE) and the electron-hole liquid (EHL).¹⁻⁴ This chapter begins by discussing the crystalline environment which determines the properties of these photoexcitations: the pertinent portions of the band structure of stressed and unstressed Ge. Introduced next is the succession of excitations which can and do exist as the photoexcitation of a Ge crystal is increased from zero. The FE and EHL excitations recombine radiatively, each with its characteristic luminescence. This luminescence and the experimental set up used for its measurement are discussed.

The next section is a terse discussion of the energy band structure of Ge. It should be skipped over and referred to as the need arises.

Ge Band Structure

Germanium is an indirect gap semiconductor. The energy band structure for Ge, which crystallizes in a diamond lattice, has conduction band minima along the $\langle 111 \rangle$ crystal directions at the Brillouin zone boundary and a valence band maximum at the zone center as is schematically illustrated in Fig. I.1. The conduction band minima are located at the Brillouin zone boundary along the $\langle 111 \rangle$ crystal axes. There are four distinct degenerate conduction band minima, each associated with a $\langle 111 \rangle$ axis (Fig. I.2 shows constant energy ellipsoids around the conduction band minima). The valence band maximum at the zone center

Fig. I.1 Ge band structure showing a conduction band minimum and the valence band maximum. Several bound photoexcited states are represented schematically with their binding energies and luminescence photon energies for LA phonon assisted recombination (from Ref. II.19).

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Fig. I.2 Constant energy ellipsoids around the conduction band minima within the first Brillouin zone. The dashed lines are $\langle 111 \rangle$ crystal directions (from Ref. I.21).

is common to both a light and a heavy hole band. While the conduction band can be accurately approximated as parabolic near its minima, the valence bands near the maximum cannot.

The electron dispersion is adequately described in terms of transverse and longitudinal effective masses m_{et} and m_{el} . The dispersion relations for the light and heavy hole bands are^{5,6}

$$E_{\pm} = Ak^2 \pm [B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{1/2}. \quad (I.1)$$

These various coefficients are displayed in Table I.1:

Table I.1

Parameter	Value	Reference
m_{et}/m_0	0.08152	a
m_{el}/m_0	1.588	a
A	13.38	b
B	8.48	b
C	0.088	b
ϵ	15.36	c
$-E_{spl}^e(\vec{\sigma} \parallel \langle 111 \rangle)$	1.05	d
$-E_{spl}^h(\vec{\sigma} \parallel \langle 111 \rangle)$	0.362	d

^aB.W.Levinger and D.R.Frankl, J. Phys. Chem. Solids 21, 281 (1961).

^bIn units of $\hbar^2/2m_0$, the values are from J.C.Hensel and K.Suzuki, Phys. Rev. B9, 4219 (1974); J.C.Hensel and G.Feher, Phys. Rev. 129, 1041 (1963).

^cR.A.Faulkner, Phys. Rev. 184, 713 (1969).

^dIn units of meV mm²/kgf these values are from S.M.Kelso, Phys. Rev. B25, 7631 (1982) and references therein.

If stress is applied along a $\langle 111 \rangle$ crystal direction, the decrease in crystal symmetry is reflected in the reduced symmetry of the band structure. The conduction band minimum along the stress axis is lowered relative to the other three (still degenerate) minima. The hole band degeneracy at the zone center is removed. As the stress is increased the indirect gap along the stress axis decreases (see Fig. 1.3), the conduction band splitting increases, and the valence band splitting increases. The conduction (valence) band splitting is given by $E_{spl}^e \sigma_{111} (E_{spl}^h \sigma_{111})$ where the $\langle 111 \rangle$ stress σ_{111} is given in kgf/mm^2 ($1 \text{ kgf} = 9.80665 \text{ N}$). A more detailed discussion of stress effects pertinent to this work is given in Ref. 1.7. The dispersion relations and densities of states are discussed in Ref. 1.8 as a function of stress.

Photoexcitation of Ge

At liquid helium temperatures ($k_B T \sim 1/3 \text{ meV}$) virtually no electrons are thermally activated across the indirect band gap of Ge ($E_g = 744 \text{ meV}$) or thermally activated to ionize shallow ($\sim 10 \text{ meV}$) donors or acceptors.

Upon introducing photons with energies above the indirect band gap electrons are excited to the conduction band. The electrons relax rapidly ($\lesssim 1 \text{ ns}$) to the conduction band minima, and holes to the valence band maximum. Through their coulomb interaction an electron and a hole can bind to form a loosely bound mobile hydrogen-like species called a Mott-Wannier exciton. Here this exciton will be called a free exciton (FE).

An effective mass calculation for the FE binding energy E_x using the simplified high stress limit band structure yields

$$E_x = \frac{e^2/\epsilon}{2a_x} \quad (1.2)$$

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Fig. 1.3 Shift in indirect band gap of Ge as a function of uniaxial stress for stresses along three symmetry axes. Slopes correspond to measurements at 80K from Ref. II.21 (from Ref. I.21).

where $\epsilon = 15.36$ is the dielectric constant of Ge and a_x is the FE Bohr radius:

$$a_x = \frac{\hbar^2}{\mu(e^2/\epsilon)} \quad (1.3)$$

The reduced mass $\mu^{-1} = (2m_{\text{et}}^{-1} + m_e^{-1})/3 + A$. The large spatial extent of the FE as characterized by the Bohr radius $a_x = 177 \text{ \AA}$ justifies the use of the dielectric constant ϵ to characterize the screened coulomb interaction. A binding energy $E_x = 2.65 \text{ meV}$ is found. For unstressed Ge, $E_x \approx 4.15 \text{ meV}$ is calculated⁹ and measured¹⁰ for the FE ground state. The corresponding Bohr radius is $a_x = 127 \text{ \AA}$.⁹

As photoexcitation is increased new species can potentially come into existence. The excitonic molecule (EM), a bound state of two excitons, has been observed¹² in Ge stressed slightly off a $\langle 100 \rangle$ axis. This stress geometry staves off the condensation of FE's into another excitation (the EHL) to higher FE densities. Even under these high FE density conditions the relative abundance of EM's relative to FE's is small due to the low EM binding energy: $E_{\text{EM}} = 0.15 \pm 0.1 \text{ meV}$. In unstressed Ge and in other stress geometries EM have not been detected.

Since excitons have integer spin, they must obey Bose-Einstein statistics. The behavior of a dense FE gas according to Bose-Einstein statistics as opposed to Boltzmann statistics has been observed¹³ under special circumstances: the authors who observed the EM in Ge used the same geometry with an additional large magnetic field parallel to the $\sim \langle 100 \rangle$ stress axis to align the FE spins and thus destabilize the EM. This enabled higher FE densities to be reached where the statistical

character of a Bose-Einstein gas could more easily be differentiated from a Boltzmann gas. The extreme limit, Bose condensation, was not observed.

As the excitation power increases, the exciton density increases. At some point the character of the system must change. As the distance between excitons approaches the spatial extent of an exciton ($\sim a_x$) the concept of an exciton becomes inadequate. One can no longer associate a single electron with a single hole in describing their interaction. In this high density limit an electron-hole plasma forms which below a critical temperature T_c becomes a two-component (electron-hole) fermi liquid. This electron-hole liquid (EHL) is composed of two interpenetrating fermi liquids, one of electrons and one of holes, each with its own fermi level. In unstressed Ge the electron fermi level is $E_f^e = 2.5$ meV; the hole fermi level is $E_f^h = 3.9$ meV; the electron-hole (e-h) pair density is $n_x = 2.3 \times 10^{17} \text{ cm}^{-3}$; the condensation energy per e-h pair is $\phi = 1.8$ meV relative to the FE; and the critical temperature $T_c \approx 6\frac{1}{2} \text{ K}$ [see Ref. 1.2 and references within].

The radii of the EHL droplets R_d do not grow indefinitely as excitation power is increased. A droplet once created will grow until an equilibrium size is reached. Here the net current of e-h pairs into the droplet through its surface ($I_{\text{source}} \propto R_d^2$) is equal to the current of e-h pairs lost from the droplet due to e-h pair recombination across the band gap ($I_{\text{sink}} \propto R_d^3$). Typical droplet radii $R_d \sim 1 \mu\text{m}$.

These EHL droplets have been shown to be stationary¹⁴ in the absence of external forces (e.g. phonon wind, strain gradient, carrier wind) by making use of the optical hysteresis in EHL droplet formation.¹⁵⁻¹⁷ As excitation power is increased from zero, EHL droplets first appear

at an excitation power P_{up} . As excitation power is decreased from above P_{up} , the last droplet disappears at the excitation power P_{down} where $P_{down} < P_{up}$. There is a range of excitation powers over which essentially no droplets are created or lost. Within this range of excitation powers a set of EHL droplets can be studied for many hours. The potential usefulness of this fact is clear when one realizes that otherwise one could study EHL droplet motion for only a few EHL lifetimes ($\tau_L = 40 \mu s$). This EHL droplet formation hysteresis is a consequence of the droplet surface energy:^{18,19} $w = 2.6 \pm 0.3 \text{ erg cm}^{-2}$.

When the Ge crystal is stressed the band structure changes and thus the FE and EHL properties change. Consider the effects of applying stress along a $\langle 111 \rangle$ crystal axis. Electrons with $\vec{k}_e$ along the stress axis are lowered in energy relative to the others. At a stress where the electron band splitting equals the electron fermi level ($\sigma = -2.5 \text{ kgf/mm}^2$), all of the electrons in the EHL will be in the electron energy ellipsoid with $\vec{k}_e$ along the stress axis. Most FE will have $\vec{k}_e$ along the stress axis at a lower stress, determined by where the valley splitting is greater than several $k_B T$. At a stress where the hole band splitting equals the hole fermi level ($\sigma = -6.3 \text{ kgf/mm}^2$), all of the holes in the EHL will be in the upper valence band. Most FE will have their holes in the upper valence band at a lower stress, determined by where the valence band splitting is greater than several $k_B T$. With the increased occupation of one electron valley at the expense of the others the kinetic energy of the EHL increases. The EHL binding energy ϕ and density n_L correspondingly decrease as does the critical temperature T_c . The calculated²⁰ high stress limit binding energy and density $\phi = 0.42 \text{ meV}$ and $n_L = 1.1 \times 10^{16} \text{ cm}^{-3}$. This is almost a factor

of five decrease in ϕ and a factor of 20 decrease in n_2 . The high stress limit FE has a binding energy $E_x \sim 2.64$ meV.

Strain Induced Potential Wells

For experiments reported in Chapter II and in Chapter III, a rectangular piece of crystalline Ge is stressed along a $\langle 111 \rangle$ crystal axis with a rounded plastic plunger.^{21,22} This stress geometry, called the Hertzian contact geometry,²³ results in a shear strain maximum inside the crystal. This feature of such stress geometries was first noticed when train wheels designed to survive the strain present at the rim of a wheel were observed to self-destruct starting at a point between rim and wheel.

The energy of an electronic excitation depends on the local strain in the crystal. The energy of an electron-hole (e-h) pair with the electron in the conduction band valley parallel to the $\langle 111 \rangle$ stress axis decreases as the indirect band gap is reduced (see Fig. I.3). A countershift in energy occurs due to a decrease in binding energy with increasing stress. Figure I.4 shows the energy per e-h pair of the EHL as a function of stress. The experimental²⁴ points were determined by measuring the wavelength shift of the EHL luminescence as a function of uniaxial stress. The solid lines are from theory.²¹ Figure I.4 shows an initial upward sloping of ΔE_{EHL} with stress. For $0 < -\sigma_{111} < 2.5$ kgf/mm² the lowering of the EHL binding energy (due to the electron band degeneracy changing from four to one) is greater than the decrease of the indirect band gap.

Fig. 1.4 Plot of the shift in energy of the electron-hole liquid with uniaxial stress along several symmetry axes. Data from Ref. 1.24. Solid lines are theory from Ref. 1.21 (from Ref. 1.21).

An e-h pair will have a lower energy in regions of higher stress if $\vec{k}_e \parallel \vec{\sigma}_{111}$ and $|\vec{\sigma}_{111}| \geq 2.5 \text{ kgf/mm}^2$. Thus an e-h pair in a stress gradient is accelerated toward regions of higher stress. A consequence of these observations is that the Hertzian contact geometry results in a strain induced potential energy well for electronic excitations with $\vec{k}_e \parallel \vec{\sigma}_{111}$ and $-\sigma_{111} > 2.5 \text{ kgf/mm}^2$.

Figure I.5 shows some calculated²¹ spatial profiles of the indirect gap ΔE_g with the EHL energy shift ΔE_{EHL} . The potential energy expanded in a Taylor series about the well bottom can be approximated as parabolic with different curvatures for positive and negative directions on the x, y, and z axes. The solid lines in Fig. I.5(b) are fits of parabolas to the strain well. The fits are quite good. I will speak generally of the geometric mean of the various curvatures

$$\alpha = (\alpha_{x+} \alpha_{x-} \alpha_{y+} \alpha_{y-} \alpha_{z+} \alpha_{z-})^{1/6} \quad (\text{I.4})$$

and discuss the strain well by modeling it as

$$U(r) = \alpha r^2 \quad (\text{I.5})$$

The strain well geometry has a number of attractive features from an experimentalist's point of view: (a) It provides well defined spatial distributions for the FE gas and the EHL. There is at most one EHL droplet in the strain well. The FE gas is distributed in the well according to Boltzmann statistics. This latter fact provides a way to measure the shape of the well bottom. (b) These distributions are far away from the crystal surfaces ($\sim 1 \text{ mm}$). This enables the experimenter to avoid the uncertainties and complications of dealing

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Fig. 1.5 Calculated variation of band gap (o) and EHL (•) energy with position inside a square Ge crystal stressed along a $\langle 111 \rangle$ axis as shown in insert. (a) Variation of energies in the direction of applied force. (b) Variation of energies along the y -axis through the well minimum. Solid lines are best fits to a parabola. The slight asymmetry in y is because Ge is not symmetric under reflection in a (112) plane (from Ref. 1.13).

with surfaces by using sufficiently low temperatures ($k_B T \ll$ well depth). (c) As mentioned in the previous section, the FE and the EHL characteristics are easily altered by varying the applied stress. This happens because the properties of these photoexcited states are determined by the band structure near the conduction band minima and the valence band maximum. These portions of the band structure are quite sensitive to modest stresses.

One added complication for the EHL confined to a strain well is due to the high compressibility²⁵ of the EHL ($\kappa_T \geq 10^{-2}$ cm²/dyne). Kelso²⁶ has measured the density distribution of a large (0.7 mm radius) EHL droplet confined to a strain well ($-\sigma = 5.5$ kgf/mm²) with curvature $\alpha = 1.7$ meV/mm². She found the central density of the EHL droplet compressed by a factor of three. To avoid EHL compression the data in Chapter III of this thesis were measured for small EHL droplets (radius ≤ 0.15 mm).

The discussion above has dealt with the effects of static strain fields on electronic excitations. An electronic excitation moves in response to static strain gradients. A natural extension of this discussion is to consider the effect of dynamic strain gradients (phonons) on electronic excitations.^{27,28} Large fluxes of phonons created as energetic carriers, photoexcited by intense light sources, thermalize. Using sharply focused intense light sources, phonons and their interaction with various photoexcited states have been studied extensively by measuring the spatial and temporal evolution of luminescence.²⁹ In studying the transport properties of photoexcited states care must be taken to determine whether the transport is ballistic (phonon wind) or diffusive.

Luminescence

The radiative recombination of FE's and the EHL results in a luminescence spectrum characteristic of their basic properties. Because Ge is an indirect gap semiconductor, a band edge phonon is required to conserve crystal momentum in the decay process (unless recombination is mediated by an imperfection in the crystal - e.g. an impurity). Because an extra particle (a phonon) is involved in the recombination the lifetimes of these photoexcitations become quite long (30-40 μ s). A decay involving a 27 meV LA phonon is illustrated in Fig. I.1. This is the dominant radiative decay route. Other luminescence lines corresponding to TA, TO, and LO phonons and no-phonon (crystal imperfection) decay are observed. In this thesis the LA phonon-assisted decay luminescence is used unless otherwise stated.

Luminescence provides a powerful tool for studying these photoexcited states. A tremendous amount of information can be extracted from measurements of luminescence intensity as a function of experimental parameters (e.g. spatial position, temperature, excitation power, stress, electric field, magnetic field). One can measure spectral line shapes, total (integrated over λ) luminescence intensities, and luminescence polarization. One can measure the relative luminescence intensities of luminescence lines for the same photoexcited species or between different species.

The dominant radiative decay path for the FE and the EHL, the LA phonon-assisted decay, is symmetry allowed. For allowed transitions it has been argued that² the optical and electron-phonon matrix elements depend only weakly on wave vector over the range of wave vectors pertinent to the FE and the EHL. This enables the FE and the EHL spectral line

shapes to be described in terms of density of state functions and fermi occupation functions.

For the FE luminescence spectral line shape

$$I_x(E) \propto D_x(E) f(E) \quad (I.6)$$

where $D_x(E)$ is the FE density of states and $f(E) = \exp(-E/k_B T)$ is the appropriate occupation function. For the range of densities achieved in the experiments in this thesis, the Boltzmann distribution is appropriate.

The zero stress FE density of states can be determined from the FE dispersion relation.⁹ For the low temperatures and relatively crude purposes it will be put to in this thesis, the FE dispersion is well approximated by a parabola. This leads to a *zero stress FE line shape*:

$$I_x(E) \propto E^{\frac{1}{2}} \exp(-E/k_B T) . \quad (I.7)$$

An additional complication, collision broadening of the spectral line shape,³⁰ is ignorable for the low temperature (1.8 K) at which the zero stress FE line shape is considered in this work. This line shape is considered here only to the extent of fixing its position so that shifts in the FE line with stress can be measured (shift energy $\gg$ line width).

It has been pointed out³¹ that the appropriate density of states for a FE gas confined to a parabolic strain well is the harmonic oscillator density of states: $D_x(E) \propto E^2$. This leads to a *strain well FE line shape*:

$$I_x(E) \propto E^2 \exp(-E/k_B T) \quad . \quad (I.8)$$

It is assumed, in writing Eq. (I.8), that the electron and hole band splittings are much greater than $k_B T$ so that only a single valence and a single conduction band need be considered. This is the case for all the stress geometry experiments reported in this thesis.

The spectral line shape of the EHL luminescence is given by a convolution of the electron and hole density of state functions:^{2,32}

$$I_L(h\nu) \propto \int_0^\infty dE_e \int_0^\infty dE_h D_e(E_e) D_h(E_h) f(E_e) f(E_h) \times \delta(E_e + E_h + E_{BB} - h\nu - \hbar\omega_{ph}) \quad . \quad (I.9)$$

Here E_{BB} is the energy difference between lowest energy electron state and the lowest energy hole state in the EHL (see Fig. I.6). The phonon energy is $\hbar\omega_{ph}$ and the energy of the luminescence phonon is $h\nu$. Figure I.6 illustrates a typical decay. The lowest energy photon occurs when electrons and holes at the band extrema recombine. The highest energy photon occurs when electrons and holes at the fermi levels recombine ($T=0$). Thus the EHL luminescence spectral line width is $E_F = E_F^e + E_F^h$. These two fermi levels are related through the electron and hole density of states to the EHL density n_L :

$$n_L = \int_0^\infty D_h(E_h) f(E_h - E_F^h) dE_h = \int_0^\infty D_e(E_e) f(E_e - E_F^e) dE_e \quad . \quad (I.10)$$

Charge neutrality requires the electron and hole densities to be equal. Given that the density of states are known⁸ Eq. (I.10) means that if

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Fig. I.6 Schematic of electron and hole Fermi liquids. Energies for a phonon assisted radiative recombination of an electron and a hole are indicated. The energy width $k_B T$ is to scale with the representative Fermi energies E_F^h and E_F^e . Widths in k space are not to scale.

any one of n_L , E_F^e or E_F^h are known then all are known. There is only one fitting parameter that determines the EHL line shape.

In fitting the spectral line shapes for a FE gas and an EHL droplet confined to a strain well Eqs. (I.8) and (I.10) are used. These line shapes when adjusted for the detector's spectral response and convolved with the spectrometer's gaussian slit function are fit to the experimental luminescence spectra. The fitting parameters are the amplitudes and positions of the lines and E_F^h .

The FE and EHL luminescence from zero stress Ge photoexcited with unpolarized light must, by symmetry, be unpolarized. If the crystal is stressed, for example along a $\langle 111 \rangle$ axis, then the symmetry is broken. In general the luminescence will be polarized.³² The EHL polarization is expected and is observed to saturate (or at least change very slowly) for stresses high enough that the hole band splitting is greater than E_F^h and the electron band splitting is greater than E_F^e . The FE polarization might be expected to saturate when the electron and hole band splittings are several times $k_B T$. The changes in polarization at higher stresses could be attributed to the warpage of the energy bands with stress. For the stresses used in Chapters II and III the polarizations are close to saturation.

The EHL may decay non-radiatively as well as radiatively. Haug³³ has calculated the decay rate for a three-carrier phonon-assisted Auger process. He calculates $[\tau_L^{-1}]_{\text{Auger}} = C n^2$ where $C = 2.16 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$. Including electron and hole correlations, the constant C should be replaced with³⁴ $C[g_{eh}(0)]^2 g_{ee}(0)$ where the g 's are spatial correlation functions. Using theoretical values³⁵ for the correlation functions (zero stress), $C \approx (2.16 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}) (2.3)^2 (0.24) = 2.7 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$;

this yields an Auger lifetime of 70 μs . This is to be compared with the experimental result³⁶ predicting a zero stress Auger lifetime $\tau_{\text{Auger}} \approx 40 \mu\text{s}/0.33 = 120 \mu\text{s}$. The 0.33 is the EHL radiative efficiency. It has been proposed that this Auger process may be responsible for a loss of carriers out through the surface of the EHL. Energetic Auger carriers near the surface could escape before thermalizing. Such a mechanism could give rise to a small charge on the EHL droplet. Thermionic emission of carriers from the droplet surface is another decay mechanism. In this case if the hole fermi energy is smaller than the electron fermi energy then the thermionic emission of holes is faster than for electrons and a small negative charge will build up.

Experimental Apparatus

A schematic of the experimental set up is shown in Fig. I.7. The microcomputer controls the apparatus and automates many of the measurements. It controls the intensity of the feedback stabilized steady state light sources: an incandescent lamp with appropriate filters or an Argon ion laser. It sends triggering pulses to the pulsed light source: a liquid N_2 cooled GaAs laser.

These light sources are used to photoexcite carriers in a piece of Ge crystal which is immersed in liquid helium in a four window cryostat. Luminescence is collected by an output lens, spectrally resolved by a $\frac{1}{4}$ meter Jarrel Ash spectrometer (890 grooves/mm grating blazed at 1 μm) and detected by a liquid N_2 cooled Ge PIN photodiode. The detector current is amplified by a relatively fast low noise preamp.

For pulsed experiments the signal is further amplified and filtered

Fig. I.7 Experimental set-up. A variety of feedback-stabilized light sources are controlled by the microcomputer. The source used for a particular experiment photoexcites a Ge crystal immersed in liquid helium in an optical cryostat. The luminescence from the photo-excited states is collected by an output lens and routed through a 1/4 meter Jarrel Ash spectrometer to an N_2 -cooled Ge PIN photodiode. For experiments using steady state excitation the luminescence is mechanically chopped and the detector output lockin detected. For pulsed experiments a transient recorder captures each decay waveform. The microcomputer automates spatial, spectral, temporal, and excitation power scans.

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to cut out high frequency noise. Then a waveform recorder digitizes the signal pulse. After the waveform has been added to the microcomputer memory another pulse is sent to retrigger the GaAs laser and restart the waveform recorder. A typical measurement might involve adding up the results of 10^4 to 10^5 pulses.

For steady state excitation experiments the luminescence is mechanically chopped and a lockin is used to detect the preamp output. The lockin output is connected to a voltage-to-frequency converter whose pulses are counted up for a specified time and added to memory in the microcomputer.

In doing steady state measurements the microcomputer can automate wavelength scans (by a stepper motor rotating the spectrometer grating), spatial scans (by a stepper motor translating the image of the crystal across the spectrometer slit), and excitation power scans (by supplying a ramp voltage connected to the light source feedback loop). For spatial or wavelength scans the signal is integrated for a preset time with the result stored in memory. The computer then steps the stepper motor and the cycle repeats itself with subsequent integration results stored in adjacent memory locations. For power scans the same procedure is followed except that in place of stepping a motor between integration points the ramp voltage controlling the light intensity is adjusted. This adjustment may include bringing the light intensity down to zero or up to some high preset power or both before the light power at which the integration takes place is incremented.

Results of any of these different types of scans were displayed on an x-y oscilloscope during the run. The finished runs were stored on magnetic tape. During an experiment it becomes necessary at times

to treat some data or plot it in more meaningful ways. To do this, the data were sent over the phone lines using a 300 baud modem to a PDP-11 computer. The PDP-11 computer used a Unix operating system and supported a number of programming languages (e.g. Basic +). Links with more powerful computers were available for more involved computations. The results could be displayed in the laboratory on the computer terminal's video display or printed on our Data Terminals and Communications model 302 printer. I wrote a general purpose point plotting routine in Basic + for our printer. This program can make linear, semilog, or log-log plots. It can plot more than one set of data with different symbols for each. The tickmarks on the coordinate axes are automatically calculated, plotted and labeled. Data to be plotted can be read in from an input file and manipulated if necessary or can be calculated within the input subroutine. Most of the figures in this thesis were traced from plots made using this program.

An infrared vidicon was used, primarily as a diagnostic tool, to check the quality of strain wells (see Ref. I.21 for representative photos). The picture seen on the monitor shows an outline of the crystal with a bright spot due to photoexcited states in the strain well luminescing. The outline of the crystal is visible because of totally internally reflected light ($n \approx 4$ for Ge) escaping out the edges of the crystal. The size of the bright spot reflects the size of the drop. Typically the droplet was observed to be about 1 mm away from any crystal surface for the strain wells of Chapter III. For stresses beyond 16 kgf/mm^2 the vidicon sensitivity rapidly tails off.

Luminescence Detector and Preamplifier

A sensitive low noise Ge PIN photodiode was used to detect the luminescence emanating from photoexcited Ge at liquid helium temperatures. The photodiode is sensitive to these wavelengths (1.6 - 1.8 μm) because it is kept at temperatures (105 - 137 K) where radiation absorption lengths are on the order of millimeters. These short absorption lengths are possible for two reasons: 1) the indirect band gap decreases with increasing temperature³⁷ (13-23 meV over the temperature range given above); 2) the thermal population of 27 meV band edge LA phonons has increased sufficiently that thermal phonon-assisted indirect gap absorption is a highly probable event. The detector was fabricated from Ge sufficiently pure ($N_A - N_D \sim 10^{10} \text{ cm}^{-3}$) that the full 7 mm depth of the photodiode is depleted at a reverse bias voltage of $\sim 300 \text{ V}$.³⁸ The large active volume of this detector enables quantum efficiencies approaching one to be achieved. The detector was used at temperatures low enough that noise from the thermal generation of free carriers was not the dominant source of noise.

The detector used for the work in Chapters II, III and IV, shown diagrammatically in Fig. I.8, was fabricated by Blair Jarret of the Lawrence Berkeley Laboratory under the supervision of Professor E. E. Haller. It is housed in an ultra-high vacuum dewar separated from a 77K cold finger by stainless steel standoffs. The temperature is varied by running current through a carefully shielded 27 ohm nichrome wire resistor located near the detector. The temperature is measured with a copper-constantin thermocouple. The input FET (selected for low noise) of the first amplification stage and a 2 Megohm feedback resistor are also kept cold ($\sim 150 \text{ K}$) to reduce amplification noise.

Ge PIN PHOTODIODE

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Fig. I.8 Schematic of the construction of the Ge PIN photodiode along with its biasing circuitry, the first amplification stage FET, and the feedback resistor R_F . The detector, FET and feedback resistor are kept permanently cold in a liquid nitrogen cold finger dewar. The detector can be heated by running current through a nearby well-shielded nichrome wire resistor. Boron nitride is an excellent heat conductor, an excellent electrical insulator, and is easily machinable. The inset shows a useful circuit model for the photodiode detector and preamp. Pins F, E, C, B, and A connect to the pins of Fig. I.10.

An external (293 K) feedback resistor can be placed in series with the internal 2 Megohm resistor if a higher preamp gain is desired and a slower time response is acceptable. The dewar hardware and electronics were prepared by John Furneaux. The detector and dewar are similar to those used for particle detectors³⁹ except for the addition of a quartz window transparent to the luminescence to be detected.

The construction of the detector is illustrated by Fig. 1.8. The PIN photodiode was made from a piece of slightly p-type ultra pure Ge with dimensions $18 \times 18 \times 7 \text{ mm}^3$. Photons enter the detector through a boron implant (p-type) on one of the $18 \times 18 \text{ mm}^2$ square faces of the crystal. Contact with the external biasing circuitry is made through a piece of indium foil pressed against the crystal. A lithium drift contact diffused into the opposing square face of the crystal serves as the n-type contact. A 10.2 mm diameter guard ring was cut through this contact down to the slightly p-type bulk of the crystal. Because the guard ring is cut through an n-type contact down to a p-type bulk, the regions of this contact inside and outside of the guard ring are electrically isolated from each other. These regions are treated separately in the external circuitry. Each region makes contact with external circuitry through indium foil attached to the crystal with an In:Ga eutectic. The region outside of the guard ring collects all surface currents. All four non-contact surfaces were passivated by sintering them with silicon oxide. This serves to give them well defined non-variable characteristics. The Li drift region outside of the guard ring was connected to ground in the external circuitry. Thus the surface currents with the associated noise did not reach the preamp as they would have for a detector without a guard ring. The contact

inside the guard ring collects electrons created within the bulk of the crystal. This includes photoexcited and thermally excited electrons.

The inset in Fig. I.8 contains a useful circuit model of the detection circuitry. The photodiode, reverse biased at -360 V, is accurately modeled as an ideal current source whose current is proportional to the incoming flux of photons: each incident photon of a given wavelength has an equal probability of exciting an electron across the indirect band gap with the absorption or emission of a band edge phonon. For each photon that excites an e-h pair one electron passes through each detector lead. The differential resistance of the detector is greater than 10^{13} ohms. This is much larger than the largest feedback resistance used ($R_F = 500$ Megohms) and justifies the modeling of the detector as a current source. Since the feedback resistance is also much less than the preamp input FET resistance, the preamp output voltage V_{out} is simply

$$V_{out} = -I_d R_F \quad (I.11)$$

where I_d is the photodiode current.

When a feedback resistor $R_F = 500 \text{ M}\Omega$ is used and the detector temperature $T = 120 \text{ K}$, a detector current $I_d \approx 0.8 \text{ fA}$ ($1 \text{ fA} = 10^{-15} \text{ A}$) can be seen with a signal-to-noise ratio of one after 64 s of integration. Upon normalizing this current noise with the bandwidth B the measurement

$$\langle I_n^2 \rangle^{1/2} (\text{Hz}^{-1/2}) = \frac{\langle I_n \rangle^{1/2}_{\text{measured}}}{\sqrt{B}} \quad (I.12)$$

where

$$B = \frac{1}{2[\text{integration time}]} \quad (I.13)$$

a current noise $\langle I_n^2 \rangle^{1/2} \approx 9 \text{ fA Hz}^{-1/2}$ is found. The Noise Equivalent Power (NEP) can be determined by calculating the incident power of radiation necessary to create a detector current equivalent to this noise current per root Hertz:

$$\text{NEP} = \left[\frac{\langle I_n^2 \rangle^{1/2}}{e} \right] \left[h\nu \right] \left[\frac{1}{q} \right] \left[\frac{1}{P_T} \right] \quad (\text{I.14})$$

Here $\langle I_n \rangle^{1/2}/e$ is the number of e-h pairs photoexcited per second in the equivalent current; $h\nu$ is the energy of the exciting photons; q (the quantum efficiency) is the absorption probability of a photon; and P_T is the probability that a photon incident on the detector will be transmitted into the crystal.

$$P_T = 1 - \left(\frac{n-1}{n+1} \right)^2 \quad (\text{I.15})$$

For Ge at 120 K the index of refraction $n = \sqrt{\epsilon} \approx 4$ so that $P_T \approx 0.64$. For $\lambda = 1.758 \text{ } \mu\text{m}$ and $q = 0.25$ (discussed below) an $\text{NEP} \approx 4 \times 10^{-14} \text{ W Hz}^{-1/2}$ is found.

To stress the high sensitivity of this detector, note that the 0.8 fA current mentioned above corresponds to ~ 5000 photoexcited e-h pairs per second, or to an incident light power of $\sim 3 \text{ fW}$. Three fW is to the power consumption of a flashlight bulb what a penny is to our national debt.

The speed of the detector is characterized by the transit time of a carrier across the 7 mm deep crystal. The photodiode is reverse biased at -360 V when in its operating mode. The entire crystal is depleted at $\sim -300 \text{ V}$ bias. For an internal field of $\sim 514 \text{ V cm}^{-1}$ and a mobility of $\mu \sim 2 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ the carrier velocities are

$v = \mu V \approx 10^7 \text{ cm s}^{-1}$. Carrier velocities in Ge saturate at approximately this speed due to phonon emission by the hot carriers.⁴⁰ For such speeds the transit time is $\sim 70 \text{ ns}$. The gain and speed of the preamp are determined by the feedback resistance and capacitance. A feedback resistance $R_F = 500 \text{ Megohms}$ provides a preamp gain of $R_F = 5 \times 10^8 \text{ VA}^{-1}$. This value of R_F combined with the feedback capacitance $C_F \sim 0.2 \text{ pF}$ (stray capacitance and capacitance of feedback resistor) result in an RC response time of $100 \mu\text{s}$. The smallest possible feedback resistor (the $2 \text{ M}\Omega$ resistor permanently mounted in the dewar) results in an RC response time of $\sim (2 \times 10^6 \text{ ohms})(0.2 \text{ pF}) \approx 0.4 \mu\text{s}$. Thus the preamp always limits the time response of the system. In practice one chooses the largest feedback resistor (to maximize preamp gain) that provides acceptable time response.

The temperature of the detector was chosen to optimize the signal-to-noise ratio for the luminescence wavelengths of interest. Figure I.9 shows the detector wavelength response for several detector temperatures. Assuming the peak in the response curves correspond to a quantum efficiency of approximately one, the quantum efficiencies for the measurements made in this thesis vary from 0.21 (for $\lambda = 1.79 \mu\text{m}$) to 0.76 (for $\lambda = 1.66 \mu\text{m}$). Noise sources are the shot noise of the detector current

$$\langle v_{\text{shot}}^2 \rangle^{1/2} = \langle I_{\text{shot}}^2 \rangle^{1/2} R_F = [2e I_{\text{shot}}]^{1/2} R_F \quad (\text{I.16})$$

and the Johnson noise from the feedback resistor

$$\langle v_{\text{Johnson}}^2 \rangle^{1/2} = [4 k_B T_{R_F} R_F]^{1/2} \quad (\text{I.17})$$

and other noise sources from the preamp (e.g. noise from the input FET).

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Fig. I.9 Detector wavelength response to a hot blackbody for several detector temperatures: (a) 105 K; (b) 117 K; (c) 136 K; (d) 145 K.

Here T_{R_F} is the temperature of the feedback resistor (~ 293 K for external resistors). The detector current I_d in Eq. (I.16) for the shot noise has several sources: the luminescence photocurrent, the background blackbody radiation photocurrent, and the current due to the thermal generation of carriers. The current I_d was measured as a function of detector temperature using a Keithley model 602 Electrometer with an opaque covering over the detector dewar window. This "dark current" showed a steeply rising component well described by the thermal generation of carriers:

$$I_{\text{thermal}} = (0.032 \text{ A K}^{-3/2}) T^{3/2} \exp\left(-\frac{3409}{T}\right). \quad (\text{I.18})$$

This component dominated the dark current for $T \geq 115$ K. For lower temperatures the blackbody photocurrent with its more gradual temperature dependence dominates the dark current. A PAR-186A lockin was used in its noise meter mode to measure the noise at the output of the preamp as a function of the detector temperature. Just as for the dark current measurements, these measurements were made with an opaque covering over the detector dewar window. The noise meter measurements showed a constant voltage noise for detector temperatures below 125 K and a steep rise in noise at higher temperatures. The steep rise in noise was consistent with shot noise. For wavelengths in the range $1.74 \mu\text{m} \leq \lambda \leq 1.79 \mu\text{m}$ corresponding to the LA phonon-assisted FE and EHL luminescence in Ge ($0 \leq -\sigma \leq 15 \text{ kgf/cm}^2$) the optimum signal-to-noise ratio is attained for detector temperatures in the range $120 \text{ K} \leq T \leq 125 \text{ K}$. Because the shot noise from the detector current rises rapidly with temperature over this temperature range and because

the signal increase with temperature is relatively gradual

$$\Delta I_d \sim (10^{-17} \text{ AK}^{-1}) \Delta T \quad (\text{I.19})$$

the optimum detector temperature depends only weakly on wavelength (for $1.74 \mu\text{m} \leq \lambda \leq 1.79 \mu\text{m}$). This detection system is not limited by background noise, but rather by preamp noise.

For steady state work where lockin detection was used, the luminescence was mechanically chopped at 670 Hz by a rotating chopper wheel. At chopping rates slower than 250 - 300 Hz 1/f noise became dominant.

One source of noise I have not yet mentioned is the sharp current spikes due to cosmic rays. This type of detector was originally developed as a particle detector. Background infrared radiation was deemed a nuisance. The detectors were typically mounted in a liquid N_2 cooled dewar with the entrance window being a thin metallic sheet. C. D. Jeffries and T. K. Lo were the first persons to use an earlier version of this type of detector for germanium EHL studies. They realized that such a detector, cooled to $T \approx 150 \text{ K}$ would have reasonable absorption lengths at EHL wavelengths. With our detector cosmic rays are the nuisance. They cannot be shielded as easily as the infrared, but they are of short duration and clipping diodes can be used to minimize their effects. A discussion of Ge PIN photodiodes from the particle detector point of view (energetic electrons, heavy charged particles, and γ -rays and x-rays) can be found in Ref. I.39 by E. E. Haller and F. S. Goulding.

The preamplifier circuitry, shown in Fig. I.10, was designed by F. Goulding of the Lawrence Berkeley Laboratory. The switch (S1) on

DETECTOR PREAMP CIRCUITRY

Δ LEADS AS SHORT AS POSSIBLE

* METAL FILM RESISTOR

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Fig. 1.10 Detector preamplifier circuitry with buffer amplifier. Designed by F. Goulding of the Lawrence Berkeley Laboratory. Cooled components are indicated as such. With the 500 Megohm feedback resistor shown, the preamp response time is ~ 0.1 ms.

the input of the buffer amplifier is in the X5 gain position. Switch position 4 corresponds to X1 gain. A cascode configuration is used to eliminate high frequency roll off due to the input FET's junction capacitance and the Miller effect. The preamp was powered by four series-connected 12 V storage batteries. This was done to avoid ground loops and power supply ripple inherent in the use of electronic power supplies.

Germanium Samples

The crystalline Ge samples used in this thesis were grown by W. Hansen and E. E. Haller at the Lawrence Berkeley Laboratory.⁴¹ Assorted characteristics of these samples are listed in Table I.2. The standard growth technique (Czochralski technique) involves pulling a rotating seed crystal out of molten Ge. A quartz (SiO_2) crucible is generally used to hold the melt. This gives rise to neutral impurity concentrations: $[\text{Si}], [\text{O}] \sim 10^{14} \text{ cm}^{-3}$. The most common growth atmosphere used was H_2 . In dislocation-free crystals a lattice divacancy-hydrogen complex is believed responsible for 80 meV acceptor states.⁴¹ In dislocated Ge, lattice vacancies are believed to be attracted to and incorporated in the dislocations during the cooling process. This results in an absence of these deep acceptors (for dislocation concentrations $\geq 10^2 \text{ cm}^{-2}$).

Most of the impurities in the Ge crystals grown at LBL are shallow impurities - binding energies $\sim 10 \text{ meV}$. The dominant acceptor is Al (10.2 meV); the dominant donor is P (12.0 meV). The concentrations of these impurities are characterized by net donor or acceptor concentrations $|N_A - N_D| \sim 10^9 + 10^{12} \text{ cm}^{-3}$. The total impurity concentration

$N_A + N_D$ is found to be less than ten times larger than $|N_A - N_D|$.

The samples were cut out of the crystals using a diamond saw with the sample faces being high symmetry directions. The samples were polished with varying grades ($10\text{ }\mu\text{m}$ - $3\text{ }\mu\text{m}$ - $1\text{ }\mu\text{m}$ - $0.01\text{ }\mu\text{m}$) of alumina grit with the exceptions of CR50 and CR38 which were polished using syton (an abrasive plus chemical etch). The syton-polished crystals and the alumina-polished crystals (not all) were then chemically etched in White etch, $3\text{HNO}_3 : \text{HF}$, followed by a rinsing in methanol or ten parts methanol to one part distilled water. This rinse acts to quench the etch. Etching times from several seconds to a minute were used. The etching process removes surface damage due to polishing and results in an electrically clean surface.

TABLE 1.2 Germanium Crystal Samples

Sample ID (if any)	Crystal ID ^a	Origin of sample along crystal	Growth direction	Growth atmosphere	Dislocations (etch pit density) (cm ⁻²)	Impurities N _A - P _D (cm ⁻³)	Special Comments
145 M	145	2.7 cm	(100)	H ₂	0	(1.5 ± 3.0) × 10 ¹¹	[O], [Si] ~ 10 ¹⁴ cm ⁻³
437 D	437	5.0 cm	(111)	H ₂	350	-2 × 10 ¹⁰	^a very high Si ~ 10 ¹⁶ cm ⁻³
437 V	437	5.0 cm	(111)	H ₂	0	-2 × 10 ¹⁰	^a very high Si ~ 10 ¹⁶ cm ⁻³
-	404	5.0 cm	(111)	H ₂	1000	-4 × 10 ⁻¹⁰ (μ _n = 4 × 10 ³ /V-s)	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	475	2.0 cm	(111)	H ₂	~100	1.5 × 10 ¹⁰	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	518	-	(100)	O ₂	?	-5 × 10 ¹¹	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	150	5.4 cm	(100)	H ₂	0	2 × 10 ¹¹ (μ _p = 2.6 × 10 ³ /V-s)	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	150	10.3 cm	(100)	H ₂	~1000	n-type	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	394	2.1 cm	(111)	H ₂	> 10 ⁴	-6 × 10 ¹⁰ (μ _n = 4 × 10 ³ /V-s)	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	393	3.0	(111)	H ₂	> 10 ³	-1.2 × 10 ¹¹ (μ _n = 4.6 × 10 ³ /V-s)	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	133	3.2 cm	(100)	H ₂	0	6 × 10 ¹⁰ (no deep acceptors)	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	381	4.4 cm	(100)	H ₂	?	6 × 10 ¹⁰	[O], [Si] ~ 10 ¹⁴ cm ⁻³
-	112	22.5 cm	(100)	H ₂ + H ₂	~10 ⁶	2.3 × 10 ¹⁴ (Ga) (μ _p = 2.7 × 10 ³ /V-s)	O, Si, Ga, P? -8 ohm-cm
-	438	11.0 cm	(111)	H ₂	3200	1 × 10 ¹¹	high C, low Si (grown in carbon crucible)
#1	400	4.0 cm	(111)	Ar	5000 (before annealing)	-3.8 × 10 ¹² (P)	" annealed
#2	400	4.0 cm	(111)	Ar	5000	-3.8 × 10 ¹² (P)	" not annealed
CR50	145	-	(100)	H ₂	0	(1.5 ± 3.0) × 10 ¹¹	[O], [Si] ~ 10 ¹⁴ cm ⁻³
CR38	146	-	(100)	H ₂	0	2 × 10 ¹¹	[O], [Si] ~ 10 ¹⁴ cm ⁻³

^a Due to a leak during growth, O₂ pulled out Si to form a film atop the melt, so there could be much less Si.

^b These are crystal identification numbers for crystals grown at LBL by M. Hansen and E.E. Haller. The dimensions of all crystals were 4 × 8 × 8 mm³ except the last two which were 3.85 × 3.95 × 2.8 mm³ and 3.85 × 3.85 × 1.75 mm³ respectively.

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- $$W = \left[\frac{2\epsilon\epsilon_0(V_a + V_{bi})}{e|N_A - N_D|} \right]^{1/2}.$$
- Here $\epsilon = 15.36$ is the dielectric constant of Ge; $\epsilon_0 = 8.85 \times 10^{-14}$ CV⁻¹cm⁻¹ is the permittivity of free space; $e = 1.6 \times 10^{-19}$ C is the electronic charge; and $V_{bi} \sim 0.2$ V is the diffusion (built in) potential. For reference see almost any semiconductor text (e.g. S.M.Sze, Physics of Semiconducting Devices (Wiley-Interscience, New York, 1969), p.89).
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CHAPTER II.

THE QUASI-EQUILIBRIUM OF PHOTOEXCITATIONS IN Ge

In this chapter the kinetics and thermodynamics of Free Carrier (FC) - Free Exciton (FE) - Electron-Hole Liquid (EHL) systems is explored. The emphasis is on photoexcitations confined to a strain induced potential well.

Free Exciton - Free Carrier Systems

In this section I will discuss the conditions under which the chemical potential μ can be used to describe free carrier (FC) - Free Exciton (FE) systems. The question is: Do these photoexcited states live long enough to be described as being in thermal and spatial¹ equilibrium?

Consider a FC-FE system. The FE and FC densities are related by the following kinetic equations:

$$\frac{dn_c}{dt} = g - \frac{n_c}{\tau_c} - (an_c^2 - bn_x) \quad , \quad (II.1)$$

$$\frac{dn_x}{dt} = -\frac{n_x}{\tau_x} + (an_c^2 - bn_x) \quad . \quad (II.2)$$

Here g is the FC generation rate; τ_c^{-1} is the FC decay rate; τ_x^{-1} is the FE decay rate; an_c^2 is the rate at which FC bind into FE; and bn_x is the rate at which FE ionizes into FC.

Timusk² has used the following relation for b :

$$b = \frac{2\pi k_B T}{h \left(\frac{\gamma_e \gamma_h}{\gamma_x} \right)} e^{-E_x/k_B T} \quad (\text{II.3})$$

where γ_e , γ_h , and γ_x are the electron, hole, and exciton degeneracies.

The rate αn_c^2 can be determined as follows: the electron mean free path to bind with a hole and form a FE is

$$l_e = \frac{1}{\sqrt{2} n_h \sigma} \quad (\text{II.4})$$

where n_h is the hole density, and σ is the cross section for an electron and a hole to bind and form an exciton. The mean rate at which electrons bind with holes to form excitons is simply the product of the rate at which one electron traveling at the mean speed

$$v_t = \sqrt{\frac{8 k_B T}{\pi m_x}} \quad (\text{II.5})$$

binds with a hole to form an exciton v_t/l_e times the concentration of electrons n_e :

$$\alpha n_c^2 = \left(\frac{v_t}{l_e} \right) n_e = \left[4 \sqrt{\frac{k_B T}{\pi m_x}} \sigma \right] n_e n_h \quad (\text{II.6})$$

By charge neutrality, $n_e = n_h \equiv n_c$, so

$$a = 4 \sqrt{\frac{k_B T}{\pi m_x}} \sigma \quad (\text{II.7})$$

The cross section σ has been measured³ as a function of temperature. It is observed to decrease with increasing temperature from

$$\sigma(2.16K) \approx 1.7 \times 10^{-10} \text{ cm}^2 \quad \text{to} \quad \sigma(4.2K) \approx 4.8 \times 10^{-10} \text{ cm}^2 \quad \text{to} \\ \sigma(4.7K) \approx 4 \times 10^{-11} \text{ cm}^2.$$

To be able to describe a FC-FE system as a quasi-equilibrium, the rate at which FC bind into excitons αn_c^2 and the rate at which FE ionize into FC βn_x must be much faster than the FC and FE decay rates:

$$\alpha n_c^2, \beta n_x \gg \frac{n_x}{\tau_x}, \frac{n_c}{\tau_c} \quad . \quad (II.8)$$

In order to evaluate these terms, values of n_x and n_c must be specified. For n_x I will use the FE density corresponding to equilibrium with the EHL. For the purpose of making these estimates I will ignore the complications of hysteresis observed in zero stress Ge. In the strain-confined geometry this complication does not exist. Equating the FE and EHL chemical potentials leads to the standard result

$$n_x = \frac{\gamma_x e^{-\phi/k_B T}}{V_{QX}} \quad (II.9)$$

where

$$V_{QX} = \left[\frac{2\pi\hbar^2}{m_x k_B T} \right] \quad (II.10)$$

Here γ_x is the FE ground state degeneracy; ϕ is the condensation energy of a FE relative to the EHL; and m_x is the FE density of states or translational mass. The value of n_c used will be that corresponding to equilibrium with the FE gas. Equating FC and FE chemical potentials leads to

$$\frac{n_c^2}{n_x} = K(T) \quad (II.11)$$

where

$$K(T) = \frac{\gamma_e \gamma_h}{\gamma_x} \left(\frac{k_B T m_e m_h}{2\pi \hbar^2 m_x} \right)^{3/2} e^{-\frac{E_x}{k_B T}}. \quad (\text{II.12})$$

Here γ_e and γ_h are the electron and hole degeneracies. If the values of n_x and n_c from Eqs. (II.9), (II.10), (II.11) and (II.12) satisfy the inequalities Eq. (II.8) then a thermodynamic quasi-equilibrium between FC's and FE's is a valid assumption. The inequalities in Eq. (II.8) can be rewritten:

$$\frac{an_c^2}{\left(\frac{n_x}{\tau_x}\right)} = a\tau_x \frac{n_c^2}{n_x} = a\tau_x K(T) \gg 1, \quad (\text{II.13})$$

$$\frac{bn_x}{\left(\frac{n_x}{\tau_x}\right)} = b\tau_x \gg 1, \quad (\text{II.14})$$

$$\frac{an_c^2}{\left(\frac{n_c}{\tau_c}\right)} = a\tau_c n_c = a\tau_c \sqrt{n_x K(T)} \gg 1, \quad (\text{II.15})$$

$$\frac{bn_x}{\left(\frac{n_c}{\tau_c}\right)} = b\tau_c \frac{n_x}{n_c} = b\tau_c \sqrt{\frac{n_x}{K(T)}} \gg 1. \quad (\text{II.16})$$

These inequalities are somewhat redundant since $an_c^2 \approx bn_x \gg n_x/\tau_x, n_c/\tau_c$ for a thermodynamic equilibrium. I trust the values of a more than b due to their experimental origin. If any of these inequalities does not hold then kinetic theory [Eqs. (II.1) and (II.2)] must be used.

I will evaluate the inequalities Eqs. (II.13), (II.14), (II.15) and (II.16) at the temperatures $T = 2.16\text{K}$, 4.2K , and 4.7K for worst case parameters in zero stress and $\langle 111 \rangle$ stressed Ge.

The zero stress estimates make use of $m_x = 0.436 m_0$,^{4,5}
 $m_e = 0.22 m_0$,⁶ $m_h = 0.35 m_0$,⁷ $E_x = 4.15 \text{ meV}$,⁸ $\tau_x = 10 \mu\text{s}$ (the smallest I've measured), $\tau_c \sim 50 \mu\text{s}$,^{9,10} and $\phi = (1.8 \pm 0.2 \text{ meV}) + (0.016 \pm 0.007 \text{ meV K}^{-2})T^2$.¹¹ The degeneracies are $\gamma_x = 16$, $\gamma_e = 8$, and $\gamma_h = 4$. The values of σ were listed just above Eq. (II.8). Table II.1 lists the results.

Table II.1 Rate ratios for zero stress

$T (^{\circ}\text{K})$	$\frac{an_c^2}{\left(\frac{n_x}{\tau_x}\right)}$	$\frac{bn_x}{\left(\frac{n_x}{\tau_x}\right)}$	$\frac{an_c^2}{\left(\frac{n_c}{\tau_c}\right)}$	$\frac{bn_x}{\left(\frac{n_c}{\tau_c}\right)}$
2.16	7.8×10^{-4}	1.8×10^{-3}	10	23
4.2	42	1.8×10^2	2×10^4	8.8×10^4
4.7	1.5×10^2	6.9×10^2	4.9×10^4	2.2×10^5

Rows having all ratios much greater than one correspond to temperatures where equilibrium thermodynamics describes the system accurately. The first two columns of ratios are independent of n_x or n_c [see Eqs. (II.13), (II.14)]. The last two columns of ratios are proportional to $\sqrt{n_x}$. With this information one can estimate how far below EHL threshold equilibrium thermodynamics can be used. At 2.16K the ratios in Table II.1 indicate that kinetic equations must be used; they indicate further that the dominant decay mechanism for e-h pairs

is through FE decay. For 4.2K and above, the ratios indicate that equilibrium thermodynamics is sufficient. This latter conclusion holds true for FE densities four orders of magnitude below those at EHL threshold; it also holds true if τ_c is two orders of magnitude shorter.²

Table II.2 below lists the ratios of rates [Eqs. (II.13), (II.14), (II.15) and II.16] where worse case parameters corresponding to the lowest stress experimental conditions of Chapter III have been used. The parameters used are: $m_e = 0.22 m_0$,⁶ $m_h = 0.1 m_0$,⁷ $m_x = 0.32 m_0$, $E_x = 3.5$ meV, $\tau_x \approx 1$ ms, $\tau_c = 100$ μ s (not measured, chosen to be pessimistic), and $\phi \approx 1.16$ meV. The degeneracies are $\gamma_x = 1$, $\gamma_e = 1$, and $\gamma_h = 1$. As in Table II.1, the FE density at EHL threshold has been used for the last two columns of ratios. For lack of a better approach, the zero stress cross sections have been scaled by the square of the ratio of Bohr radii - stressed to unstressed: $\sigma(2.16K) \approx 2.4 \times 10^{-10} \text{ cm}^2$, $\sigma(4.2) \approx 6.7 \times 10^{-11} \text{ cm}^2$, and $\sigma(4.7K) \approx 5.6 \times 10^{-11} \text{ cm}^2$.

Table II.2 Rate ratios for $\langle 111 \rangle$ stress.

T (°K)	$\frac{an_c^2}{\left(\frac{n_x}{\tau_x}\right)}$	$\frac{bn_x}{\left(\frac{n_x}{\tau_x}\right)}$	$\frac{an_c^2}{\left(\frac{n_c}{\tau_c}\right)}$	$\frac{bn_x}{\left(\frac{n_c}{\tau_c}\right)}$
2.16	0.51	12	87	2×10^3
4.2	3.8×10^3	2.2×10^5	4.1×10^4	1.7×10^6
4.7	1.5×10^4	6.8×10^5	8.4×10^4	3.9×10^6

The worst case results at 2.16K are somewhat marginal for the first ratio. This ratio, however, depends exponentially on E_x and thus

increases with increasing stress. The progression of values of this ratio that correspond to the data of Chapter III are 0.51, 1, 2.3, 5.8, 8, 8.7, 15, Equilibrium thermodynamic calculations should be reasonably accurate at several of the higher stresses. In spite of these results, the decay kinetics of the FE gas at 2.16K are not significantly altered, even in the case where $n_c^2 = 0.5(n_x/\tau_x)$. This can be seen clearly by looking at the kinetic equations (II.1) and (II.2). The rate at which FC combine to form FE depends quadratically on n_c . This dependence acts to keep n_c relatively close to the thermal equilibrium concentration (within an order of magnitude or so). At the EHL threshold at 2.16K, equilibrium thermodynamics [Eqs. (II.11), (II.12)] predicts $n_x/n_c \approx 1.7 \times 10^3$. Even if n_c were to increase an order of magnitude, which given the quadratic behavior of the $e+h \rightarrow FE$ reaction would be hard to do, the bulk of the excited electrons and holes would still be in the form of FE's. The FE's would still dominate the behavior of the FC-FE system. This is true even for n_x an order of magnitude or so below the EHL threshold value of n_x .

This result justifies Eq. (III.12) in Chapter III, which assumes that all FE loss mechanisms can be incorporated into a decay term of the form n_x/τ_x . Here τ_x is in general a function of n_x . It should not depend on the history of the system (e.g. steady state vs pulsed photoexcitation). The free carrier densities for the first several stresses in Chapter III may depend on the kinetics and thus the past history of the system. Because n_c is much smaller than n_x , FC decay is negligible for reasonable FC lifetimes and can be neglected.

Consider a FE-FC system confined to a strain-induced potential well. Assume the system is well characterized by equilibrium thermodynamics.

The FE and FC spatial distributions can be calculating by requiring the chemical potentials for a FE And for an unbound e-h pair to be independent of position and equal to each other. The resulting distributions will be accurate if the FE diffusion length

$$L_x = \sqrt{D_x \tau_x} \quad (\text{II.17})$$

is large compared to the spatial extent of the FE gas. Here D_x is the FE diffusion length. For a parabolic strain well [see Eqs. (I.4), (I.5)] the spatial extent (Δr) of the FE gas is characterized by

$$\alpha(\Delta r)^2 = k_B T \quad (\text{II.18})$$

or

$$\Delta r = \sqrt{k_B T / \alpha} \quad (\text{II.19})$$

So we must have

$$\frac{L_x}{\Delta r} \gg 1 \quad (\text{II.20})$$

or

$$D_x \gg \frac{k_B T}{\tau_x \alpha} \quad (\text{II.21})$$

Using typical values of τ_x (~ 1 ms) and α (~ 3 meV/mm) and a temperature $T = 2.17$ K, this means $D_x \gg 0.62 \text{ cm}^2 \text{ s}^{-1}$. The FE diffusion constant will be dealt with in a later section. The following discussion assumes that Eq. (II.20) is valid.

The electron and hole chemical potentials are

$$\mu_e = k_B T \ln(n_e V_{Qe}) + \alpha_e r^2 \quad (\text{II.22})$$

$$\mu_h = k_B T \ln(n_h V_{Qh}) + \alpha_h r^2 \quad (\text{II.23})$$

where the quantum volumes for electrons V_{Qe} and holes V_{Qh} are defined in a manner analogous to Eq. (II.10).

The FE chemical potential is

$$\mu_x = k_B T \ln(n_x V_{Qx}) + \alpha_{FE} r^2 - E_x \quad (\text{II.24})$$

Equating $\mu_x = \mu_e + \mu_h$ yields

$$n_x = n_e n_h \left[\frac{V_{Qe} V_{Qh}}{V_{Qx}} e^{\frac{E_x + (\alpha_e + \alpha_h - \alpha_{FE}) r^2}{k_B T}} \right] \quad (\text{II.25})$$

The degeneracies γ_e , γ_h , and γ_x are all equal to one ($-\sigma \geq 5 \text{ kgf/mm}^2$) and have been neglected. Charge neutrality assures $n_e = n_h \equiv n_c$. Because the binding of an electron and a hole doesn't effect the indirect band gap we have $\alpha_{FE} = \alpha_e + \alpha_h$. The effect of the binding energy E_x is accounted for explicitly in E_x which is a function of stress and thus of r . Thus Eq. (II.25) becomes

$$n_x = n_c^2 \left[\frac{V_{Qe} V_{Qh}}{V_{Qx}} e^{\frac{E_x}{k_B T}} \right] \equiv \frac{n_c^2}{K(T)} \quad (\text{II.26})$$

which is precisely Eqs. (II.11) and (II.12). The strain well does not, to this approximation, alter the equation describing local FE-FC chemical equilibrium.

Requiring the FE chemical potential [Eq. (II.24)] to be independent of position determines the spatial distribution of FE. If E_x is expanded as a function of r about the well bottom, the quadratic term $\left[\frac{d^2 E_x}{dr^2} \Big|_{r=0} \right] r^2$ can be incorporated with $\alpha_{FE} r^2$ to form an effective curvature $\alpha = \alpha_{FE} - \left[\frac{d^2 E_x}{dr^2} \Big|_{r=0} \right]$ for FE in the strain well. The contribution due to E_x is approximately $-0.1 \alpha_{FE}$. The resulting FE distribution is

$$n_x(r) = n_x(0) e^{-\frac{\alpha r^2}{k_B T}} \quad (II.27)$$

In reality α will be different for the three axes of the crystal [see Eq. (I.4)]. Experimentally these α can be determined by fitting spatial profiles of FE luminescence. The FE luminescence emanating per unit volume from a given point is

$$I_x = \frac{n_x(x, y, z)}{\tau_{rx}} \quad (II.28)$$

where τ_{rx} is the FE radiative lifetime. Assuming τ_{rx} changes negligibly for FE within $k_B T$ of the well bottom, a spatial scan of the luminescence can be interpreted as a spatial scan of the FE density. In practice the image of the strain well is scanned across the slit of the spectrometer by translating the output lens [see Fig. I.7] with the spatial resolution limited by the width of the spectrometer slit. The well parameter α corresponding to the axis along which the luminescence was scanned is determined by fitting a slit convolved Eq. (II.27):

$$I_x(y) \propto \left\{ \operatorname{erf}\left[\left(y + \frac{s}{2}\right)\sqrt{\alpha}\right] - \operatorname{erf}\left[\left(y - \frac{s}{2}\right)\sqrt{\alpha}\right] \right\} \quad (\text{II.29})$$

where s is the width of the image of the spectrometer slit as perceived from the strain well. Figure II.1 shows a FE spatial scan and the fit (triangles) of Eq. (II.29). The well parameter found was $\alpha = 2 \text{ meV/mm}^2$ along a $\langle 1\bar{1}0 \rangle$ crystal axis perpendicular to the $\langle 111 \rangle$ stress axis.

FE-FC System: Decay Mechanisms

In this section measurements of the total FE luminescence intensity emanating from a strain well are discussed. In order to compare theory to experiment the equations describing the system must be integrated over the volume of the well.

The sum of the two rate equations (II.1) and (II.2) is

$$\frac{d}{dt} (n_x + n_c) = g - \frac{n_x}{\tau_x} - \frac{n_c}{\tau_c} \quad (\text{II.30})$$

This result combined with Eq. (II.26), which relates n_c to n_x , yields a differential equation in the variable n_x :

$$\frac{d}{dt} \left(n_x + \sqrt{n_x K(T)} \right) = g - \frac{n_x}{\tau_x} - \frac{\sqrt{n_x K(T)}}{\tau_c} \quad (\text{II.31})$$

where the equilibrium constant $K(T)$ is defined in Eqs. (II.26) and (II.12).

Equation (II.31) must be integrated over the volume of the strain well using Eq. (II.27). Assuming $k_B T \ll$ well depth, the total number of FE in the strain well is:

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Fig. II.1 Fit of an exciton spatial distribution measured at 2.9K to Eq. (II.29). The resulting curvature is $\alpha = 2 \text{ meV/mm}^{-2}$. The position axis is along a crystal $\langle 1\bar{1}0 \rangle$ axis at right angles to the $\langle 111 \rangle$ stress axis. Sample CR50.

$$N_x = \int n_x(r) d^3r = \left(\frac{\pi k_B T}{\alpha} \right)^{3/2} n_x(0) \quad . \quad (II.32)$$

Similarly, the total number of FC in the strain well is:

$$\begin{aligned} N_c &= \sqrt{K(T)} \int n_x^{1/2}(r) d^3r \\ &= \left(\frac{2\pi k_B T}{\alpha} \right)^{3/2} \sqrt{n_x(0) K(T)} \\ &= \left(\frac{4\pi k_B T}{\alpha} \right)^{3/4} \sqrt{K(T)} N_x^{1/2} \\ &\equiv \sqrt{AN_x} \end{aligned} \quad (II.33)$$

where

$$A \equiv a(k_B T)^3 e^{-\frac{E_x}{k_B T}} \quad (II.34)$$

and

$$a \equiv \left(\frac{2m_e m_h}{\alpha \hbar^2 m_x} \right)^{3/2} \quad . \quad (II.35)$$

Thus the integral of Eq. (II.31) is

$$\frac{d}{dt} (N_x + \sqrt{AN_x}) = g - \frac{N_x}{\tau_x} - \frac{\sqrt{AN_x}}{\tau_c} \quad . \quad (II.36)$$

Solutions to this equation for steady state and pulsed excitation can be compared to experimental measurements of FE luminescence intensity (I_x). This assertion assumes that the FE radiative decay rate τ_{rx}^{-1} does not vary significantly for the bulk of the FE in the well. That τ_{rx}^{-1} should vary for FE in the strain well follows from

the changing properties of the FE with stress. There are a range of stresses accessible to excitons several $k_B T$ from the well bottom. I will show that these variations in τ_{rx}^{-1} are small. The radiative decay rate τ_{rx}^{-1} is proportional to the probability density for an electron at the site of a hole: $|\psi_x(0)|^2$. Here ψ_x is the FE wave function. A simple hydrogenic model for the FE (see the Photoexcitations in Ge section of Chapter I) predicts

$$|\psi_x(0)|^2 = \frac{1}{(\pi a_x^3)} \propto E_x^3. \quad (II.37a)$$

So

$$\frac{1}{\tau_{rx}} \propto E_x^3. \quad (II.37b)$$

The FE binding energy is seen to vary with stress [see Fig. III.5]. From this information I calculate that the average τ_{rx}^{-1} at $T=2.16K$ is about 3% faster than the rate corresponding to the bottom of the well. At 4.7K the average rate is about 6% faster than that for the well bottom. These variations are not large enough to significantly effect the comparison of I_x to N_x . A comment concerning the FC-FE chemical equilibrium constant $K(T)$ is in order here [see Eq. (II.26)]. This constant has an exponential dependence on $E_x/k_B T$. In the worst case (lowest stress, highest temperature) this results in a 20% smaller value of N_c with N_x essentially unchanged. This does not appreciably effect the discussion in the previous section where these considerations were neglected.

Consider Eq. (II.36) for steady state excitation:

$$g = \frac{N_x}{\tau_x} + \frac{\sqrt{AN_x}}{\tau_c} \quad (II.38)$$

where $N_c = \sqrt{AN_x}$. Here A [see Eq. (II.34)] is strongly dependent on temperature, and τ_x and τ_c may also depend on temperature. Figure II.2 shows the results of a steady state experiment in which I_x was measured at a number of temperatures for two different carrier generation rates: g_0 and $2g_0$. These I_x , measured at different temperatures, are accurately proportional to the number of FE N_x because the temperatures used ($T < 4.8K$) are too low for thermal populations of band edge phonons to effect the indirect gap radiative decay rate. Also, the temperature effect discussed in the previous paragraph is small. The generation rate g_0 was three-fourths of that needed to create the EHL at 2.16K. The $-\sigma \approx 8.5 \text{ kgf/mm}^2$ strain well had a curvature $\alpha \approx 2 \text{ meV/mm}^2$ (measured along a $\langle 1\bar{1}0 \rangle$ axis perpendicular to the $\langle 111 \rangle$ stress axis).

Figure II.2 shows I_x leveling off at low temperatures and decreasing rapidly at high temperatures. This low temperature behavior is consistent with FE decay dominating FC decay ($N_x/\tau_x \gg N_c/\tau_c$). In this case Eq. (II.38) reduces to

$$N_x = g\tau_x \quad (II.39)$$

Furthermore, the ratio of the FE luminescence intensities $I_x(2g_0)/I_x(g_0)$ approaches two asymptotically as the temperature is lowered (see Fig. II.3). Both the temperature independence of I_x at low temperatures and the linear dependence of I_x on g argue that Eq. (II.39), with τ_x weakly dependent on temperature, accurately describes the system.

The high temperature solution to the quadratic equation (II.38),

$$N_x = \frac{(g\tau_c)^2}{a} \frac{e^{\frac{E_x}{k_B T}}}{(k_B T)^3} \quad (II.40)$$

Fig. II.2 Free exciton (FE) luminescence intensity I_{FE} is plotted as a function of T^{-1} for two excitation powers: g_0 (lower data) and $2g_0$ (upper data). The circles are experimental data points. The lower solid line is the best fit of the data to Eq. (II.41). The upper solid line is plotted using the fitting parameters from the lower curve. Sample CR50. XBL 8212-12218

XBL 7212-12216

Fig. II.3 The ratio of the free exciton (FE) luminescence intensities I_{FE} at the excitation powers $2g_0$ and g_0 are plotted for several temperatures. These ratios are taken from the data of Fig. II.2. Note the ratio approaches two asymptotically as the temperature is lowered. At the higher temperatures the ratio reaches four. More recent data (like that in Fig. II.2) that is not yet fully analyzed show intensity ratios that asymptotically approach values consistent with a quadratic dependence of I_{FE} on g at high temperatures. The larger error bars for higher temperatures are due to smaller signals (see Fig. II.2). Sample CR50.

corresponds to FC decay dominating FE decay ($N_c/\tau_c \gg N_x/\tau_x$). Notice that this relation predicts that N_x depends quadratically on g . The ratio of intensities $I_x(2g_0)/I_x(g_0)$ plotted in Fig. II.3 reaches four at the highest temperatures that could safely be reached by overpressuring our liquid helium cryostat. A value of four for this ratio is consistent with a quadratic dependence of I_x on g . Auger processes can also give rise to nonlinear relations between N_x and g . However these relations would yield $I_x(2g_0)/I_x(g_0)$ ratios less than two (e.g. $2^{1/3} \approx 1.26$). Another experimental observation that supports this picture is that the temperature ($\sim 4K$) marking the transition between the high and low temperature regimes increases with increasing excitation power. [Higher excitation powers increase N_x/N_c and thus $(N_x/\tau_x)/(N_c/\tau_c)$.]

Difficulties arise, however, when quantitative agreement is sought between experiment (Fig. II.2) and the solution to Eq. (II.38):

$$N_x = g\tau_x [(1+p) - \sqrt{(1+p)^2 - 1}] \quad (II.41)$$

where

$$p \equiv \left(\frac{a\tau_x}{2g\tau_c^2} k_B^3 \right) T^3 e^{-\frac{E_x}{k_B T}} \quad (II.42)$$

The lower solid line in Fig. II.2 is the best fit of Eq. (II.41) to the data for the e-h pair generation rate g_0 ($\sim 2 \times 10^{11}$ e-h pairs/sec).

The upper curve uses the same parameters except $g = 2g_0$. For $\tau_x \approx 1$ ms the values for the best fit correspond to $E_x = 5.4$ meV and $\tau_c \sim 30$ μ s.

This value of E_x is larger than the spectroscopically measured value [$E_x(8.5 \text{ kgf/mm}^2) = 3.35$ meV - see Fig. III.5]. Schowalter et al.¹² have

independently noted similar results. (Other portions of the work in this section^{13,14} have been done independently by Schowalter et al.) They found the best fit E_x to increase with the well curvature α . They also claim that the best fit E_x is not strongly dependent on stress. They concluded that none of the decay models they considered adequately described the temperature dependence of the FE decay.

It is possible that a component of the FC decay rate is thermally activated. This could potentially remove the above discrepancy between the measured activation energy and the spectroscopically measured FE binding energy E_x . A possible mechanism for this is thermally activated decay on traps (shallow, ~ 10 meV deep traps). However, since differently shaped strain wells in the same crystal yield different activation energies, some other mechanism seems more likely. It is possible, though, that differing strain gradients might in some way effect the activation energy. Another possible mechanism involves FC recombination at the crystal surface^{13,15} or in low stress regions of the crystal where decay is rapid. The FC concentrations may be low at the top of the well (the surface with the lowest potential energy), but the decay rates are correspondingly fast.

The distribution of FC in parabolic strain well follows from Eqs. (II.26) and (II.27). It is

$$n_c(r) = n_c(0) e^{-\frac{(\alpha/2)r^2}{k_B T}} \quad (II.43)$$

About 2% of the FC in a parabolic strain well lie higher in the well than $5 k_B T$. At 4K this corresponds to 1.7 meV above the well bottom. This is quite comparable to the following upper limit on the experimental

well depth for the experiment of Fig. II.2: In this experiment the well curvature along a $\langle 1\bar{1}0 \rangle$ axis perpendicular to the $\langle 111 \rangle$ stress axis was $\alpha \approx 2 \text{ meV/mm}^2$. The distance from well bottom to crystal surface along this $\langle 1\bar{1}0 \rangle$ direction was 1.4 mm. The quadratic FC potential well $U = \alpha r^2/2$ [see Eq. (II.43)] cuts through this surface 2 meV above the well bottom. In reality the upper reaches of the well flare out to meet the crystal surface.¹⁶ In addition, the potential energy at the crystal surface under the stressing plunger is probably lower [see Fig. I.5].¹⁶ Thus the depth of the well for FC could be on the order of 1 meV. For $T = 4\text{K}$, which is approximately where the data in Fig. II.2 switches from one regime [Eq. (II.39)] to the other [Eq. (II.40)], this would imply substantial FC densities at the crystal surfaces.

I will assume the following temperature dependence for the surface decay of FC:

$$\frac{1}{\tau_c} \propto \exp \left[-\frac{W_c}{k_B T} \right]. \quad (\text{II.44})$$

Here the FC activation energy for decay, W_c , is identified with the depth of the well. If the FC diffusion length $L_c = \sqrt{D_c \tau_c}$ is much longer than the distance from well bottom to surface then the decay process is not transport limited. Estimates at the end of this chapter indicate that the above steady state experiment is not transport limited. Equilibrium thermodynamics arguments should suffice.

Examination of Eq. (II.40) suggests that twice the FC activation energy, $2W_c$, plus the FE binding energy E_x (3.35 meV; see Fig. III.5) should be equal to the measured activation energy ϕ :

$$\phi = E_x + 2W_c. \quad (\text{II.45})$$

This implies $W_c \approx 1$ meV, which is consistent with the value estimated for W_c in the above discussion.

It is now accepted that the strain field of an inhomogeneously stressed crystal can be thought of as a superposition of an inhomogeneous strain (strain well) and a uniform strain. Indeed the above argument concerning well depth indicates that there must be some residual shear stress at the crystal surface. For a strain well with a given maximum stress, the depth of the strain well relative to the surface should decrease as the well curvature α decreases. As the curvature approaches zero the stress is uniform and the well depth is zero. For a given well curvature α it is reasonable to expect a given well depth, relatively independent of stress. It is interesting to note that Schowalter et al.¹² measured the activation energy in a variable stress experiment. They found the activation energy to be the same for wells with 7.8 and 9.8 meV indirect band gap shifts. For the model proposed in this section this behavior corresponds to the well curvature remaining unchanged, and the added stress increasing the uniform strain field. The lowest stress (4.8 meV band gap shift) at which they¹² measured an activation energy ($\phi \approx 8.8$ meV) was for a steep well of curvature $\alpha = 18$ meV/mm². For such a steep low stress well the component of uniform strain should be small. Thus we should have $2W_c \approx 4.8$ meV. With $E_x \approx 3.65$ meV [from Fig. III.5], the activation energy from Eq. (II.45) is $\phi = 8.45$ meV. This prediction is in good agreement with their measured result $\phi = 8.8$ meV. At a higher stress (5.5 meV band gap shift) they measured an activation energy $\phi = 5.8$ meV for a shallower well $\alpha = 8.8$ meV/mm². From this measured ϕ and using $E_x \approx 3.5$ meV [from Fig. III.5], Eq. (II.45) yields $2W_c \approx 2.3$ meV.

This is consistent with an approximately 2.5 meV band shift uniform strain.

Thus it appears all the measurements above can be understood in the context of FC decay at the crystal surface.

We have also measured the decay of FE luminescence. For pulsed excitation, Eq. (II.36) can be rewritten

$$\begin{aligned} \frac{dN_x}{dt} &= - \left(\frac{1 + \frac{\tau_x}{\tau_c} \sqrt{\frac{A}{N_x}}}{1 + \frac{1}{2} \sqrt{\frac{A}{N_x}}} \right) \frac{N_x}{\tau_x} \\ &= - \left(\frac{1 + \frac{N_c/\tau_c}{N_x/\tau_x}}{1 + \frac{1}{2} \frac{N_c}{N_x}} \right) \frac{N_x}{\tau_x} \end{aligned} \quad (II.46)$$

Clearly if $N_c \ll N_x$ and $N_c/\tau_c \ll N_x/\tau_x$, the solution to this equation corresponds to an exponential FE decay with a lifetime τ_x . This limiting case corresponds to low temperatures. A trend toward exponential decay is observed experimentally (see Fig. II.4) as the temperature is lowered. An opposite extreme limit occurs where $N_c \gg N_x$ and $N_x/\tau_x \gg N_c/\tau_c$. In this limit the FE decay is exponential with a lifetime of $\tau_c/2$. Because this limit occurs at temperatures too high or at immeasurably low FE concentrations, it has not been seen. In between these limits the decay is non-exponential (unless $\tau_c = 2\tau_x$). The bracketed quantity in Eq. (II.46) can be incorporated with τ_x into an effective FE decay time constant:

Fig. II.4 Luminescence decay curves measured for a strain confined free exciton (FE) gas. Note the striking non-exponential decay. The FE decay faster as their numbers decrease. Curves (a) and (b) were measured at the same temperature (3.2K) for two different stresses: (a) $\sigma = -10 \text{ kgf/mm}^2$; (b) $\sigma = -7.5 \text{ kgf/mm}^2$. Curves (b) and (c) were measured at the same stress but at different temperatures: (b) $T = 3.2\text{K}$; (c) $T = 4.7\text{K}$. Sample CR50.

$$\tau_{\text{eff}} = \tau_x \left(\frac{1 + \frac{1}{2} \sqrt{\frac{A}{N_x}}}{1 + \frac{\tau_x}{\tau_c} \sqrt{\frac{A}{N_x}}} \right) \quad (\text{II.47})$$

where $\sqrt{A/N_x} = N_c/N_x$. As the decay proceeds N_x decreases and τ_{eff} decreases (increases) if $\tau_c < 2\tau_x$ ($\tau_c > 2\tau_x$). Because τ_{eff} is always observed to decrease as N_x decreases we conclude that $\tau_c < 2\tau_x$ for temperatures $2.16 \leq T \leq 4.8\text{K}$. Further note that Eq. (II.47) for τ_{eff} decreases monotonically from τ_x to $\tau_c/2$. This means that $\tau_c/2$ should be smaller than any τ_{eff} measured. At 2.16K the lowest limit that can be found from any of our stress data is $\tau_c \leq 1.6$ ms. At high temperatures (4.7K) limits as low as $\tau_c \leq 100$ μs have been noted.

Figure II.5 shows measurements of τ_{eff} as a function of T^{-1} for three different values of I_x (or N_x). All measurements were made on the same strain well ($-\sigma \approx 6.5$ kgf/mm²). The τ_{eff} for all three I_x level off and approach the same value for low temperatures. This is consistent with an approach to exponential decay. The effective lifetime is thermally activated.

The solution to the FE decay equation (II.46) is a transcendental equation in N_x :

$$N_x = N_{x_0} e^{-\frac{t-t_0}{\tau_x}} \left(\frac{1 + \sqrt{\frac{A}{N_{x_0}}} \frac{\tau_x}{\tau_c}}{1 + \sqrt{\frac{A}{N_x}} \frac{\tau_x}{\tau_c}} \right)^{2 - \frac{\tau_c}{\tau_x}} \quad (\text{II.48})$$

Due to the multitude of fitting parameters the only reasonably trustworthy result from decay curve fits is τ_x . We noted a monotonic increase in τ_x with stress from τ_x (-7.6 kgf/mm²) = 1.29 ms to τ_x (12 kgf/mm²) = 1.55 ms

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Fig. 11.5 The decay rate τ_{eff}^{-1} of the free exciton luminescence (I_{FE}) was measured as a function of temperature for three values of I_{FE} . The lifetimes τ_{eff} are plotted vs T^{-1} . The values of I_{FE} corresponding to the symbols are in the ratios 10 (Δ) : 5 (o) : 1 ($\square$). The lifetime τ_{eff} is clearly thermally activated. All measurements were made using the same strain well. Sample CR50.

for a series of FE decay measurements made at 3.14K. Within the combined errors, these τ_x scale with the measured FE binding energies [see Fig. III.5] according to Eq. (II.37) [a scaling law for radiative decay rates]. The magnitudes are in general agreement with the τ_{rx} displayed in Table III.5.

In summary: The rate of FE decay is observed to increase as the density of FE decreases (FE die of loneliness). This rules out all Auger mechanisms for FE decay; Auger rates decrease with decreasing particle concentrations. Steady state excitation measurements at low temperatures are consistent with FE decay being the dominant e-h pair loss mechanism. At higher temperatures the FE luminescence intensity approaches a quadratic dependence on excitation power. This is consistent with the ionization of FE with increasing temperature and the subsequent dominance of FC decay over FE decay. Both steady state and decay measurements of FE luminescence indicate the existence of a thermally activated FC decay mechanism. The activation energy attributed to FC decay is consistent with the estimated depth of the strain well. The decay of FC at the crystal surface is proposed as a possible explanation of the thermally activated decay. This model makes the assumption that either FE decay at the surface is negligible or does not become the dominant mode of FE decay until higher temperatures. It is also assumed that the FC recombination rate in bulk Ge is not fast. Finally, at high temperatures where $k_B T$ is on the same order as the well depth, details of the solutions which relied on a parabolic well will vary. Analysis of newer data that could require a generalization of the contents of this section is in progress.

Strain Confined Free Exciton — Electron-Hole Liquid System

In this section I will discuss the equilibrium thermodynamics of a FE gas-EHL droplet system confined to a strain induced potential well. Temperatures will be assumed low enough that FC concentrations can be neglected. The EHL is a very compressible liquid.^{17,18} Different portions of an EHL in a non-uniform potential will differ in density. For the slowly varying potentials and small droplet sizes dealt with in this thesis compression effects are small. I will assume negligible compression in the discussion below. Other considerations involve the surface tension of the droplet and the effects of FE gas pressure on the equilibrium FE density. The pressure of the FE gas has been discussed in the Ph.D. thesis of John E. Furneaux.¹⁹ He found that the FE gas pressure has a negligible effect on the character of the system for all temperatures and stresses at which the FE gas and EHL droplet can coexist.

The effects of surface tension have their largest effect for large surface-to-volume ratios (i.e. for small drops). I will show that surface energy effects are negligible for the smallest measureable droplet size of Chapter III ($R_d \sim 20 \mu\text{m}$). Laplace's equation $\Delta p = 2\sigma/R_d$ gives the additional pressure inside a droplet of radius R_d due to the surface tension σ . The surface tension causes a difference in the Gibbs free energy per particle between the FE gas and the EHL of

$$\Delta\mu = \frac{\Delta p}{n_d} = \frac{2\sigma}{R_d n_d} \quad . \quad (\text{II.49})$$

I will show that $\Delta\mu \ll \phi$ where ϕ is the condensation energy of a FE relative to the EHL. The special case $\phi = \Delta\mu$ corresponds to the critical radius R_c of the droplet. For radii $R_d < R_c$ the droplet is

energetically unstable. Parameters for highly stressed Ge will be used to get a worst case estimate of $\Delta\mu$. The surface tension scales with temperature as

$$\sigma = w \left[1 - \left(\frac{T}{T_c} \right)^2 \right] \quad (\text{II.50})$$

for small T/T_c . I will use the zero stress value of $w = 2.4 \text{ ergs cm}^{-2}$ scaled by the ratio of EHL binding energies for high stress and zero stress. For 2.16K, I find $\sigma \approx 10^{-4} \text{ erg cm}^{-2}$. This implies $\Delta\mu = 2.5 \times 10^{-3} \text{ meV}$ for $R_g = 20 \text{ }\mu\text{m}$. This is not a significant fraction of the high stress value of $\phi \approx 0.5 \text{ meV}$. The critical radius $R_c \approx 0.1 \text{ }\mu\text{m}$, far smaller than can be seen experimentally. As is expected from these calculations, we have never seen hysteresis effects in a strain confined FE-EHL system.

With these considerations aside, the characteristics of a FE gas - EHL droplet system in thermodynamic equilibrium can be described by equating their chemical potentials and requiring them to be independent of position.

We choose the zero of energy such that the FE and EHL chemical potentials are:

$$\mu_x(r) = k_B T \ln(n_x V_{Qx}) + \alpha r^2, \quad r \geq R_g \quad (\text{II.51})$$

$$\mu_g(r) = -\phi + \alpha r^2, \quad r \leq R_c \quad (\text{II.52})$$

where ϕ is the condensation energy of a FE relative to the EHL and the FE quantum volume V_{Qx} is given by Eq. (II.10). At $r = R_g$ the FE and EHL chemical potentials must be equal. This condition determines

the FE concentration in equilibrium with the EHL at $r = R_d$:

$$n_x(R_d) = \frac{e^{-\frac{\phi}{k_B T}}}{V_{Qx}} \quad (II.53)$$

This fixes μ_x at one value of r . Requiring μ_x in Eq. (II.51) to be independent of position determines the spatial distribution of FE outside of a droplet of radius R_d :

$$n_x(r) = n_x(R_d) e^{-\frac{\alpha(r^2 - R_d^2)}{k_B T}} \quad (II.54)$$

Assuming $k_B T$ is much less than the depth of a real strain well, the total number of FE in the strain well is given by

$$\begin{aligned} N_x(R_d) &= 4\pi \int_0^\infty n_x(r) r^2 dr \\ &= n_x(R_d) \left(\frac{\pi k_B T}{\alpha} \right)^{3/2} \left[e^{U^2} \operatorname{erfc}(U) + \frac{2U}{\sqrt{\pi}} \right] \end{aligned} \quad (II.55)$$

where $U = R_d \sqrt{\alpha/(k_B T)}$. Assuming the FE radiative decay rate τ_{rx}^{-1} is constant within several $k_B T$ of the well bottom [see discussion of Eq. (II.37b)], the result, Eq. (II.55), should be proportional to the measured FE luminescence. Note that $N_x(R_d) \approx \text{constant}$ for R_d small. This is in accordance with the following intuitive argument: The spatial extent of the FE gas in the bottom of a strain well is characterized by $\alpha(\Delta r)^2 = k_B T$, or $\Delta r = \sqrt{k_B T/\alpha}$. Putting a small EHL droplet in the well bottom ($R_d \ll \Delta r$) fixes n_x at the well bottom according to Eq. (II.53). Upon increasing R_d upward from zero the spatial distribution of FE will be perturbed only when the radius of the droplet starts to

approach Δr . Until then $N_x \approx \text{constant}$. This behavior is clearly evident in the first two figures of Chapter III. For R_d large, $N_x \propto R_d$. To see this intuitively, consider that the FE gas extends a distance above the droplet determined by $\alpha(r^2 - R_d^2) \approx k_B T$. For R_d large and $k_B T / \alpha$ small this yields a skin of FE around the droplet with a thickness $\Delta r \approx k_B T / (\alpha R_d)$. Multiplying by the surface area results in $N_x \propto R_d$.

Free Exciton Diffusion

The two most important scattering mechanisms that limit the diffusion of FE in ultra-pure liquid helium temperature Ge are FE-FE scattering (self diffusion) and scattering with thermal LA phonons.

The FE diffusivity D_x is given in terms of a FE scattering time τ by

$$D_x = \frac{k_B T}{m_x} \tau \quad (II.56)$$

Self Diffusion. The mean time between FE scatterings is given by $\tau = \ell / \bar{v}$ where

$$\ell = \frac{1}{\sqrt{2} n_x \sigma} \quad (II.57)$$

is the mean free path between FE collisions and

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m_x}} \quad (II.58)$$

is the average speed of a FE. Here σ is the total cross section for FE-FE scattering, n_x is the FE density, and $m_x = 0.436 m_0$ is the FE translational mass.^{4,5} Thomas et al¹¹ have determined an effective

FE-FE collision radius of $220 \pm 80 \text{ \AA}$ from the collision broadening of the FE spectral lineshape. A radius of $220 \text{ \AA}$ predicts that the self diffusion of FE is substantial for the conditions of the diffusion experiment discussed in Chapter V. Because the diffusion profiles measured in Chapter V are independent of excitation power (i.e. of FE density) I believe that the correct collision radius is at least on the low end of their error limits. This is close to the FE Bohr radius a_x which I will use as the collision radius in the discussion below.

Assuming $\sigma = \pi a_x^2$ the diffusivity for the self scattering of FE at zero stress is

$$D_{xs} = (3 \times 10^{16} \text{ cm}^{-1} \text{ s}^{-1} \text{ K}^{-1/2}) \frac{T^{1/2}}{n_x} \quad (II.59)$$

FE Diffusion: Scattering by LA phonons. The mean scattering time for FE with LA phonons is²⁰

$$\tau_p = \frac{2\sqrt{2}}{3} \pi \frac{\rho s^2 \hbar^4}{m_x^{3/2} E^2} \frac{1}{(k_B T)^{3/2}} \quad (II.60)$$

For Ge, with $m_x = 0.436 m_0$, density $\rho = 5.32 \text{ g cm}^{-3}$, sound velocity $s = 1.6 \times 10^5 \text{ cm s}^{-1}$ and deformation potential $E = 2 \text{ eV}$,²¹ this yields

$$\tau_p \approx (3.8 \times 10^{-9} \text{ K}^{3/2} \text{ s}) T^{-3/2} \quad (II.61)$$

Measurements by Tamor and Wolfe²² for τ_p in Si found good agreement with Eq. (II.60). Tamor and Wolfe²³ have measured $\tau_p(2K) \approx 0.53 \pm 0.07 \text{ ns}$ for the EHL in Ge. The equivalence of τ_p for the EHL and τ_p for the FE has been demonstrated convincingly [p.143 of Ref. II.6]. This implies

Eq. (II.61) is a factor of 2.5 high. Measurements of τ_p for electrons and holes separately have also been made. Hensel and Suzuki²⁴ have measured $\tau_p(1.8K) \sim 5 \times 10^{-10} s$ for holes, while Ito et al²⁵ have measured $\tau_p(1.8K) \sim 10^{-9} s$ for electrons. These measurements are in the same ratio as their density of states masses^{6,7} to the 3/2 power. This is expected from Eq. (II.60). However, the magnitudes predicted by Eq. (II.60) are a factor of 4.4 high. I take the measurement of τ_p by Tamor and Wolfe²³ as the most accurate value, so I will use the τ_p of Eq. (II.61) scaled down by 2.5. With this scaled down τ_p the predicted FE diffusivity due to scattering with LA phonons is:

$$D_{xp} = [(530 \pm 70) \text{ cm}^2 \text{ s}^{-1} \text{ K}^{1/2}] T^{-1/2} . \quad (\text{II.62})$$

To combine diffusivities due to different scattering mechanisms, the scattering rates (τ^{-1}) are added. Thus diffusivities [see Eq. (II.56)] add in reciprocal:

$$\frac{1}{D_x} = \frac{1}{D_{xs}} + \frac{1}{D_{xp}} \quad (\text{II.63})$$

or

$$D_x = \left[[(1.9 \pm 0.25) \times 10^{-3} \text{ cm}^{-2} \text{ s K}^{-1/2}] T^{1/2} + (3.3 \times 10^{-17} \text{ cm s K}^{1/2}) n_x T^{-1/2} \right]^{-1} . \quad (\text{II.64})$$

Pokrovskii and Svistunova²⁶ claim to have measured $D_x = 1500 \text{ cm}^2 \text{ s}^{-1}$ at 3K. The largest possible value for D_x from Eq. (II.64) corresponds to $D_x = D_{xp} = 306 \text{ cm}^2 \text{ s}^{-1}$, almost an order of magnitude smaller than their result. In their experiment they measured the diffusion length L_x and the FE lifetime τ_x . They inferred $D_x = L_x^2 / \tau_x$. The EHL lifetime

reported was a factor of two low. Furthermore, I am not convinced that the ionizing electric fields they used to make their measurements didn't interfere with the processes they were trying to measure. For these reasons I discount their measurements of D_x .

I have measured D_x at 4.2K by direct imaging of FE diffusion profiles.¹⁵ The experiment is discussed in Chapter V of this thesis. The value $D_x(4.2K) = 250-300 \text{ cm}^2\text{s}^{-1}$ that I reported verbally⁵¹ is consistent with the phonon scattering diffusivity $D_{xp} = (260 \pm 35) \text{ cm}^2\text{s}^{-1}$ predicted from Eq. (II.62). The diffusion profiles were consistent with those expected for diffusion mediated by LA phonons, but it is difficult to rule out the existence of a small component of D_{xs} . The maximum D_{xs} that Eq. (II.59) predicts for this experiment is given by the following considerations: The maximum FE density is determined from a calorimetry measurement of the laser pulse energy, and an effective volume occupied by the FE. An effective volume can be determined by examining the spatial extent of the first diffusion profiles. This yields a rough estimate for the peak FE concentration of $n_x \sim 10^{14} \text{ cm}^{-3}$. The value of D_{xs} predicted by Eq. (II.59) is $D_{xs}(4.2K) = 615 \text{ cm}^2\text{s}^{-1}$. Combined with $D_{xp}(4.2K) = 260 \text{ cm}^2\text{s}^{-1}$ from Eq. (I.81) the total diffusivity is predicted to be $D_x = 183 \text{ cm}^2\text{s}^{-1}$. This is somewhat low compared to the value determined in Chapter V. This would seem to indicate that there is room for improvement in the FE-FE scattering cross section appropriate for the self diffusion of FE.

It is of interest to estimate D_x for excitons in stressed Ge. For the work of Chapter III it is of critical importance that the FE

diffusion length L_x be much greater than the spatial extent of the FE gas Δr .

The phonon contribution $D_{xp}(2.16K) = 360 \text{ cm}^2 \text{ s}^{-1}$ where Eq. (II.62) has been used. The highest FE density occurs for the highest stress. Using Eqs. (II.9) and (II.10), and $\phi \sim 0.5 \text{ meV}$, I estimate $n_x \sim 10^{14} \text{ cm}^{-3}$. This results in $D_{xs} \sim 467 \text{ cm}^2 \text{ s}^{-1}$ and $D_x \sim 200 \text{ cm}^2 \text{ s}^{-1}$. So for FE in this strain well D_x should vary from $200 \text{ cm}^2 \text{ s}^{-1}$ for high FE densities near the droplet to $360 \text{ cm}^2 \text{ s}^{-1}$ for the lower densities of FE higher in the well. For $\tau_x \approx 790 \mu\text{s}$ and a well curvature $\alpha \approx 3 \text{ meV mm}^{-2}$ we have from Eqs. (II.17) and (II.18), $L_x/\Delta r = 16$.

In discussing the FE-FC system's decay kinetics, the FC diffusion length should be checked to see if FC decay at the surface is transport limited (i.e. if $L_c/\Delta r \lesssim 1$). For the experiment of Fig. II.2 the FE densities are so low that self diffusion is entirely negligible. The smallest $D_x = D_{xp} = 243 \text{ cm}^2 \text{ s}^{-1}$ corresponds to the highest temperatures. This model for FC decay assumes the bulk value of τ_c is long. Logic would indicate $(\tau_c)_{\text{bulk}} > (\tau_x)_{\text{bulk}}$ because FC don't carry around a convenient recombination partner as do carriers bound in FE. For $(\tau_x)_{\text{bulk}} \sim 1 \text{ ms}$ and using D_x above as a lower bound on D_c we find $L_c = \sqrt{D_c \tau_c} \gtrsim 5 \text{ mm}$. The distance between well bottom and crystal surface ($\Delta r \sim 1 \text{ mm}$) is the important spatial dimension with which to compare L_x . We find $L_c/\Delta r \gtrsim 5$. There are no transport limiting problems with this steady state experiment. For some high temperature, high stress FE decays there may be some transport limited decay. This would depend on the accuracy of Eq. (II.59).

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CHAPTER III. THE ENHANCEMENT FACTOR

Introduction

This chapter reports the first absolute measurement of the density dependence of the enhancement factor for the electron-hole liquid (EHL) in Ge. This enhancement factor, the ratio of the electron density at the site of a hole to the mean EHL density, provides a valuable and sensitive test for the predictions of various many-body approximation schemes.¹⁻⁴ The measured enhancement factors agree quantitatively with the results of both the FSC approximation of Vashishta, Bhattacharyya, and Singwi² and the Jastrow variational calculation of Chakraborty and Pietiläinen.⁴ Comments are made on experimental and interpretational difficulties in the one published experiment⁵ dealing with the enhancement factor as a function of EHL density.

To enhance the utility of many-body theory calculations it is essential to compare the results of various approximation schemes with experiment. A uniquely useful physical system for this purpose is the electron-hole liquid (EHL). The EHL consists of two interpenetrating Fermi liquids, one of electrons and one of holes. It exists in optically excited Ge at liquid helium temperatures. The EHL droplets studied contain large numbers (10^6 to 10^{14}) of electron-hole (e-h) pairs. Various EHL parameters, such as ground state binding energy and density, can easily be varied in the laboratory. The EHL density, for example, can be varied by applying a stress to, applying a magnetic field to, or changing the temperature of the crystal containing the EHL. By applying stress, density variations of over a factor of 10 are achievable. Finally, the EHL system's characteristics are known accurately² for the

purpose of theoretical calculations, and the many-body calculation results are not small corrections. Other Fermi liquids such as neutron stars, nuclei, and electrons in metals have various disadvantages when used to test many-body theory approximations: physical parameters cannot be altered experimentally; the number of constituent particles is small; many-body effects are small corrections; or the system's characteristics are not known accurately for the purpose of theoretical calculation.

In this experiment the enhancement factor $g_{eh}(0)$ of the EHL is determined for a number of EHL densities. The enhancement factor is the e-h spatial correlation function evaluated at zero e-h separation and normalized to the average plasma density. An alternate way of saying this is that the enhancement factor $g_{eh}(0)$ is the electron density at the site of a hole divided by the mean electron density:

$$g_{eh}(0) = \frac{\text{electron density at the site of a hole}}{\text{mean electron density}}. \quad (\text{III.1})$$

If the electrons and holes in the EHL were totally uncorrelated, then the electron density near a given hole would be independent of the distance from that hole and would equal the average electron density. In this case the enhancement factor $g_{eh}(0)$ would be equal to one. If the electrons and holes are correlated through their coulomb attraction such that the electron density at the site of a hole is twice the mean electron density, then the enhancement factor $g_{eh}(0)$ is equal to two. The $g_{eh}(0)$ from this work are between 3.4 and 4.4.

In measuring $g_{eh}(0)$ as a function of EHL density n_L the EHL density is made to vary by altering the germanium band structure through

the application of stress. The Ge band structure near the conduction band minima and the valence band maximum determines the characteristics of the EHL. The application of stress (along a $\langle 111 \rangle$ crystal axis in this experiment) significantly alters these portions of the band structure. This in turn results in significant changes in the properties of the EHL (e.g. density).

This measurement of the electron-hole correlation function provides an especially sensitive test for the prediction of many-body approximation schemes: Several calculations¹⁻⁴ for the EHL have yielded substantially different predictions for the density dependence of $g_{eh}(0)$ while still being in reasonable agreement with experiment for EHL densities and ground state energies.

The only prior experiment dealing with the density dependence of $g_{eh}(0)$ in stressed Ge was performed by Chou and Wong.⁵ To "estimate semiquantitatively" a quantity proportional to $g_{eh}(0)$ as a function of EHL density, Chou and Wong assumed a sample independent model of EH decay. Their model assumes a one to one correspondence between the EHL density n_L and the EHL lifetime τ_L :

$$\frac{1}{\tau_L} = A[n_L g_{eh}(0)] + B[n_L g_{eh}(0)]^2 \quad (\text{III.2})$$

where the coefficients A and B of the radiative and Auger terms are taken to be independent of stress. While other work dealing with EHL decay mechanisms has been done⁶ in moderately stressed Ge ($\sigma = -6 \text{ kgf/mm}^2$ where $1 \text{ kgf} = 9.80665 \text{ N}$),^{7,8} I will leave discussion of these experiments till later.

At a stress and EHL density for which Chou and Wong measured $\tau_L =$

0.5 ms, a lifetime $\tau_{\frac{1}{2}} = 0.75$ ms was measured in this work. The $\tau_{\frac{1}{2}}$ measured in this work are consistently longer than their $\tau_{\frac{1}{2}}$. This indicates that either their sample independent model is not appropriate or their decay data is at fault.

A possible problem with their experiment lies in the shallow $\sim \frac{1}{2}$ meV deep strain induced potential well they claim to have used. They did no spatial imaging of luminescence to check the quality of their strain well. Relative to the crystal beneath their stressing plunger, the well depth may have been as little as $\frac{1}{4}$ meV deep.⁸ This shallow well implies a large volume of free exciton (FE) gas with a potentially significant loss term due to FE recombination at the crystal surface which is only several $k_B T$ above the bottom of the well. The resulting net flux of e-h pairs out through the EHL droplet surface can make the measured EHL decay rate faster than the bulk EHL decay rate.

The method of determining $g_{eh}(0)$ discussed in the next section has the advantage of being independent of EHL recombination models. In this experiment a FE gas and at most one EHL droplet are confined to a strain induced potential well^{8,9} in an ultrapure Ge crystal at temperature $T = 2.16$ K. The shallowest strain well used was at least several meV deep. The results reported here are derived from spatial, spectral, temporal, and excitation power scans of Fe and EHL luminescence. The $g_{eh}(0)$ determined from these measurements are not significantly altered by the compression¹⁰ of the EHL in the strain well. The measurements made on droplets having the highest EHL compression are those measurements made on the largest droplets. A worst case (highest stress) estimate yields a 5% average compression. For most EHL measurements the compression was much less.

This experiment provides, for the first time, an absolute determination of $g_{eh}(0)$ vs n_l and the extraction of $g_{eh}(0)$ from the data relies on only a few simple and verifiable assumptions.

Measurement Scheme

To see how a measurement of the enhancement factor $g_{eh}(0)$ can be approached experimentally, recall that $g_{eh}(0)$ is proportional to the probability of an electron being at the site of a hole. The radiative decay rate of an electron and a hole is also proportional to the probability of an electron being at the site of a hole. A study of radiative decay rates should lead to a measurement of $g_{eh}(0)$. From a treatment¹¹ of the LA phonon assisted FE and EHL radiative recombination rates we have

$$\frac{\tau_{rx}}{\tau_{rl}} = \frac{g_{eh}(0)n_l}{|\psi_x(0)|^2} \quad (\text{III.3})$$

where τ_{rx} and τ_{rl} are the LA phonon assisted FE and EHL radiative lifetimes and $\psi_x(0)$ is the FE wave function evaluated at zero e-h separation. Equation (III.3) states that the ratio of the EHL and the FE radiative decay rates is equal to the electron density at the site of a hole in the EHL divided by the electron density at the site of hole in a FE ($|\psi_x(0)|^2$).

Radiative lifetimes are difficult to determine experimentally so the FE and EHL radiative efficiencies are introduced:

$$e_{rx} = \frac{\left(\frac{1}{\tau_{rx}}\right)}{\left(\frac{1}{\tau_x}\right)} \text{ and } e_{rl} = \frac{\left(\frac{1}{\tau_{rl}}\right)}{\left(\frac{1}{\tau_l}\right)}. \quad (\text{III.4})$$

Incorporating these definitions in Eq. (III.3) and solving for $g_{eh}(0)$:

$$g_{eh}(0) = \left(\frac{e_{rl}}{e_{rx}} \right) \frac{\tau_x}{\tau_l} \frac{|\psi_x(0)|^2}{n_l} . \quad (III.5)$$

To express $|\psi_x(0)|^2$ in terms of experimentally measurable quantities consider the results of a simple effective mass theory calculation using s-wave wave functions:

$$|\psi_x(0)|^2 = \frac{1}{(\pi a_x^3)} \quad (III.6)$$

$$E_x = \frac{e^2/\epsilon}{2a_x} . \quad (III.7)$$

Here a_x is the FE Bohr radius, E_x is the FE binding energy relative to free carriers and $\epsilon = 15.36$ is the dielectric constant¹² used to characterize the screened coulomb interaction. The effective mass approximation should be valid for the Mott-Wannier exciton in Ge with its large spatial extent as characterized by a_x . Combining Eqs. (III.5), (III.6), and (III.7) we have:

$$g_{eh}(0) = \left(\frac{e_{rl}}{e_{rx}} \right) \frac{\tau_x}{\tau_l} \frac{1}{n_l} \frac{1}{\pi} \left(\frac{2\epsilon E_x}{e} \right)^3 . \quad (III.8)$$

All terms on the right hand side of this equation are either known or accessible to experiment.

The FE binding energy E_x is determined by spectroscopically measuring the shift in energy of the FE luminescence $\Delta E_{LUM}(\sigma)$ with stress in the spirit of Feldman, Chou and Wong:¹³

$$E_x(\sigma) = E_x(0) + [\Delta E_g(\sigma) - \Delta E_{LUM}(\sigma)]. \quad (III.9)$$

Here the zero stress FE binding energy $E_x(0) = 4.15 \text{ meV}^{14} \pm 0.1 \text{ meV}^{15}$

The band gap shift is^{7,8}

$$\Delta E_g(\sigma) = (-0.839)|\sigma| \text{ meV} \quad (III.10)$$

with σ in kgf/mm^2 . The stress σ is determined from the energy shift in the EHL luminescence.⁸ Finally

$$\Delta E_{LUM}(\sigma) = \frac{hc}{\lambda_{\text{peak}}(\sigma)} - \frac{hc}{\lambda_{\text{peak}}(0)} - 0.35 \text{ meV}. \quad (III.11)$$

The 0.35 meV is due to the different luminescence line-shapes for FE in unstressed Ge and for a strain confined FE gas [see Eq. (I.7) and (I.8)].

The lifetimes τ_x and τ_l are measured from luminescence decay (see Fig. III.1); the EHL density n_l is measured by fitting the EHL luminescence lineshape;¹⁶ and the ratio of radiative efficiencies e_{rl}/e_{rx} is determined from the experiment described below.

Consider a steady state experiment measuring the combined FE and EHL luminescence intensity, $I_x + I_l$, as a function of e-h pair generation rate G (see Fig. III.2).

Below the EHL threshold the number of free excitons N_x is determined by the steady state equation

$$G = \frac{N_x}{\tau_x}. \quad (III.12)$$

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Fig. III.1 Luminescence intensity is plotted semilogarithmically vs time for (a) the electron-hole liquid droplet, (b) the free exciton gas, and (c) the total luminescence. The electron-hole liquid has disappeared by 4 ms. Curve (a) shows a transition from bulk to surface decay for the droplet. Typically the GaAs laser was pulsed at lower than a 100 Hz rate with pulse energies less than 2 μ J. Sample CR50.

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Fig. III.2 Luminescence intensity is plotted vs excitation power for (a) the electron-hole liquid droplet, (b) the free exciton gas, and (c) the total luminescence. All curves are scaled vertically to have the same height at 10 μW . The electron-hole liquid threshold is clearly visible in (a) and (b). No hysteresis in electron-hole liquid formation is seen within experimental resolution. Sample CR50.

Other decay paths (see discussion leading up to and after Table II.2) are absorbed into τ_x . The measured FE luminescence intensity I_x is related to N_x by

$$I_x = \frac{N_x}{\tau_{rx}} e_{cx} \quad (\text{III.13})$$

where the FE collection efficiency e_{cx} is the ratio of the FE luminescence collected and detected to that emitted. An EHL collection efficiency e_{cl} is similarly defined. Combining Eqs. (III.12) and (III.13) the luminescence vs generation rate slope below the EHL threshold is

$$\frac{dI}{dG} = \frac{dI_x}{dG} = e_{rx} e_{cx}. \quad (\text{III.14})$$

Above the EHL threshold both FE and EHL exist, and the number of e-h pairs N_x in FE and N_l in the EHL droplet are related to the generation rate G by the steady state equation

$$G = \frac{N_x}{\tau_x} + \frac{N_l}{\tau_l}. \quad (\text{III.15})$$

Similar to the FE case, the measured EHL luminescence intensity I_l is related to N_l by

$$I_l = \frac{N_l}{\tau_{rl}} e_{cl}. \quad (\text{III.16})$$

Combining Eqs. (III.15) and (III.16) and using the experimental observation (see Figs. III.1 and III.2) and theoretical expectation [see discussion below Eq. (II.55)] that $N_x \approx$ constant just above the EHL

threshold, we find the slope dI/dG just above EHL threshold to be

$$\frac{dI}{dG} = \frac{dI_l}{dG} = e_{rl} e_{cl}. \quad (\text{III.17})$$

Any slope in I_x vs G above the EHL threshold can be measured and subtracted out.

Taking the ratio of the slope just above [Eq. (III.17)] to that just below [Eq. (III.14)] the EHL threshold we have

$$\frac{\left(\frac{dI}{dG}\right)_{\text{above}}}{\left(\frac{dI}{dG}\right)_{\text{below}}} = \left(\frac{e_{rl}}{e_{rx}}\right) \left(\frac{e_{cl}}{e_{cx}}\right). \quad (\text{III.18})$$

An optical hysteresis in EHL droplet formation which would complicate the above discussion has not been observed, within experimental resolution, for the strain confined FE gas - EHL droplet system used. Upon separately measuring the ratio of FE and EHL collection efficiencies e_{cl}/e_{cx} we obtain the desired ratio of radiative efficiencies e_{rl}/e_{rx} . The factors involved in measuring the ratio of collection efficiencies are discussed in appendix IIIA.

Actually a pumping efficiency relating excitation power to e-h pair generation rate G should be included, but has been found to be constant over the range of excitation powers used and is thus neglected in the above discussion. This was demonstrated by measuring the ratio of slopes [Eq. (III.18)] for vastly different pumping conditions: sharply focussed surface excitation, and broad focus surface excitation from an Argon ion laser and various wavelength volume-excitation sources (volume excitation means a long absorption length). Within the several percent accuracy of the measurements, all the ratios of slopes [Eq.

(III.18)] were equal.

Measurement Scheme Validity

An assumption inherent in the use of both steady state and decay measurements for the terms in Eq. (III.8) is the existence of a thermodynamic quasi-equilibrium (i.e. both thermal and spatial¹⁷) within the FE-EHL system. To compare steady state and decay measurements these measurements must be made on the same physical system. All steady state and decay measurements for a given strain well, and thus for a given EHL density, were performed at the same temperature (2.16 K) within the same day. This avoided the problem of having to apply exactly the same stress in exactly the same way on separate days.

Three criteria must be satisfied for the FE, EHL system to be in thermodynamic quasi-equilibrium.

- (a) The e-h pairs in the EHL droplet must be in thermal and spatial¹⁷ quasi-equilibrium.
- (b) The FE gas must be in thermal and spatial¹⁷ quasi-equilibrium with itself.
- (c) The FE gas must be in spatial¹⁷ quasi-equilibrium with the EHL droplet.

If any of these conditions are not met, then equilibrium thermodynamics is not appropriate and a more general transport picture must be considered.

Given a carrier-phonon scattering time $\tau_p \sim 1$ ns the FE, EHL system is well characterized by the lattice temperature for the low excitation powers (μ W) and long time scales (ms) of this experiment. The parameters characterizing the speed of response of the EHL to perturbations

which are the plasma frequency and the inter- and intra-band relaxation times, all correspond to approximately 0.1 ps time scales¹⁸ in unstressed Ge. When scaled for the larger less dense EHL droplets typically found in the strain confined geometry the time scales involved are still much faster than the fastest (0.1 ns) time scales of this experiment. In addition the transit time of a carrier across a diameter of a droplet at the Fermi velocity $V_F = \sqrt{2E_F/m}$ is much smaller than the experimental time scales. Using worst case values $m = 0.4 m_0$, $E_F \approx 2$ meV and $R_d \approx 150 \mu\text{m}$ the transit time is less than 4 ns. The electrons and holes are to a good approximation in quasi-equilibrium for the time scales of this experiment.

For the FE gas to be in spatial¹⁷ equilibrium with itself, the FE diffusion length $L_x = \sqrt{D_x \tau_x}$ must be large compared to the spatial extent of the FE gas. If we approximate the bottom of the strain induced potential well with a parabola:

$$U = \alpha r^2 \quad (\text{III.19})$$

the spatial extent of the FE gas is characterized by $\alpha(\Delta r)^2 = k_B T$ or

$$\Delta r = \sqrt{k_B T / \alpha}. \quad (\text{III.20})$$

Taking worst case values of α and τ_x from our data, we find $L_x / \Delta r \gtrsim 16$; the FE gas is in diffusive equilibrium with itself to an excellent approximation. This is making use of the FE diffusion constant D_x calculated from Eq. (II.64) corresponding to the highest stress data reported in this work.

To ensure spatial¹⁷ equilibrium between the EHL droplet and the FE gas, the net flux of FE out of (for decays) or into (for steady state) the EHL droplet must be small compared to the equilibrium flux of e-h pairs back and forth across the EHL droplet surface. For decays the EHL droplet acts as a FE source that keeps the number of FE approximately constant for small drop sizes. The net current outward is

$$4\pi R^2(J_{\text{out}} - J_{\text{in}}) = \frac{N_x}{\tau_x}. \quad (\text{III.21})$$

For steady state excitation a FE flux inward compensates for the droplet's bulk recombination loss of carriers. The net current inward is

$$4\pi R^2(J_{\text{in}} - J_{\text{out}}) = \frac{N_\ell}{\tau_\ell}. \quad (\text{III.22})$$

To be able to treat these systems as in quasi-equilibrium, and thus able to ignore transport, we must have

$$\left| \frac{J_{\text{out}} - J_{\text{in}}}{J_\infty} \right| \ll 1 \quad (\text{III.23})$$

where J_∞ is the flux of e-h pairs back and forth across the droplet surface in the limit of infinite carrier, FE, and EHL lifetimes. Simple thermodynamic and kinetic arguments [see Eq. (IIIB-1)] yield

$$J_\infty = S \frac{4\pi m_x}{h^3} (k_B T)^2 \exp\left(-\frac{\phi}{k_B T}\right) \quad (\text{III.24})$$

where

m_x = FE translational mass.

ϕ = EHL ground state binding energy per e-h pair relative to the FE.

S = absorption probability for a FE incident on the EHL droplet. [Generally $S = 1$ is assumed in nucleation work in Ge. In S_1 $S \sim 0.05$ fits nucleation work though people are cautious of this low value.]

The typical EHL radii in this experiment range from 20 μm to 150 μm as determined from spatial imaging and the scaling law

$$I_L(R_L) \propto R_L^3. \quad (\text{III.25})$$

This relation follows straightforwardly from Eq. (III.16) and

$$N_L = \frac{4}{3} \pi R_L^3 n_L. \quad (\text{III.26})$$

From Eqs. (III.21) and (III.24) and an expression for N_x [see Eq. (II.55)] we have, using worst case values for decays,

$$\left| \frac{J_{\text{out}} - J_{\text{in}}}{J_{\infty}} \right| \approx \frac{1}{S} \left(\frac{0.87}{R_L^2} \right) \text{ independent of } \phi R_L \text{ in } \mu\text{m}. \quad (\text{III.27})$$

The right hand side of this equation includes a term proportional to the FE volume, $(\Delta r)^3 = (k_B T / \alpha)^{3/2}$ [see Eq. (III.20), (III.21) and (II.55)].

If the FE volume is a factor of two larger due to the finite depth of the well and the flaring of the strain well out to meet the crystal surface, then $|(J_{\text{out}} - J_{\text{in}}) / J_{\infty}|$ is increased by a factor of two. If, in addition, the absorption probability $S \sim 10^{-2}$ we have a pessimistic

estimate

$$\left| \frac{J_{out} - J_{in}}{J_{\infty}} \right| \approx \frac{1.74}{R_l^2}; R_l \text{ in } \mu\text{m}. \quad (\text{III.28})$$

For $R_l = 20 \mu\text{m}$ this ratio is ~ 0.44 and the quasi-equilibrium description of FE-EHL system is suspect. For $R_l = 100 \mu\text{m}$ this ratio is 1.74×10^{-2} and the quasi-equilibrium description is justified.

When measuring τ_l from semilog plots of $I_x + I_l$ [see discussion below Eq. (III.33)] the region of the decay curve corresponding to a FE-EHL quasi-equilibrium is easily recognizable. This region is characterized by the exponential decay (straight line on semilog) of $I_l + I_x$. For small droplets not in the quasi-equilibrium regime the decay curve will deviate from exponential decay. For large droplets compression of the EHL starts increasing the decay rate. The measurements of τ_l for this work were performed on an EHL droplet small enough to have negligible compression effects, but large enough to be in the exponential quasi-equilibrium regime. Since the decay curves remain exponential down to $20 \mu\text{m}$ drop sizes the absorption probability used above ($S \sim 10^{-2}$) is an underestimate.

From Eqs. (III.22), (III.24) and (III.26) we have, using worst case steady state values,

$$\left| \frac{J_{out} - J_{in}}{J_{\infty}} \right| \approx \frac{7.2 \times 10^{-5}}{S} R_l; R_l \text{ in } \mu\text{m}. \quad (\text{III.29})$$

In the steady state experiment measuring $\epsilon_{rl}/\epsilon_{rx}$ the slope of $I_l + I_x$ is measured just above EHL threshold. A volume of EHL corresponding to a droplet with a radius smaller than $40 \mu\text{m}$ is sufficient to measure

this slope. For a 40 μm droplet and $S \sim 10^{-1}$ we have a pessimistic estimate

$$\left| \frac{J_{\text{out}} - J_{\text{in}}}{J_{\infty}} \right| \approx 2.9 \times 10^{-2}. \quad (\text{III.30})$$

For the conditions under which τ_L and e_{rL}/e_{rx} measurements are performed the FE gas - EHL droplet system is accurately described as being in thermodynamic quasi-equilibrium. The use of the steady state and decay measurements in the expression for $g_{\text{eh}}(0)$ [Eq. (III.8)] is justified.

Experimental Details

All measurements were performed on an ultrapure (net electrical impurity concentration $N_A - N_D \approx 2 \times 10^{11} \text{ cm}^{-3}$), dislocation free Ge crystal with dimensions $3 \times 4 \times 4 \text{ mm}^3$ (CR50 — see Table I.2). A strain induced potential well was created by applying an inhomogeneous stress along a $\langle 111 \rangle$ crystal direction with a spherical Delrin plunger. An infrared vidicon and video monitor were used to show the well bottom to be at least 1 mm away from any crystal surface. This experimental geometry has the advantage of providing well defined FE and EHL spatial distributions isolated from crystal surfaces with at most one EHL droplet in the well.

All measurements were performed with the crystal immersed in superfluid liquid helium in the temperature range $2.15 \text{ K} < T < 2.17 \text{ K}$. This avoids scattering of the luminescence by helium gas bubbles. At these temperatures the EHL is less compressible and the FE gas is restricted to a smaller volume in the well bottom than is the case for higher temperatures. The temperature is not so low that we cannot measure FE

luminescence below EHL threshold for modest to high stresses. Data were taken for a range of stresses from $\sim 6.3 \text{ kgf/mm}^2$ to $\sim 15.2 \text{ kgf/mm}^2$ where $1 \text{ kgf} = 9.80665 \text{ N}$. The bottom of the strain induced potential wells were characterized by curvatures $\alpha \approx 3 - 4 \text{ meV/mm}^2$.

A schematic of the experimental apparatus is shown in Fig. III.3. Steady state volume excitation of the crystal was achieved with a feed-back stabilized tungsten lamp followed by a silicon filter and $1.59 \mu\text{m}$ interference filter. The luminescence was mechanically chopped, spectrally resolved, and detected by a liquid N_2 cooled germanium PIN photodiode. The detector output was amplified, lockin detected, and digitally integrated in the microcomputer which controlled the experiment. The microcomputer automated measurements where wavelength, spatial position, or excitation power were varied.

For transient measurements a liquid nitrogen cooled GaAs laser was used for pulsed excitation and a waveform digitizer captured the full range of each decay. The microcomputer integrated the results of many pulses of the experiment. The waveform digitizer is what makes this experiment possible. If a boxcar integrater is used instead and the decay curve is sampled at 100 points, then the boxcar is 100 times slower than the waveform digitizer. With each pulse of the laser the boxcar looks at only 1% of the curve, while the waveform digitizer can look at 100%. Measurements which now take $\frac{1}{2}$ hour with the waveform recorder would take 50 hrs using a boxcar integrater.

It is important to note that the luminescence was mechanically chopped in the steady state experiments. Normally the excitation source is chopped rather than the luminescence. This is done to reduce the amount of unwanted chopped background light from entering the detection

apparatus. In the present case, the lifetimes of the photo-excited states are on the same order as the reciprocal chopping rate. Because the lifetimes are a function of excitation power, the phase of a chopped excitation source signal is a function of excitation power. For the lockin available for this experiment this phase shifting would have resulted in distorted signals. A chopping rate much slower than the 667 Hz rate used was an alternate possibility, but 1/f noise and the difficulty of chopping the spatially wide light beam made it impractical.

Data and Discussion

A typical set of decay data is shown in Fig. III.1. Plotted semi-log vs time are the EHL(a), FE(b), and FE plus EHL(c) luminescence intensities. The measured decay curves for the FE-EHL system contain an EHL threshold time past which the EHL droplet no longer exists. The threshold time is evident from the disappearance of the EHL decay curve (a) into the noise and the kink in the FE curve (b) due to the sudden loss of a FE source (the EHL droplet). The spectrometer grating used to spectrally resolve the EHL(a) and FE(b) luminescence was replaced with a mirror to measure the total (FE plus EHL) luminescence decay curve (c). The EHL curve (a) shows a transition from the dominance of bulk EHL decay to a dominance of surface decay as the surface to volume ratio of the EHL droplet increases with time.

$$\frac{\text{surface area}}{\text{volume}} = \frac{4\pi R_L^2}{\frac{4}{3}\pi R_L^3} = \frac{3}{R_L} \quad (\text{III.31})$$

The EHL lifetime τ_L was measured high enough on the decay curve to avoid

boil off (surface decay) effects, and for small enough drop sizes to avoid EHL compression effects on the lifetime. Alternatively τ_{ℓ} can be measured from the $I_{\ell} + I_x$ decay curve (c) as indicated in the discussion below Eq. (III.33). A faster than exponential FE decay is seen past the EHL threshold time in curves (b) and (c). The FE lifetime was measured just past the EHL threshold time $t = 4$ ms. Just before the EHL threshold time the FE luminescence intensity is approximately constant. The decay curves of Fig. III.1 correspond to a stress of $\sigma = -9.7 \text{ kgf/mm}^2$.

A typical set of luminescence intensity vs excitation power data, used to determine $e_{r\ell}e_{c\ell}/e_{rx}e_{cx}$, is shown in Fig. III.2. The EHL(a) and FE(b) curves help to accurately locate the EHL droplet threshold while the slopes of the FE plus EHL curve (c) above and below threshold yields $(e_{r\ell}/e_{rx})(e_{c\ell}/e_{cx})$. The luminescence detection system's wavelength and polarization response was independently measured, thus determining the ratio of collection efficiencies $e_{c\ell}/e_{cx}$ needed to isolate the ratio of radiative efficiencies $e_{r\ell}/e_{rx}$. Note the constant FE luminescence intensity above threshold.

No EHL formation hysteresis was observed. The EHL formation threshold, whether approached by lowering excitation power or increasing excitation power, occurred at a fixed excitation power within our experimental resolution.

Since the FE decay curves are non-exponential, the measured decay rate $1/\tau_x$ depends on where along the decay curve it is measured. Similarly the FE radiative efficiency part of $e_{r\ell}/e_{rx}$ depends on where below EHL threshold the slope of the power scan is measured. In order for the product $(1/\tau_x)(e_{r\ell}/e_{rx})$ to yield $1/\tau_{rx}$ care must be taken that both measure-

Fig. III.3 Experimental set-up. A variety of feedback stabilized light sources are controlled by the microcomputer. The source used for a particular experiment photoexcites a Ge crystal (CR50) immersed in super-fluid ($T = 2.16\text{K}$) liquid helium in an optical cryostat. The luminescence from the photoexcited states is collected by an output lens and routed through a 1/4 meter Jarrel Ash spectrometer to an N₂ cooled Ge PIN photodiode. For experiments using steady state excitation the luminescence is mechanically chopped and the detector output lockin detected. For pulsed experiments a transient recorder captures each decay waveform. The microcomputer automates spatial, spectral, temporal, and excitation power scans.

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ments are made the same distance below EHL threshold (corresponding to equivalent FE distributions).

The results of several measurements are displayed in Table III.1 below:

Table III.1

$-\sigma$ (kgf/mm ²)	τ_x (μ s)	τ_l (μ s)	$\frac{e_{rl}e_{cl}}{e_{rx}e_{cx}}$	$\frac{e_{cl}}{e_{cx}}$	$\frac{n_l}{(10^{16} \text{ cm}^{-3})}$	$\frac{E_x}{(\text{meV})}$
6.3 $\pm$.1	975 $\pm$ 10	570 $\pm$ 30	0.71 $\pm$.04	1.04 $\pm$.03	4.6 $\pm$.2	3.51 $\pm$.25
7.5 $\pm$.1	1150 $\pm$ 30	620 $\pm$ 20	0.80 $\pm$.04	1.33 $\pm$.04	4.0 $\pm$.2	3.41 $\pm$.17
9.7 $\pm$.1	1180 $\pm$ 40	760 $\pm$ 40	0.75 $\pm$.04	1.02 $\pm$.03	3.5 $\pm$.2	3.26 $\pm$.17
10.7 $\pm$.1	1165 $\pm$ 40	803 $\pm$ 10	1.00 $\pm$.05	1.20 $\pm$.04	3.0 $\pm$.2	3.18 $\pm$.17
12.0 $\pm$.1	1290 $\pm$ 110	915 $\pm$ 10	1.00 $\pm$.05	1.16 $\pm$.03	2.75 $\pm$.1	3.13 $\pm$.17
13.0 $\pm$.1	1112 $\pm$ 70	950 $\pm$ 20	1.04 $\pm$.05	0.99 $\pm$.03	2.62 $\pm$.1	2.99 $\pm$.17
14.2 $\pm$.1	957 $\pm$ 45	960 $\pm$ 30	1.47 $\pm$.07	0.98 $\pm$.03	2.55 $\pm$.1	2.98 $\pm$.17
14.7 $\pm$.1	890 $\pm$ 20	1010 $\pm$ 40	1.53 $\pm$.08	1.00 $\pm$.03	2.5 $\pm$.1	2.91 $\pm$.17
15.2 $\pm$.1	790 $\pm$ 30	1053 $\pm$ 50	1.58 $\pm$.08	0.97 $\pm$.03	2.42 $\pm$.1	2.92 $\pm$.17

The experimental EHL lifetimes are plotted with error bars in Fig. III.4 with the results of several other experiments.^{5,6,9,19} The EHL lifetime reported in Refs. III.6 and III.19 was measured using the same piece of Ge crystal used in this work (CR50). The data point (circle in Fig. III.4) of Refs. III.6 and III.19 matches up nicely with the data points from this work. In this work and in Refs. III.6 and III.19 care was taken to measure τ_l for EHL droplets small enough to make the reduction of τ_l due to EHL compression negligible. The other measure-

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Fig. III.4 Experimental electron-hole liquid lifetimes are plotted vs stress. The data from this work are plotted with error bars (sample CR50). The circle is from Refs. III.6 and III.19 which use the same piece of Ge. The solid line⁵ and dashed line⁹ (sample CR38) measurements were made on different pieces of Ge. The square data point is the zero stress result.

ments^{5,9} were made using two different pieces of Ge crystal (Ref. III.9 used crystal CR38 — see Table I.2). In both experiments the measured τ_L are different from each other and smaller than the τ_L of this work. The scatter in the measured τ_L could be due to several factors: (1) τ_L could be reduced due to EHL compression [possibly the case for Ref. III.9]; (2) τ_L could be reduced due to a large surface loss of e-h pairs caused by too shallow of a strain well [possibly the case for Ref. III.5]; or (3) part of the EHL decay rate could be sample dependent (i.e. recombination on impurities and crystal imperfections). In all cases a monotonic increase in τ_L is observed as |stress| increases (EHL density decreases).

The FE binding energies E_x are plotted vs stress in Fig. III.5. Also plotted are the results of Feldman, Chou and Wong.¹³ These latter results have been adjusted through the use of the zero stress $E_x = 4.15$ meV¹⁴ in Eq. (III.9) instead of the 4 meV they used. These adjusted results and our results lie within 7% of each other.

The EHL densities n_L adjusted for EHL compression, are plotted with prior measurements^{5,9,13,20,21} and theoretical predictions²² in Fig. III.6. A typical fit of the EHL and FE lineshapes is shown in Fig. III.7. The measurements necessary to estimate the compression of the EHL are discussed below.

Compression of the EHL in an inhomogeneously strained crystal can alter EHL density and lifetime measurements. To estimate the compression¹⁰ of an EHL droplet in a strain well it is necessary to know the radius of the EHL droplet in question and the curvature²³ α at the bottom of the strain induced potential well to which it is confined. Below EHL threshold the FE density distribution in a parabolic well $U(r)$

XBL 8211-3327

Fig. III.5 Measured FE binding energies E_x are plotted vs stress. Data from this work (sample CR50) are plotted with error bars. Actually differences in E_x are measured and the measured zero stress E_x ¹⁴ (Δ) is used to fit one value of E_x which then fixes the rest [see Eq. (III.9)]. Feldman, Chou, and Wong⁵ used $E_x = 4 \text{ meV}$ at zero stress ($\bullet$). Their results, translated upward 0.15 meV to agree with the zero stress $E_x = 4.15 \text{ meV}$ used in this work, are plotted as ($\circ$). The theoretical high stress limit $E_x = 2.65 \text{ meV}$ is indicated by the arrow.

XBL 8211-3312

Fig. III.6 Electron-hole liquid densities n are plotted vs stress. Along with the measurements from this work (+ — sample CR50) two theory curves²² are plotted. Several other experimental results are plotted: (Δ),⁵ ($\circ$),⁹ (∇),¹³ ($\bullet$),²⁰ and ($\blacksquare$).²¹ The theoretical³ high stress limit density is indicated by the arrow.

XBL 8211-3326

Fig. III.7 Luminescence intensity is plotted vs photon energy. The curve is the best fit to the experimental free exciton, electron-hole liquid luminescence lineshape (o). The experimental spectral resolution is indicated in the upper right corner of the figure. The condensation energy ϕ of the exciton relative to the liquid is $\phi = 0.48$ meV in this case ($-\sigma = 15.2$ kgf/mm²). The liquid density inferred from this fit is $n = 0.24 \times 10^{17}$ cm⁻³. The sum of the electron and hole Fermi levels is $E_F = 3.63 \pm 0.12$ meV. The exciton binding energy $E_x = 2.9$ meV. The peak intensity corresponds to a 107 fA detector current. Sample CR50.

$= \alpha r^2$ is given by the simple Boltzman factor relation $n(r) = n(0)\exp[-\alpha r^2 / (k_B T)]$. The curvature α for the FE distribution was measured in a steady state excitation experiment by scanning an image of the luminescing FE distribution across the spectrometer slit [see Fig. III.8]. This curvature, when corrected for stress dependences of binding energies, is the curvature needed to characterize the strain well for the EHL. Typically $\alpha \approx 3 - 4 \text{ meV}/\mu\text{m}^2$. The other parameter needed, the EHL droplet radius R_ℓ , was measured similarly by scanning an image of the droplet across the spectrometer slit [see Fig. III.9]. The droplet radius is thus known for one steady state excitation power for which the EHL compression can be estimated.¹⁰ The worst case (large droplet and high stress) compression of the EHL was 14% at the well bottom and an average 5.6% compression for the droplet as a whole. Most cases were much better. Compression of the EHL potentially effects density n_ℓ and lifetime τ_ℓ measurements. The droplet radius R_ℓ and the EHL density n_ℓ were both measured at the same excitation power. Typically $R_\ell \approx 80 \mu\text{m}$. To find the time along the decay curves corresponding to the same R_ℓ consider that the ratio I_{tot}/I_x (threshold) should be equal for decay and steady state total luminescence curves ($I_{\text{tot}} = I_\ell + I_x$) where the R_ℓ are equal.²⁴ The droplet radius can be inferred for other steady state excitation powers and as a function of time for decay experiments by using the scaling relation

$$R_\ell = R'_\ell [I_\ell / I'_\ell]^{1/3} \quad (\text{III.32})$$

and the measured I_ℓ curve. This follows from the relations $I_\ell = (N_\ell / \tau_{\ell\ell}) e_{c\ell}$ and $N_\ell = 4/3 \pi R_\ell^3 n_\ell$ as discussed above (see Eq. (III.25)). Vol-

XBL 8211-3325

Fig. III.8 Free exciton luminescence intensity is plotted as a function of position across the strain well. The curve is the least squares fit to a gaussian. The spatial resolution is indicated in the upper right corner of the figure. The peak intensity corresponds to an 8 fA detector current. Sample CR50.

XBL 8211-3324

Fig. III.9 Electron-hole liquid luminescence intensity is plotted as a function of position across the strain well. The curve is a least squares fit to determine the droplet radius. The spatial resolution is indicated in the upper right corner of the figure. The peak intensity corresponds to a 169 fA detector current. Sample CR50.

umes of EHL corresponding to as little as a 20 μm radius droplet can be seen above the noise. In general $R_d \leq 150 \mu\text{m}$ for these measurements.

The EHL lifetime τ_l should be measured for small droplets where compression effects are negligible because the radiative efficiency e_{rl} [see Eq. (III.4)] is measured for small droplet radii. The radiative lifetime $\tau_{rl} = \tau_l / e_{rl}$ is not expected to be as sensitive to compression effects as is n_l . This is because $1/\tau_{rl} \propto g_{eh}(0)n_l$ [see Eq. (III.2)] and $g_{eh}(0)$ is expected to increase as n_l decreases. However, faith need not be put in this assumption in order to determine τ_l for small droplets. Consider the decay equation

$$\frac{d(N_l + N_x)}{dt} = -\frac{N_l}{\tau_l} - \frac{N_x}{\tau_x} \quad (\text{III.33})$$

describing the decay of e-h pairs in the EHL (N_l) and in the FE gas (N_x). Just above EHL threshold N_x is observed to be approximately constant. Using Eqs. (III.4), (III.13), and (III.16) the above equation becomes

$$\frac{d}{dt} \left(I_l + \frac{e_{rl} e_{cl}}{e_{rx} e_{cx}} I_x \right) = - \frac{\left(I_l + \frac{e_{rl} e_{cl}}{e_{rx} e_{cx}} I_x \right)}{\tau_l} \quad (\text{III.34})$$

To determine τ_l simply plot $I_l + \frac{e_{rl} e_{cl}}{e_{rx} e_{cx}} I_x$ semilog and read off the decay constant. This curve is generally found to have the same exponential decay rate for times corresponding to both small and large droplet radii. This puts to rest worries about compression effects and also about quasi-equilibrium uncertainties for small droplet radii in decays.

From the above discussion we have $I_x(t)$, $I_l(t)$, and $I_l(R_d)$. Thus we can find $I_x(R_d)$. This result can be compared with the theoretical expectation [Eq. (II.55)]:

$$I_x(R_L) = I_x(0)[e^{u^2} \operatorname{erfc}(u) + 2u/\sqrt{\pi}] \quad (\text{III.35})$$

where $u = R_L \sqrt{\alpha/(k_B T)}$; $R_L = R_L'(I_L/I_L')$ ^{1/3}.

Figure III.10 is a semilog plot of the FE and EHL decay curves which will be used to compare the theoretical and experimental $I_x(R_L)$. Due to the spectral resolution of the spectrometer and the relatively small energy separating the FE and EHL luminescence curves, the EHL luminescence is not totally discriminated against in the FE decay curve.

Figure III.11 shows a similog plot of $I_L(t)$ and $I_x(t) - I_x(\text{threshold})$. If the change in the I_x curve above threshold is entirely due to EHL luminescence then these two curves should be identical. They are clearly not identical. Figure III.12 shows a plot of the best fit theory

$I_x(R_L) - I_x(0)$ [Eq. (III.35)] and the experimental $I_x(R_L) - I_x(0)$ as a function of R_L . Clearly the changes in I_x above threshold are not entirely accounted for by FE luminescence alone. Figure III.13 shows a plot of the best fit theory $I_x(R_L) - I_x(0)$ [Eq. (III.35)] plus $I_L(R_L)$ as a function of R_L . Clearly the fit, which includes a fraction of I_L comparable in magnitude to the theory $I_x(R_L) - I_x(0)$, is excellent.

The only fitting parameter in the theory $I_x(R_L) - I_x(0)$ was $\sqrt{\alpha R_L'^2/(k_B T)}/I_L'^{1/3}$. The best fit value of this parameter is in agreement with the measured $\alpha/(k_B T)$, R_L' and I_L' within experimental uncertainty. As a final comment, note that an examination of Eq. (III.35) shows that $I_x \approx$ constant for small R_L , and for large R_L the FE luminescence I_x changes linearly with R_L . This latter regime has been seen by Ohyama and Otsuka.²⁵

The self-consistency of these various results and comparisons of these results with those of other works adds to the confidence in the integrity of these measurements and of the picture of the strain con-

XBL 8211-3323

Fig. III.10 Luminescence intensity is plotted semilog vs time for (a) the electron-hole liquid, and (b) the free exciton gas. Sample CR50.

XBL 8211-3322

Fig. III.11 Luminescence intensity is plotted semilog vs time for the liquid $I(t)$ (o), and the above-threshold exciton signal $I_x(t) - I_x(\text{threshold})$ (□). If the change in I_x above threshold were due to electron-hole liquid (EHL) luminescence alone the curves would lie on top of each other. The EHL luminescence alone is not sufficient. Sample CR50.

XBL 8211-3321

Fig. III.12 Luminescence intensity is plotted vs droplet radius. The (●) are the best fit to (□) $I_X(t) - I_X$ (threshold) assuming no electron-hole liquid (EHL) luminescence is being measured. Exciton luminescence alone is not sufficient. This is expected since the EHL luminescence is not entirely discriminated against experimentally. Sample CR50.

XBL 8211-3320

Fig. III.13 Luminescence intensity is plotted vs droplet radius. The ($\bullet$) are the best fit to ($\square$) $I_x(t) - I_x(\text{threshold})$ assuming some portion of the electron-hole liquid (EHL) luminescence is being measured. The best fit indicates the above threshold change in $I_x(t)$ has EHL and exciton components of comparable magnitude. Sample CR50.

finned FE gas-EHL droplet system used to generate the self-consistency checks. Table III.2 contains the enhancement factors, $g_{eh}(0)$, determined from Eq. (III.8) and the results displayed in Table II.1. Also in Table III.2 is r_s where

$$r_s = \left(\frac{3}{4\pi n_l} \right)^{1/3} / n_l. \quad (\text{III.36})$$

Here $a_x = 177 \text{ \AA}$ is the high stress limit FE Bohr radius.

Table III.2

$-\sigma$ (kgf/mm ²)	n_l (10 ¹⁶ cm ⁻³)	r_s	$g_{eh}(0)$
6.3 ± .1	4.6 ± 0.2	0.978 ± .016	3.4 ± 0.6
7.5 ± .1	4.0 ± 0.2	1.025 ± .017	3.41 ± 0.6
9.7 ± .1	3.5 ± 0.2	1.071 ± .018	3.48 ± 0.6
10.7 ± .1	3.0 ± 0.2	1.128 ± .019	4.0 ± 0.6
12.0 ± .1	2.75 ± 0.1	1.161 ± .019	4.2 ± 0.7
13.0 ± .1	2.62 ± 0.1	1.180 ± .020	3.9 ± 0.7
14.2 ± .1	2.55 ± 0.1	1.191 ± .020	4.37 ± 0.8
14.7 ± .1	2.5 ± 0.1	1.199 ± .020	4.1 ± 0.8
15.2 ± .1	2.42 ± 0.1	1.215 ± .020	3.91 ± 0.8

The enhancement factors from Table III.2 are plotted with error bars in Fig. III.14 along with various theoretical predictions¹⁻⁴ and a zero stress experimental determination of $g_{eh}(0)$ due to Westervelt.²⁶ A detailed discussion of these results will be made in the next section.

Some additional results, obtained from fitting the FE and EHL

XBL 8211-3319

Fig. III.14 Enhancement factors $g_{eh}(0)$ are plotted vs $r_s = [3/(4\pi n_2)]^{1/3}/a_x$ where $a_x = 177 \text{ \AA}$ is the high stress limit free exciton Bohr radius. The results from this work (sample CR50) are plotted with slant-topped error bars. The width of the slanted tops is the uncertainty in r_s . The tops are slanted because the expressions for r_s and $g_{eh}(0)$ both depend on n_2 . The (*) data point is from Ref. III.26. The solid curves are from Ref. III.2, the dashed curve is from Ref. III.4.

spectral lineshapes is displayed in Table III.3:

Table III.3

$-\sigma$ (kgf/mm ²)	E_F^h (meV)	E_F^e (meV)	ϕ (meV)	$E_B = \phi + E_x$ (meV)
6.3 ± 0.1	2.27 ± 0.11	2.12 ± 0.11	1.16 ± 0.12	4.67 ± 0.28
7.5 ± 0.1	2.25 ± 0.11	1.93 ± 0.10	0.90 ± 0.09	4.31 ± 0.19
9.7 ± 0.1	2.31 ± 0.12	1.79 ± 0.09	0.60 ± 0.06	3.86 ± 0.18
10.7 ± 0.1	2.23 ± 0.11	1.62 ± 0.08	0.65 ± 0.06	3.83 ± 0.18
12.0 ± 0.1	2.21 ± 0.11	1.52 ± 0.08	0.61 ± 0.06	3.74 ± 0.18
13.0 ± 0.1	2.23 ± 0.11	1.49 ± 0.07	0.55 ± 0.06	3.54 ± 0.18
14.2 ± 0.1	2.25 ± 0.11	1.46 ± 0.07	0.50 ± 0.05	3.48 ± 0.18
14.7 ± 0.1	2.27 ± 0.11	1.45 ± 0.07	0.46 ± 0.05	3.37 ± 0.18
15.2 ± 0.1	2.23 ± 0.11	1.40 ± 0.07	0.48 ± 0.05	3.4 ± 0.18

The hole Fermi level E_F^h (□) and electron Fermi level E_F^e (■) are plotted vs stress in Fig. III.15. Other data^{5,20} are plotted along with two theoretical predictions²² for each of E_F^e and E_F^h . All E_F^h data points are open symbols. All E_F^e data points are solid symbols. The Fermi levels from this work fall in between the two theory curves for both holes and electrons. The Fermi levels for holes and electrons from this work disagree with those of Chou and Wong⁵ by less than 20%.

The values of ϕ (the condensation energy of a FE relative to the EHL) from Table III.3 are obtained from the fitting parameter involving the translation of the FE lineshape relative to the EHL lineshape. These ϕ are plotted with the measurements of Feldman, Chou, and Wong¹³ in Fig. III.16. The agreement is reasonable. I have observed that the

Fig. III.15 The hole Fermi level E_F^h and the electron Fermi level E_F^e are plotted vs stress. Open symbols are E_F^h data points. Solid symbols are E_F^e data points. Also plotted are theoretical curves:²² two for E_F^h and two for E_F^e . The E_{split}^e and E_{split}^h lines indicate the energy splitting between upper and lower bands for the electrons and holes. For E_F^h to the right of E_{split}^h only one hole band is occupied. For E_F^e to the right of E_{split}^e only one electron valley is occupied. The data from this work (sample CR50), plotted as squares, correspond to one conduction and one hole band being occupied. These Fermi levels fall in between the two theoretical curves for both holes and electrons. Chou and Wong⁵ data are plotted as triangles. Thomas and Pokrovskii's²⁰ data are plotted as circles. XBL 8211-3318

XBL 8211-3317

Fig. III.16 The condensation energy ϕ of a free exciton relative to the electron-hole liquid is plotted vs stress. The results of this work (sample CR50) are plotted with error bars. Other experimental data are plotted ($\square$).¹³ The zero stress $\phi \approx 1.8$ meV is indicated by an arrow as is the theoretically expected³ high stress limit $\phi = 0.42$ meV.

FE luminescence intensity at EHL threshold, I_x (threshold) scales with $\exp(-\phi/k_B T)$ [see Eqs. (II.53) and (II.55)]. This dependence of I_x at threshold on ϕ explains what prevented the measurement of $g_{eh}(0)$ down to lower stresses. The FE signal became too small. To set the scale for the ϕ in Fig. III.16, the theoretical high stress limit ϕ is predicted to be 0.42 meV.² The zero stress ϕ is predicted to be 1.74 meV³ and is measured experimentally to be $\phi \approx 1.8 \pm 0.2$ meV.^{27,28} The value $\phi = 1.74$ meV is consistent with the theoretical EHL binding energy³ of 5.89 meV and the measured $E_x = 4.15 \pm 0.1$ meV.^{14,15}

A variety of information concerning radiative efficiencies and radiative lifetimes can be determined from the results displayed in Tables III.1 and III.2. The ratio of radiative efficiencies e_{rl}/e_{rx} is determined from the fourth and fifth columns of Table III.1. The ratio of radiative lifetimes is determined from

$$\frac{\tau_x}{\tau_l} = \left(\frac{e_{rl}}{e_{rx}} \right) \frac{\tau_x}{\tau_l}. \quad (\text{III.37})$$

An upper bound for e_{rl} is given by (e_{rl}/e_{rx}) because $e_{rx} \leq 1$. Because $e_{rl} \leq 1$ we have

$$e_{rl} \leq \min \left[\frac{e_{rl}}{e_{rx}}, 1 \right]. \quad (\text{III.38})$$

Given this upper bound on e_{rl} a lower bound on τ_{rl} is

$$\tau_{rl} \geq \frac{\tau_l}{\min \left[\frac{e_{rl}}{e_{rx}}, 1 \right]}. \quad (\text{III.39})$$

From arguments analogous to those leading up to Eqs. (III.38) and (III.39) we have an upper bound on e_{rx} :

$$e_{rx} < \min \left[\frac{e_{rx}}{e_{rl}}, 1 \right] \quad (\text{III.40})$$

and a lower bound on τ_{rx} :

$$\tau_{rx} > \frac{\tau_x}{\min \left[\frac{e_{rx}}{e_{rl}}, 1 \right]} \quad (\text{III.41})$$

Table III.4 displays the results of these calculations.

Table III.4

$-\sigma$ (kgf/mm ²)	$\frac{e_{rl}}{e_{rx}}$	$\frac{\tau_{rx}}{\tau_{rl}}$	(e_{rl}) upper bound	(e_{rx}) upper bound	(τ_{rl}) lower bound (μ s)	(τ_{rx}) lower bound (μ s)
6.3 ± .1	0.68 ± .04	1.17 ± .09	0.68 ± .04		838 ± 66	975 ± 10
7.5 ± .1	0.06 ± .03	1.11 ± .08	0.60 ± .03		1033 ± 69	1150 ± 30
9.7 ± .1	0.73 ± .04	1.14 ± .10	0.73 ± .04		1041 ± 82	1180 ± 40
10.7 ± .1	0.83 ± .05	1.21 ± .08	0.83 ± .05		969 ± 58	1165 ± 40
12.0 ± .1	0.86 ± .05	1.22 ± .13	0.86 ± .05		1064 ± 63	1290 ± 110
13.0 ± .1	1.05 ± .06	1.23 ± .11		0.95 ± .06	950 ± 20	1171 ± 100
14.2 ± .1	1.50 ± .09	1.49 ± .12		0.67 ± .04	960 ± 30	1423 ± 120
14.7 ± .1	1.53 ± .09	1.35 ± .10		0.65 ± .04	1010 ± 40	1369 ± 116
15.2 ± .1	1.63 ± .09	1.22 ± .10		0.61 ± .04	1053 ± 50	1295 ± 113

Note that τ_{rx}/τ_{rl} is constant (within experimental error) over the stress range of these data. All lower bounds for τ_{rl} are approximately

1 ms. All lower bounds for τ_{rx} are approximately 1.2 ms.

Information concerning the decay mechanisms for the EHL can be obtained by studying $1/\tau_l$ as a function⁵ of $n_l g_{eh}(0)$:

$$\frac{1}{\tau_l} = A + B(gn_l) + C(gn_l)^2. \quad (\text{III.42})$$

Here A is a decay rate independent of n_l . This could be due to recombination at impurities. A radiative no-phonon luminescence has been seen for the EHL in zero stress Ge at about 736 meV.²⁹ This no-phonon EHL luminescence is not seen in the crystal used in this experiment ($I_{\text{no-phonon}}/I_{\text{LA phonon}} \lesssim 10^{-3}$) even though no-phonon exciton luminescence is seen quite clearly. I have seen no-phonon EHL luminescence in crystals with higher concentrations of Si, Ga, or P. At no time was any no-phonon luminescence (FE or EHL) detected coming from a strain well. A density independent decay rate intermediated by the 80 meV deep acceptor level could exist. This level is always present in dislocation free Ge crystals grown in hydrogen. It is the only deep acceptor level occurring in measurable concentrations ($N_A \sim 2 - 4 \times 10^{11} \text{ cm}^{-3}$). The radiation of e-h pairs decaying through this level falls outside the spectral response of the Ge photo-diode used here.

The term in Eq. (III.42) linear in gn_l is the radiative decay rate. The term quadratic in gn_l is an Auger decay rate. This expression for a three particle Auger decay rate is obtained through the use of the Kirkwood superposition approximation. This approximation for a three particle correlation function in terms of products of two particle correlation functions should be used with caution in highly correlated systems. Actually the Auger term in this approximation should also in-

clude an electron-electron or hole-hole correlation function: $g_{ee}(0)$ or $g_{hh}(0)$. These terms, however, are predicted² to have a negligible dependence on n_l and are incorporated into B. Note that if $A = 0$, the Eq. (III.42) becomes identical to Eq. (III.2).⁵

A plot of τ_l^{-1} vs gn_l using the data in Tables III.1 and III.2 is shown in Fig. III.17. If these data are fit to Eq. (III.42) the fit is poor because there are too many fitting parameters for the quality of the data. Restrictions on the coefficients of A, B, and C can be established by fitting the data to two out of the three decay rate terms in Eq. (III.42).

If the data is fit to $\tau_l^{-1} = A + B(gn_l)$ the coefficient A is negative. This unphysical result indicates that an Auger rate must be included.

If the density independent and Auger decay rates are the dominant decay rates ($B(gn_l) \ll A$ and $B(gn_l) \ll C(gn_l)^2$) the data fits to

$$\frac{1}{\tau_l} = (0.42 \pm 0.09) + (0.57 \pm 0.06)(gn_l)^2 \quad (\text{III.43})$$

where n_l is in units of 10^{17} cm^{-3} and τ_l is in ns. The value of $g_{eh}(0)$ consistent with Eq. (III.43) and the zero stress EHL lifetime ($\sim 40 \text{ ns}$) and density ($2.3 \times 10^{17} \text{ cm}^{-3}$) is $g_{eh}(0) = 2.9 \pm 0.4$. These results lead to the zero stress density independent and Auger efficiencies:

$$e_{d1} = A\tau_l = 0.02$$

and

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Fig. III.17 The electron-hole liquid decay rate τ_{EHL}^{-1} is plotted vs $g_{EH}(0)n_L$. The inset shows the data on a more compressed scale. Here the results of this work correspond to the short segment near the origin. The (*) in the inset corresponds to the zero stress case using the theory³ value of $g_{EH}(0) = 2.33$. The arrow on the finer scale horizontal axis points to the theoretically expected minimum $g_{EH}(0)n_L$. Sample CR50.

$$e_{\text{Aug}} = C(gn_l)^2 = 0.98.$$

The zero stress theoretical³ $g_{\text{eh}}(0) = 2.33$ is not in serious disagreement with the value found above. The zero stress experimental^{30,31} $e_{\text{rl}} = 0.25 \rightarrow 0.33$ and $e_{\text{Aug}} = 0.67 \rightarrow 0.75$ are in definite disagreement with the above efficiencies.

The final pair of decay rates to consider neglects the density independent decay rate A. The data fits to

$$\frac{1}{\tau_l} = (0.68 \pm 0.15)(gn_l) + (0.31 \pm 0.11)(gn_l)^2 \quad (\text{III.44})$$

where n_l is in units of 10^{17} cm^{-3} and τ_l is in ms. The value of $g_{\text{eh}}(0)$ consistent with Eq. (III.44) and the zero stress EHL lifetime (40 μs) and density ($2.3 \times 10^{17} \text{ cm}^{-3}$) is $g_{\text{eh}}(0) \approx 3.5 \pm 1.5$. These results lead to the zero stress radiative and Auger efficiencies:

$$e_{\text{rl}} = Bgn_l\tau_l = 0.22 \pm 0.1$$

and

$$e_{\text{Aug}} = C(gn_l)^2 = 0.78 \pm 0.1.$$

The zero stress theoretical³ $g_{\text{eh}}(0) = 2.33$ and the experimental^{30,31} $e_{\text{rl}} = 0.25 - 0.33$ are in agreement with these results.

The coefficients A, B, and C can be smoothly varied between those of Eq. (III.43) and Eq. (III.44) while maintaining the same quality fit with the data. This puts the following limits on the coefficients

A, B, and C:

$$(0.57 \pm 0.06) \gtrsim C \gtrsim (0.31 \pm 0.11)$$

$$0 \lesssim B \lesssim (0.68 \pm 0.15)$$

$$(0.42 \pm 0.09) \gtrsim A \gtrsim 0. \quad (\text{III.45})$$

The fit, Eq. (III.44), with $A = 0$ agrees with the zero stress experimental results. Assuming this fit is correct, Eq. (III.44) can be used to determine τ_{rl} and e_{rl} for the stresses used in this work. The exciton τ_{rx} and e_x can then be calculated from the values of τ_{rx}/τ_{rl} and e_{rl}/e_{rx} in Table III.4. The results of these calculations are displayed in Table III.5.

Table III.5

$-\sigma$ (kgf/mm ²)	$\epsilon_{eh}(0)n_l$ (10 ¹⁷ cm ⁻³)	τ_{rl} (μ s)	e_{rl}	τ_{rx} (μ s)	e_{rx}
6.3	1.57 $\pm$ 0.29	970 $\pm$ 287	0.59 $\pm$ 0.17	1135 $\pm$ 336	0.86 $\pm$ 0.25
7.5	1.37 $\pm$ 0.25	998 $\pm$ 296	0.62 $\pm$ 0.18	1108 $\pm$ 328	1.03 $\pm$ 0.3
9.7	1.22 $\pm$ 0.22	1173 $\pm$ 347	0.65 $\pm$ 0.19	1337 $\pm$ 396	0.88 $\pm$ 0.26
10.7	1.20 $\pm$ 0.20	1232 $\pm$ 365	0.65 $\pm$ 0.19	1491 $\pm$ 442	0.78 $\pm$ 0.23
12.0	1.16 $\pm$ 0.21	1388 $\pm$ 411	0.66 $\pm$ 0.19	1693 $\pm$ 502	0.76 $\pm$ 0.23
13.0	1.02 $\pm$ 0.19	1382 $\pm$ 409	0.69 $\pm$ 0.2	1700 $\pm$ 504	0.65 $\pm$ 0.19
14.2	1.11 $\pm$ 0.22	1435 $\pm$ 425	0.67 $\pm$ 0.2	2138 $\pm$ 633	0.45 $\pm$ 0.13
14.7	1.03 $\pm$ 0.21	1473 $\pm$ 436	0.69 $\pm$ 0.2	1988 $\pm$ 589	0.45 $\pm$ 0.13
15.2	0.95 $\pm$ 0.19	1500 $\pm$ 444	0.70 $\pm$ 0.2	1830 $\pm$ 542	0.43 $\pm$ 0.13

Note that these radiative lifetimes and radiative efficiencies are consistent with the limits placed on them (see Table III.4). Further note that τ_{rx} scales approximately with E_x^3 as discussed below Eq. (II.36).

Kelso and Furneaux⁶ have performed experiments using the same piece of Ge used in this work (CR50 — see Table I.2) in which the EHL decay mechanisms were studied. In the first part of the paper Kelso discusses a measurement of τ_d for an EHL droplet as a function of droplet radius. The droplet size was varied from a small droplet with negligible compression to a large droplet with density variations measured to be up to 3.5 times the uncompressed density. Given the measured EHL density distribution and the measured decay rate for a number of different sized droplets the coefficients A, B, and C of Eq. (III.42) can be determined. At the time Ref. III.6 was published a constant $g_{eh}(0)$ was assumed. Using numbers and advice kindly supplied by Sue Kelso I have re-evaluated this data using a density dependent $g_{eh}(0)$. There is some flexibility depending on the model of $g_{eh}(0)$ vs n_d used. Evaluating the various decay efficiencies at the uncompressed density ($n_d = 0.47 \times 10^{17} \text{ cm}^{-3}$) of this experiment there are several trends: The density independent decay efficiency is small ($\epsilon_{d1} \lesssim 0.2$); the radiative efficiency is large ($\epsilon_{r1} \gtrsim 0.8$); and the Auger efficiency is small and negative. This latter result is unphysical. Given the extensive deconvolutions and difficult measurements involved in this experiment these results are understandable.

The second part of Kelso and Furneaux's⁶ paper involves Furneaux's measurements of the magneto-oscillations of EHL luminescence for a small ($R_d \lesssim 125 \text{ } \mu\text{m}$) droplet confined to a strain induced potential well. It

is argued that $e_{di} \gtrsim 0.5$. Including boil off at e-h pairs from the EHL droplet in the analysis of the luminescence decay makes the lower bound on e_{di} even larger. Conservatively I estimate from this data that $e_{di} > 0.55$. Using the measured $\tau_l = 0.5$ ms this yields the density independent decay lifetime $\tau_{di} < 0.91$ ms. It should not be possible to measure an EHL lifetime longer than τ_{di} because the decay rate of τ_{di}^{-1} is only part of the total decay rate τ_l^{-1} . Lifetimes as long as 1.05 ± 0.05 ms have been measured in this work. This is a definite contradiction. Fitting the τ_l^{-1} vs gn_l data plotted in Fig. III.17 results in an unphysical negative radiative efficiency if A is forced to be the τ_{di}^{-1} from above. One assumption clearly stated in this experiment concerns the efficiency with which carriers are photo-excited and drawn into the strain well. The analysis relies on the assumption that this pumping efficiency is independent of the magnitude of the fixed orientation magnetic field. A change in pumping efficiency with field comparable with the change in gn_l with field would account for the discrepancy.

It should be noted that all the discussion following Eq. (III.42) assumes that the coefficients A, B, and C are constants independent of or at least very slowly varying with stress. Chou and Wong⁵ estimate from Smith et al's.³² work that the radiative recombination rate for electrons with the $|3/2, \pm 1/2\rangle$ hole states is smaller than the radiative recombination rate for electrons with the $|3/2, \pm 3/2\rangle$ hole states by 24%. One might expect this difference to cause the coefficient B to decrease as stress is increased and the $|3/2, \pm 3/2\rangle$ band passes through the Fermi level (~ -6.5 kgf/mm²). This is not the case however because hole band that remains occupied at high stresses is the heavy hole band at low stresses. Since the density of states is proportional to the $3/2$

power of the effective mass the relative occupancy of the light to heavy hole bands is¹⁶ approximately $(m_{hh}/m_{lh})^{3/2} = 24$. Here m_{hh} and m_{lh} are respectively the heavy and light hole band masses. The hole band which remains occupied at high stresses contains $\sim 96\%$ of the holes in the EHL at zero stress and thus has the dominant effect on B throughout the stress range.

Enhancement Factor Results and Discussion

The enhancement factors resulting from this work are plotted with slanted top error bars are plotted in Fig. III.14 as a function of $r_s = [3/(4\pi n_x)]^{1/3}/a_x$ where $a_x = 177 \text{ \AA}$ is the high stress limit FE Bohr radius. The width of the slanted tops is the uncertainty in r_s . The tops are slanted because the expressions for r_s and $g_{eh}(0)$ both depend on n_x . These results are slightly different from those presented in Ref. III.33 due to a refinement of the FE + EHL luminescence lineshape fits and the collection efficiencies. One more data point has been included.

The lone "solid square" data point is from a zero stress experimental determination of $g_{eh}(0)$ by Westervelt.²⁶

The curves are the results of several many-body approximations^{2,4} for a model system assuming isotropic electron and hole bands, and equal electron and hole masses. The legitimacy of such model systems for use in $g_{eh}(0)$ calculations is suggested by the following: The exchange-correlation energy of the EHL has been shown to be independent of the different band structure characteristics of semiconductors.³⁴ The lowest curve is that predicted by the Hubbard Approximation (HA) and the Random Phase Approximation (RPA). The upper two curves are the results of more sophisticated approximations. The FSC approximation² takes into account

multiple scattering between the plasma components to infinite order in an approximate way. The dashed curve is the result of a variational calculation⁴ as opposed to the solid curves which are the results of perturbative methods. A separate FSC calculation³ of $g_{eh}(0) = 2.33$ for the zero stress case ($r_g \approx 0.57$) has been made. The same paper reports an infinite stress limit $g_{eh}(0) = 6.8$ corresponding to $r_g = 1.57$. Figure III.15 plots $g_{eh}(0)$ between these two limiting values of r_g (higher densities, smaller r_g , can be reached by applying a magnetic field^{30,31}).

Within experimental error the $g_{eh}(0)$ from this work agree quantitatively with the results of the FSC approximation² and also with the results of the Jastrow variational calculation.⁴ There is a clear disagreement with the HA and RPA predictions.

The spatial correlation function $g_{eh}(r)$ is both computationally and physically a sensitive parameter. In the theoretical formalism $g_{eh}(r)$ typically shows up in the form of $\int g_{eh}(r)r^2 dr$ or integrals of this integral. In order for $g_{eh}(0)$ to converge the calculations must be very carefully iterated to a highly accurate solution. This is analogous to standard perturbation theory with $g_{eh}(r)$ corresponding to the Schrödinger wave function (a spatial correlation function). Recall that one needs only first order wave functions to get second order energy eigenvalues. Thus $g_{eh}(r)$ is a more sensitive test of the theory than is the EHL binding energy. That $g_{eh}(r)$ evaluated at $r = 0$ is the quantity to be checked with experiments gives rise to another potential difficulty: Central cell corrections may be necessary to describe the close range particle interactions. To date no such corrections have been incorporated into $g_{eh}(0)$ calculations. All calculations have made use of effective mass theory which under some circumstances³⁵ has failed to describe

accurately wave functions in semiconductors.

The $g_{eh}(0)$ calculations were all done assuming zero temperature. However since $k_B T/E_F^{e,h} \leq 0.13$ the corrections should be small.

There is room for improvement in the experimental working equations for $g_{eh}(0)$. One obvious place is in relating E_x to $|\psi_x(0)|^2$ [Eqs. (III.6) and (III.7)]. In addition to making a more sophisticated effective mass calculation, the above considerations of central cell corrections and the applicability of the effective mass approximation are of concern here too. Difficulties arise when perturbation theory is used, due to the large electron mass anisotropy.

In spite of these potential sources of difficulty there is good agreement between theory and experiment. Confidence in the accuracy of the effective mass theory could be justified due to the large FE Bohr radius in spite of the added complications of the band structure.

In summary, this experiment provides the first absolute determination of $g_{eh}(0)$ as a function of EHL density. The resulting $g_{eh}(0)$ are in good agreement with the most sophisticated theoretical predictions,^{2,4} and do not agree with the HA and RPA predictions.

APPENDIX IIIA. LUMINESCENCE COLLECTION EFFICIENCY

In order to determine the enhancement factor $g_{eh}(0)$ it is necessary to characterize the relative efficiency with which the detection apparatus collects and detects FE and EHL luminescence (e_{cx}/e_{cl}). [See Eq. (III.18).]

The characteristics of the luminescence and of the detection system pertinent to e_{cx}/e_{cl} are as follows: The FE and EHL luminescence differ in frequency, and degree of polarization, and are emitted from different spatial distributions within the crystal. A camera lens focusses a portion of the escaping luminescence onto the split plane of a $\frac{1}{2}$ meter spectrometer. The luminescence passing through the slit is spectrally resolved by a polarization sensitive diffraction grating with 890 grooves/mm and a 1 μ m blaze. The luminescence leaving the spectrometer is focussed on a liquid nitrogen cooled Ge PIN photodiode. The decrease in the Ge bandgap with increasing temperature is responsible for the shifting wavelength response of the detector with temperature.

To determine the ratio of FE and EHL collection efficiencies e_{cx} and e_{cl} one needs to consider:

(a) The relative efficiency with which the camera lens collects the luminescence from the differing spatial distributions.

(b) The spectrometer's spectral response due to both the wavelength resolution of the slits used and the grating's spectral response.

(c) The grating's polarization response.

(d) The detectors wavelength response.

(a) If the FE distribution outside of the EHL droplet is modeled as

[see Eq. (II.54)]

$$n_x(r) = n_x(R_L) \exp\left(-\frac{\alpha(r^2 - R_L^2)}{k_B T}\right) \quad (\text{IIIA-1})$$

n_x is down to 10% of its peak value $n_x(R_L)$ a distance

$$r = \sqrt{R_L^2 - \frac{k_B T}{\alpha} \ln\left(\frac{1}{10}\right)} \quad (\text{IIIA-2})$$

from the well bottom. For $R_L = 100 \mu\text{m}$, $\alpha = 3.5 \text{ meV}/\mu\text{m}^2$ and $T = 2.16\text{K}$. Equation (IIIA-2) yields $r = 0.36 \text{ mm}$ or a diameter of 0.72 mm .

The image of the 4 mm slits demagnified by 0.47 by the output lens is $(4 \text{ mm})(0.47) = 1.9 \text{ mm}$ at the plane of the droplet. The FE and EHL spatial distributions fall well within this 1.9 mm region. The amount of light routed into the spectrometer from a given point is proportional to the solid angle occupied by the output lens as viewed from this point. The variation in this solid angle is less than one part in 10^4 across the FE, EHL distribution. Spatial effects on e_{cl}/e_{cx} are insignificant.

(b) The diffraction grating spectral response differs by less than 1% over the spectral width of the FE and EHL luminescence ($\sim 4 \text{ meV}$). The measured slit function for 4 mm slits (FWHM $\sim 13 \text{ meV}$) has an average 10% effect on e_{cl}/e_{cx} . This effect is calculated by scaling the high resolution FE and EHL spectral scans with the measured slit function for 4 mm slits.

(c) The effects of polarization on e_{cl}/e_{cx} are determined from measurements of the polarization response of the spectrometer and the polarization of the luminescence.

The spectrometer's polarization response is characterized by measuring the ratio of the output signals $I_{\parallel}/I_{\perp}$ corresponding to input light beams of equal intensity polarized parallel to and perpendicular to the slits. Over the range of wavelengths of interest in this experiment $I_{\perp}/I_{\parallel} = 2.8$; the spectrometer passes light polarized perpendicular to the slits most efficiently.

The stress is applied along a $\langle 111 \rangle$ crystal axis which is parallel to the spectrometer slits. The polarization of the LA phonon assisted FE and EHL luminescence has been measured by Pokrovskii and Svistunova³⁶ for $\langle 111 \rangle$ stress from zero to -12 kgf/mm^2 . They measured FE and EHL polarizations in the range $-0.22 \gtrsim P \gtrsim -0.15$ for stresses in the range $6.3 \text{ kgf/mm}^2 \leq -\sigma \leq 12 \text{ kgf/mm}^2$. The polarization P is defined as

$$P = \frac{I_{\perp} - I_{\parallel}}{I_{\perp} + I_{\parallel}}. \quad (\text{IIIA-4})$$

Here $I_{\perp}$ and $I_{\parallel}$ are the luminescence intensities measured with polarizations perpendicular to and parallel to the stress axis. Pokrovskii and Svistunova claim only a qualitatively accurate description of the FE and EHL polarizations (P_x and P_z) due to the sensitivity of their measurements to the preparation of their crystal surfaces. I measured polarizations in the range $-0.47 \lesssim P \lesssim -0.34$. Over the range of stresses used in the $g_{\text{eh}}(0)$ experiment the polarizations measured and the results of Pokrovskii and Svistunova both find $P_x < P_z$. If polarization effects were neglected $e_{\text{cl}}/e_{\text{cx}}$ would be underestimated by at most 6%, the size of the largest polarization correction factor.

(d) The detector response for photon energies near the band gap of the liquid N_2 cooled Ge detector was determined by measuring the spec-

trum of a hot blackbody (see Fig. I.9). The slow wavelength dependence of the blackbody curve was estimated from the short wavelength end of the wavelength scan. The resulting detector response near the FE and EHL wavelengths is well approximated by a straight line. By scaling the FE and EHL spectra with this detector response function a detector response collection efficiency is determined. These collection efficiencies vary from 0.88 to 0.93 for the various stresses and detector temperatures used in the $g_{eh}(0)$ experiment.

Combining collection efficiencies due to all of the factors mentioned above, the final ratio of EHL and FE collection efficiencies are all within the range $0.97 < e_{cl}/e_{cx} < 1.33$.

APPENDIX IIIB. CURRENT DENSITY OF e-h PAIRS BETWEEN A FE GAS AND AN EHL

In the limit of infinite FE and EHL lifetimes the flux of e-h pairs entering J_{in} and leaving J_{out} the EHL through its surface are equal. I label this flux J_{∞} . It can be evaluated through the following simple arguments.

The flux of FE incident on the EHL surface is $J = \frac{1}{2} n_x(R_L) \bar{v}_x$. Here $n_x(R_L)$ is the equilibrium FE concentration at the surface of the EHL [see Eqs. (II.53) and (II.10)], and $\bar{v}_x = \sqrt{8k_B T / \pi m_x}$ is the thermal average speed of a FE. Assuming a fraction S of the incident FE are absorbed, the equilibrium back and forth flux of e-h pairs across the EHL surface is

$$J_{\infty} = S \frac{4\pi m_x}{h^3} (k_B T)^2 \exp\left(-\frac{\phi}{k_B T}\right). \quad (\text{IIIB-1})$$

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CHAPTER IV.

THE OPTICAL HYSTERESIS OF ELECTRON-HOLE LIQUID
NO-PHONON LUMINESCENCEIntroductory Remarks on Hysteresis

It has been noted experimentally¹ that there is a hysteresis in the formation and destruction of electron-hole droplets (EHD) in Ge. The observed hysteresis can be explained in terms of the surface tension of the EHD, and classical nucleation theory generalized to include the effects due to finite electron-hole liquid (EHL) lifetime.^{2,3,4} Detailed studies of the EHD hysteresis have yielded values for the surface energy of the EHD^{4,5} ($w = 2.6 \pm 0.3 \text{ erg cm}^{-2}$), and the condensation energy of free excitons (FE) relative to the EHL ($\phi = 1.9 \pm 0.2 \text{ meV}$).⁴ Use has been made of this optical hysteresis to put an upper bound on the diffusion coefficient for EHD ($D \leq 10^{-9} \text{ cm s}^{-1}$) and thus a lower bound on the binding energy of EHD to crystal defects ($B \geq 5 \text{ meV}$).⁶

In the model of Westervelt,^{2,3,4} the response of Ge to photoexcitation proceeds as follows (a spatially uniform e-h pair generation rate is assumed for simplicity): As the e-h pair generation rate g is increased from zero, the density of the FE gas increases. At $g = g_+$ where the density of the FE gas is supersaturated by a factor of $n/n_s = 7.46$, the homogeneous nucleation of EHD starts to take place [the saturated FE density n_s is given by Eq. (II.9)]. It is found that the shift in the supersaturation ratio for inhomogeneous nucleation (at defects) is not large.³ The EHD quickly reach an equilibrium radius determined by the EHL lifetime τ_L and density of the coexisting supersaturated FE gas $n_+ \approx 7.46 n_s$. As excitation power is increased, more EHD nucleate and

the density of the FE gas remains constant. The steady state equation describing this behavior is (the equation for the "upgoing hysteresis curve"):

$$g = \frac{n_+}{\tau_x} + \frac{N_d \nu_+}{\tau_d} \quad (IV.1)$$

Here N_d is the number of EHD, ν_+ is the number of e-h pairs in an EHD in equilibrium with the supersaturated FE gas of density n_+ , and τ_x is the FE lifetime.

Upon reducing the e-h pair generation rate g the density of the FE gas is reduced and the size of the EHD in equilibrium with the FE gas becomes smaller (ν decreases). The number of drops N_d remains constant. When the density of the FE gas decreases to a supersaturation ratio² of $n/n_g = 2.08$, EHD start to break up. For lower excitation powers the density of the FE gas remains constant at $n_- = 2.08 n_g$ and N_d decreases. The steady state equation describing this behavior is (the equation for a portion of the "downgoing hysteresis curve"):

$$g = \frac{n_-}{\tau_x} + \frac{N_d \nu_-}{\tau_d} \quad (IV.2)$$

At some e-h pair generation rate g_- smaller than g_+ all EHD are gone ($g_- = n_-/\tau_x$).

Westervelt has found good experimental agreement⁴ with the predictions of this model. It has been clearly demonstrated⁴ that the number of EHD is constant at the top of the downgoing hysteresis curve. There has been some controversy over the predicted EHD radii being smaller than those measured in light scattering experiments. The differences have

generally been attributed by Westervelt⁴ to experimental conditions for which nucleation theory is not applicable. As mentioned above, Westervelt et al⁶ have found evidence that EHD are bound on crystal defects. Westervelt et al⁴ found a significant correlation between g_+/g_- and the net electrical impurity concentration $|N_A - N_D|$. This is evidence that the observed nucleation of EHD takes place on shallow electrical impurities, at least for the more impure crystals.

Fishman⁷ has recently proposed that EHD in ultra-pure Ge crystals nucleate on spatial concentration fluctuations of electrically inactive impurities. Electrically inactive impurities, such as silicon and oxygen, can reach concentrations of 10^{14} - 10^{16} cm⁻³ even in the purest of Ge crystals [see Table I.2]. Fishman proposes that concentration fluctuations of such impurities cause lattice deformations, and these deformations give rise to slight potential energy variations. Fishman estimates that the energy change for a drop of radius 0.1 μ m can be greater than 0.5 meV. This change could be positive or negative. Fishman's model seems plausible, however, it is difficult to evaluate the reliability of his experiment due to the translator's unusual skill in making ambiguities in critical places.

The experiments of this chapter are intended to explore the hypotheses of Westervelt et al⁴ and Fishman⁷ concerning the nucleation sites of EHD. Use is made of EHL no-phonon luminescence attributed to the proposed binding sites.

No-Phonon Luminescence as a Probe of Nucleation Binding Sites

Because Ge has an indirect energy band gap, photoexcited e-h pairs in Ge generally require the emission or absorption of a $\langle 111 \rangle$ zone edge phonon to recombine. Localized defects, such as impurities, remove the translational symmetry of the crystal and require a distribution of wave vectors for a proper description. Because translational symmetry is violated, crystal momentum is no longer a strictly conserved quantum number. An e-h pair at an impurity can recombine without involving a phonon. An alternate way of seeing this is to observe that because the defect requires a distribution of wave vectors to describe (including zone edge wave vectors) an e-h pair interacting with this defect should have a non-zero no-phonon recombination matrix element. Luminescence lines corresponding to the radiative recombination of an e-h pair (in an exciton or in an EHD) where no phonon is involved will be called "no-phonon" lines. The no-phonon lines observed in this thesis were generally of much lower intensity ($\leq 1\%$) than the most intense luminescence lines (LA phonon lines).

Let N_i be the concentration of the impurity responsible for a no-phonon line. The shape of the EHL no-phonon (EHL_{NP}) hysteresis curves can be quite sensitive to N_i . Figure IV.1 shows two limiting cases: (a) a single isolated impurity is within an EHD; (b) many impurities are within an EHD. Inside the EHL only e-h pairs within about one Bohr radius of an impurity can recombine without involving a zone edge phonon. For more distant e-h pairs the field of the impurity is screened out by the electron-hole plasma. The smallest drop sizes studied here are predicted to be many Bohr radii across. This means that the EHL_{NP} luminescence intensity emanating from a single isolated impurity inside a single EHD is a constant for all achievable drop radii.

(a)

(b)

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Fig. IV.1 Two electron-hole drops (EHD) of radius R are represented schematically. Defects or impurities are represented by the dots. Two limiting cases for impurity concentration are shown: (a) less than one impurity per drop, (b) more than one impurity per drop. The impurity concentration N_i separating these two limits is $N_i = (4\pi R_0^3/3)^{-1}$. An impurity is shown in (a) with its sphere of influence whose radius is the Bohr radius a_x . The electron-hole plasma acts to screen the field of the impurity at distances greater than a_x .

In the case of high impurity concentration, an EHD has many impurities within its bounds. Assuming the distribution of impurities is uniform, the number contained in an EHD is proportional to the volume of that EHD. In this case the intensity of the EHL_{NP} line for one drop should scale with the volume of that drop. Of course if the droplet gets small enough, the transition is made to the behavior of the one isolated impurity; the intensity of the EHL_{NP} line should level off as the drop gets smaller. Figure IV.2 shows what the hysteresis curves for the EHL_{NP} line should look like for both of these limits. Plotted with the EHL_{NP} curves are some EHL_{TA} (TA phonon assisted recombination) hysteresis curves (scaled to the same height). The intensity of the EHL_{TA} luminescence from a drop is proportional to the total volume of that drop. Thus the EHL_{TA} lines are proportional to the total volume of EHL in the system.

For the upgoing hysteresis curves, the number of EHD's increases. The size of the EHD's remain constant. For the EHL_{TA} line the upgoing curve is thus proportional to the number of EHD. The EHD might or might not nucleate on impurities. For both cases the upgoing hysteresis curve for an EHL_{NP} line due to isolated impurities should also be proportional to the number of drops. Finally, in the case of many impurities within each drop, each drop added to the system should on average contain the same number of impurities. Thus the upgoing hysteresis curve for an EHL_{NP} line in the many-impurity case should be proportional to the number of drops. All of the upgoing hysteresis curves should have the same shape.

As the e-h pair generation rate g is decreased, the number of EHD is initially constant. The radii of the EHD decrease. At the e-h pair generation rate $g = g_c$, the EHD are all reduced to the critical size v_- .

Fig. IV.2 The electron-hole liquid (EHL) luminescence intensity is plotted as a function of a spatially uniform e-h pair generation rate g . The solid lines are for TA phonon assisted luminescence. The dashed lines are for no-phonon luminescence. The peak EHL_{NP} signal is scaled to equal the peak EHL_{TA} signal. For g increasing from zero the EHL_{TA} and EHL_{NP} curves coincide. The EHL_{NP} curves in (a) correspond to the low impurity concentration limit of Fig. IV.1(a) with the impurity binding an EHD. The high impurity concentration limit of Fig. IV.1(b) would yield EHL_{TA} and EHL_{NP} lines coinciding for both increasing and decreasing g . The EHL_{NP} curves in (b) correspond to a transition from many to one impurity per EHD as the drop size decreases. Upon increasing g from zero drops first appear at $g = g_+$. Upon subsequently decreasing g drops first start disappearing at $g = g_-$. All drops are gone for $g < g_-$.

luminescence intensity

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From this point on the size of the EHD that exist is constant, but the number of EHD decreases. The downgoing EHL_{TA} line is shown with a kink in it corresponding to the onset of drop annihilation at $g = g_c$. In the isolated impurity case consider two subcases: (1) the EHD is not bound to the impurity and can "shrink" off the impurity with downgoing excitation; (2) the EHD is bound to the impurity and the drop will "shrink" around it with downgoing excitation. For the former case the downgoing hysteresis curve is proportional to the total EHL volume of the system and thus has the same shape as the EHL_{TA} curve. For the second case, the downgoing hysteresis curve for the EHL_{NP} line is constant until $g = g_c$ where drops start disappearing. After that it drops to zero at the downgoing threshold g_- . Finally, in the case of many impurities within each drop, the downgoing EHL_{NP} hysteresis curve should be proportional to the volume of the EHL as is the case for the EHL_{TA} curve. These two curves should thus coincide over the full length of the downgoing hysteresis curve. I have shown the special case in Fig. IV.2(b) where there is a transition from the many-impurity to the single-impurity case as the EHD radius decreases. Alternatively, if the impurity concentration is non-uniform, this could correspond to EHD shrinking toward higher impurity concentrations.

Measurements of luminescence decay for the EHL_{NP} line and the EHL_{TA} line should exhibit features analogous to those discussed above for the downgoing hysteresis curves. Figure IV.3 shows the expected shapes for the various cases. The phonon and no-phonon curves are scaled to have the same height. The decay curve for the single isolated impurity that binds an EHD remains constant until drops start disappearing. The decay curve for the many impurity case is the same as that for the EHL_{TA} . The dashed line is for the case where there is a transition from the

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Fig. IV.3 The electron-hole liquid (EHL) luminescence intensity is plotted semilogarithmically vs time for spatially uniform pulsed photoexcitation. The solid lines are for TA phonon-assisted luminescence. The dashed lines are for no-phonon luminescence. The EHL_{NP} curves in (a) and (b) are for the impurity concentration cases of Figs. IV.2(a) and IV.2(b) respectively; they are analogous to the downgoing excitation power curves of Fig. IV.2.

many impurity to the single isolated impurity case as the drop radii decrease. Alternatively, if the impurity concentration is non-uniform, this could correspond to EHD shrinking toward higher impurity concentrations.

It is informative to compare droplet volumes with the volume per impurity for the conditions of the experiments in this chapter. At $T = 1.8\text{K}$, the predicted⁴ EHD radius for upgoing hysteresis curves is $R^+ \approx 1\text{ }\mu\text{m}$ for inhomogeneous nucleation. For downgoing hysteresis, the minimum drop radius is $R^- \approx 0.13\text{ }\mu\text{m}$. At the top of the downgoing hysteresis curves, an impurity concentration that would yield one impurity per drop is $N_1 \approx 2.4 \times 10^{11}\text{ cm}^{-3}$. Near the bottom of the downgoing hysteresis curve the impurity concentration that would yield one impurity per drop is $N_1 \approx 10^{14}\text{ cm}^{-3}$. An impurity concentration $\sim 10^{15}\text{ cm}^{-3}$ would under these circumstances be in the limiting case of many impurities over the full range of the downgoing hysteresis curve and the decay. An impurity concentration $\sim 10^{13}\text{ cm}^{-3}$ would start in the many impurity case and finish in the isolated impurity case. An impurity concentration of $\sim 10^{11}\text{ cm}^{-3}$ would be in the isolated impurity case for the full range of the downgoing hysteresis curve. These estimates of course rely on the predicted radii. If the excitation level on the upgoing hysteresis curve is not increased very slowly, there will be smaller droplets formed and more of them.^{3,4} Thus one could potentially be in the single isolated impurity case for impurity concentrations of $\sim 10^{12}\text{ cm}^{-3}$ or so.

A comment is in order concerning the hysteresis of the FE and bound exciton (BE) luminescence lines. A schematic of ideal FE hysteresis curves is shown in Fig. IV.4. These lines will have a hysteresis characterized by the density n_+ of the supersaturated FE gas along the upgoing

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Fig. IV.4 The free exciton (FE) luminescence intensity is plotted as a function of a spatially uniform e-h pair generation rate g . The arrows indicate whether the curves correspond to increasing or decreasing g . The values g_+ , g_c , and g_- are the same as those in Fig. IV.2

curve, and by the density n_- of the FE gas along the lower portion of the downgoing curve. Thus the FE luminescence intensity along an upgoing hysteresis curve will be greater than along a downgoing hysteresis curve. For the EHL hysteresis curves the opposite is true; the downgoing curves lie above the upgoing curves. This provides a simple test for the character of the species responsible for a given luminescence line.

In a real experiment, a distribution of excitation powers is achieved within a crystal and the corners in the idealized curves of Figs. IV.2, IV.3 and IV.4 are rounded out.

Ge Crystals and their Spectra

To do this experiment it was essential to have a variety of ultra-pure and carefully doped Ge crystals. For these crystals we are indebted to E. E. Haller of the Lawrence Berkeley Laboratory.

The crystals selected for the study fell into two categories:

- 1) High Si content — purposefully doped $[Si] \sim 10^{14} - 10^{16} \text{ cm}^{-3}$.
Crystals grown in quartz crucibles (SiO_2) usually contain $\sim 10^{14} \text{ cm}^{-3}$ of Si.
- 2) Crystals with net electrical impurity concentration $|N_A - N_D|$ high enough to provide sizable EHL_{NP} lines, but low enough that the single isolated impurity case should be applicable.

The search for the best crystals was done by measuring the no-phonon luminescence spectra. The spectra of some of the crystals tested for this experiment are discussed below. Further information on their characteristics is displayed in Table I.2.

Crystals Not Used

Figure IV.5 shows a spectrum from sample 112. The pair of lines toward shorter wavelengths are the no-phonon lines. The pair of lines to their right are the TA phonon-assisted lines. The sharp lines are due to excitons. The broad lines are due to the EHL. Sample 112 has a shallow electrical impurity concentration: $N_A - N_D = 2.4 \times 10^{14} \text{ cm}^{-3}$. This concentration is too high for the single isolated impurity case discussed in the previous section. A small hysteresis ($g_+/g_- \sim 1$) was observed for this crystal. This finding is in agreement with the expectations and experimental results of Westervelt et al.⁴ that were discussed several paragraphs below Eq. (IV.2).

Figure IV.6 shows a spectrum from sample 438. This spectrum was measured using poor spectral resolution in order to detect the no-phonon FE and EHL lines. This sample, grown in a graphite crucible, has "high" carbon content and low Si content.

Figure IV.7 shows the spectrum of two ultra-pure Ge samples: (a) 145M, and (b) 404. Neither of these crystals shows EHL_{NP} luminescence. Both spectra contained a BE_{NP} line and an EHL_{TA} line. A third ultra-pure sample (475) was tested and no no-phonon luminescence of any type was seen.

Crystals Used

Figure IV.8 shows the spectrum of sample 437V (dislocation free). The spectrum of sample 437D (dislocated) was measured to be identical to that of sample 437V. These samples are n-type with $|N_A - N_D| = 2 \times 10^{10} \text{ cm}^{-3}$ believed due to phosphorous. An effort was made to grow a high Si content into these crystals ($\sim 10^{16} \text{ cm}^{-3}$). Due to a leak in the atmosphere chamber during growth, a SiO₂ film formed on top of the melt. The actual Si

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Fig. IV.5 Luminescence spectrum of sample 112. The two broad lines are EHL luminescence. The two sharp lines are exciton luminescence. The pair of lines at longer wavelengths are TA phonon-assisted luminescence. The pair at shorter wavelengths are no-phonon luminescence. This crystal has a net electrical impurity concentration due to Ga of $N_A - N_D = 2.4 \times 10^{16} \text{ cm}^{-3}$.

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Fig. IV.6 Luminescence spectrum of sample 438. Weak no-phonon exciton and EHL luminescence are seen. Low spectral resolution was used in order to optimize the luminescence crystal. This crystal was grown in a graphite crucible. The net electrical impurity concentration $N_A - N_D = 10^{11} \text{ cm}^{-3}$ is probably due to phosphorous.

Fig. IV.7 Luminescence spectra of two ultra-pure samples:
(a) 145M, and (b) 404. No EHL no-phonon luminescence
is seen.

XBL 6212-12293

Fig. IV.8 Luminescence spectrum of sample 437V. This sample is n-type with a net electrical impurity concentration $|N_A - N_D| = 2 \times 10^{10} \text{ cm}^{-3}$. The Si concentration should be quite high: $[\text{Si}] = 10^{15} - 10^{16} \text{ cm}^{-3}$.

concentration could be $\sim 10^{14} - 10^{16} \text{ cm}^{-3}$. These concentrations are high enough to have many impurities inside a single EHD for all but possibly the smallest EHD. Rolf Martin⁸ has tentatively identified BE_{NP} lines in some Berkeley grown crystals with silicon. Considering the high silicon content of crystal 437 it is reasonable to suspect Si for the BE_{NP} line.

Figure IV.9 shows the spectrum of sample 400 #2. The spectrum of 400 #1 was measured and found to be identical to that of 400 #2. The spectra corresponding to excitons, EHL, and one new line are grouped together for no-phonon, TA phonon assisted, LA phonon assisted, and TO phonon assisted luminescence in a progression from low to high wavelengths. The new luminescence line and its phonon assisted counterparts were found to exist at the same wavelengths as the low wavelength end of the EHL spectrum. Its no-phonon line has a hysteresis characteristic of excitons: the upgoing hysteresis curve lies above the downgoing hysteresis curve. We tentatively identify these lines with a multi-exciton complex. From his experiments on another piece of this crystal, Rolf Martin⁸ has tentatively identified the BE_{NP} line with phosphorous. The net concentration of electrical impurities for this "high" phosphorous content crystal is $N_A - N_D = -3.8 \times 10^{12} \text{ cm}^{-3}$. The single isolated impurity model should be accurate for the lower excitation part of the downgoing EHL_{NP} hysteresis curve. How much of this curve is characterized by the single isolated impurity model depends on the actual EHD radius for the upgoing curve. This crystal was grown in a graphite crucible and has a correspondingly "high" concentration of carbon and low concentrations of silicon and oxygen.

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Fig. IV.9 Luminescence spectrum of crystal 400 #2. The spectrum magnified by $\times 7$ is also plotted. The no-phonon, TA phonon-assisted, LA phonon-assisted, and TO phonon-assisted luminescence are shown (from short to longer wavelengths). A sharp line exists between the exciton and EHL lines. We attribute it to a multi-exciton complex. This crystal was grown in a graphite crucible. The net electrical impurity concentration for this "high" phosphorous content crystal is $N_A - N_D = -3.8 \times 10^{12} \text{ cm}^{-3}$.

Experimental Procedure

The experimental apparatus and the general procedures for making measurements were dealt with in detail in Chapter I. In this section I will describe the time history of the excitation power used to measure the hysteresis curves. The source, a feedback-stabilized incandescent lamp with a $1.52 \mu\text{m}$ interference filter, was chosen for its stability and long absorption length in Ge ($\sim 1.25 \text{ mm}$). The crystal sizes were $\sim 8 \times 8 \times 4 \text{ mm}$.

Figure IV.10 shows the time histories for upgoing and downgoing hysteresis curves. For upgoing hysteresis curves the excitation power was increased from zero to the desired value. Several seconds later the detection apparatus started integrating the luminescence signal for a preset time. Next the light intensity was reduced to zero for several seconds to erase the memory of the system. This cycle was then restarted with the lamp power incremented by a preset amount. After the lamp power was cycled and incremented the desired number of times the experiment was stopped. Figure IV.10(a) shows a time history of the excitation power for an upgoing hysteresis experiment.

The time history of the excitation power for a downgoing hysteresis experiment is shown in Fig. IV.10(b). The difference is the insertion of several seconds of high excitation power between the regions of zero excitation and the regions where the luminescence signal is integrated.

Measured Hysteresis and Decay Curves

Figure IV.11 shows the hysteresis curves for both the EHL_{NP} and the EHL_{TA} lines for crystal 437D. The curves were scaled to have the same peak intensity. The upgoing hysteresis curves coincide nicely as is

Fig. IV.10 The time histories of the excitation power g for (a) upgoing hysteresis curves, and (b) downgoing hysteresis curves. The luminescence signal was integrated during the intervals Δt . Between each cycling of the excitation power, the lamp intensity was brought to zero. The shortest time interval used for any part of these excitation power histories was 5 seconds.

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Fig. IV.11 Electron-hole liquid (EHL) luminescence intensities measured for the TA phonon assisted (EHL_{TA}) line and the no-phonon (EHL_{NP}) line for upgoing and downgoing excitation power scans (see Fig. IV.10). The solid curves are for the EHL_{TA} line; the dots are for the EHL_{NP} line. The upgoing data lie below the downgoing data. Crystal 437D.

expected. The downgoing hysteresis curves have the same characteristics as those in Fig. IV.2(b). Because the excitation power in the experiment is not uniform, the corners on the ideal model should be rounded out. The observed hysteresis supports the model where an EHD contains many impurities. The deviation of the downgoing EHL_{NP} curve from the downgoing EHL_{TA} curve could be for one of several reasons:

- 1) The transition from many to one impurity in an EHD could be made as the drop radii decrease. This case is illustrated in Fig. IV.2(b).
- 2) The impurities in the many per drop limit could be distributed non-uniformly. The drops could be shrinking toward the higher impurity concentrations.

Figure IV.12 shows the luminescence decay for sample 437D in response to pulsed photoexcitation using a GaAs laser diode. The decay curve for the EHL_{NP} line was scaled to have the same peak intensity as the decay curve for the EHL_{TA} line. The EHL_{NP} decay is observed to deviate from the EHL_{TA} decay curve in the same manner as occurred in the downgoing hysteresis curves.

Figure IV.13 shows the hysteresis curves for both the EHL_{NP} and the EHL_{TA} lines for crystal 400 #2. The EHL_{NP} curves were scaled to match the upgoing EHL_{NP} curve to the upgoing EHL_{TA} curve. Within the noise the match between upgoing hysteresis curves is quite good. Comparison of the downgoing hysteresis curves clearly indicates that the dominant EHL_{NP} luminescence site is an isolated impurity that binds EHD.

Figure IV.14 shows the upper end of another set of EHL_{NP} and EHL_{TA} hysteresis curves. The maximum excitation power for these curves was

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Fig. IV.12 Electron-hole liquid (EHL) luminescence intensities measured for the TA phonon assisted (EHL_{TA}) and the no-phonon (EHL_{NP}) line in response to pulsed photo-excitation by a GaAs laser. Sample 437D.

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Fig. IV.13 Electron-hole liquid (EHL) luminescence intensities measured for the TA phonon assisted (EHL_{TA}) line and the no-phonon (EHL_{NP}) line for upgoing and downgoing excitation power scans (see Fig. IV.10). The upgoing data lie below the downgoing data. Sample 400 #2.

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Fig. IV.14 Electron-hole liquid (EHL) luminescence intensities measured for the TA phonon assisted (EHL_{TA}) line and the no-phonon (EHL_{NP}) line for the higher excitation powers of upgoing and downgoing excitation power scans (see Fig. IV.10). The upgoing data lie below the downgoing data. Sample 400 #2.

2.7 times the maximum excitation power used in Fig. IV.13. Again the deviations in the downgoing hysteresis curves clearly indicate that the dominant EHL_{NP} luminescence site is an isolated impurity that binds EHD.

Measurements of EHL_{TA} and EHL_{NP} luminescence decay are planned.

Results and Conclusions

Because these experiments were performed using low excitation powers and a stable light source (excluding pulsed measurements) the nucleation theory of Westervelt^{2,3,4} should be applicable. Because the light intensities were not cycled infinitely slowly, the EHD radius for the upgoing hysteresis curve should be smaller than that predicted^{3,4} by inhomogeneous nucleation theory. The isolated impurity case should be realized for higher impurity concentrations.

The upgoing hysteresis curves for the EHL_{TA} and EHL_{NP} lines were observed to have the same shape. The shapes for the downgoing curves were dramatically different from each other. The discussions in previous sections indicate that there are two possible explanations for such behavior:

- 1) At least some EHD become bound on isolated impurities.
- 2) There are a large number of impurities within the EHD.

The concentrations may be non-uniform.

For the high Si content crystal (437) there are several possible explanations for the observed downgoing hysteresis curves. Because the Si content of this otherwise ultra-pure crystal is $\sim 10^{15} \text{ cm}^{-3}$ there should be many Si atoms inside an EHD for all drop sizes. This assumes of course

that the Si atoms don't clump significantly and the EHD nucleate away from such clumps. If the impurity responsible for the EHL_{NP} line is uniformly distributed and there are many impurity per drop, then the downgoing hysteresis curves for the EHL_{NP} and the EHL_{TA} lines should have the same shape. They are observed to have different shapes. If the EHL_{NP} line is due to Si alone, then the data would be explained if the EHD shrink toward regions with higher Si concentration. This would be consistent with Fishman's⁷ model where EHD in ultra-pure Ge bind on concentration fluctuations of non-electrical impurities. Another possible explanation for the observed hysteresis is that there are two sources of EHL_{NP} radiation: 1) an isolated impurity to which the EHD bind, and 2) many impurities within an EHD (non-electrical Si or possibly O). In this case there should still be a sizable deviation between the upper regions of the EHL_{NP} and the EHL_{TA} downgoing hysteresis curves. We conclude that data for this crystal supports a model where EHD are bound on concentration fluctuations of impurities (many per drop). For this crystal the most likely non-electrical impurity is Si.

For the high phosphorous content crystal (400 #2) there are several possible explanations for the observed downgoing hysteresis curves.

There is a sharp deviation between the downgoing EHL_{NP} and EHL_{TA} hysteresis curves at the highest excitation powers. From this observation it must be concluded that the EHD are binding to defects that are localized (smaller than the size of the EHD). Furthermore, the binding site is responsible for the EHL_{NP} line. It is possible that there could be another defect type (many per EHD) contributing to the EHL_{NP} line, but its contribution must be small. The localized defect could be either an isolated defect (e.g. a single impurity atom), or a sharply clustered

collection of defects (e.g. sharply clustered impurities). For this crystal, shallow neutral electrical impurities are a candidate $[N_A - N_D] = [4\pi(0.4 \mu\text{m})^3/3]^{-1}$. If these impurities are incorporated into Ge as single isolated impurities, then the largest acceptable EHD radius for this data is $R_d \sim 0.4 \mu\text{m}$. If the impurities are clustered this upper limit increases. Another possible binding site for EHD is clustered non-electrical impurities. Because the concentration of EHD in Ge crystals is typically $\sim 10^5 - 10^7$ EHD/cm³ the EHD could in fact be bound to defects of such low concentration that they are not readily characterized. But we do know they are binding on the defect responsible for the EHL_{NP} line and the most probable candidate for this is phosphorous.

The argument can be made for the many impurity case, that a reduction in concentration will decrease the EHL_{NP} signal. Thus for other ultra-pure Ge crystals it is still possible that EHD bind to them, but the luminescence is weaker and less easily seen. The possibility also exists that in crystals grown differently the binding site may be altered sufficiently that it is non-radiative. Alternatively, other nucleation sites may become preferable.

If EHD nucleate on shallow electrical impurities, the intensity of the EHL_{NP} line might be expected to be insensitive to the concentration of these impurities. The concentration of EHD is typically $10^5 - 10^7$ EHD/cm³. The concentration of shallow neutral electrical impurities is in most crystals three to five orders of magnitude higher. There are several possible reasons why we don't see significant EHL_{NP} luminescence intensities in the more electrically pure crystals: it could be that clusters of electrical impurities are responsible for the EHL_{NP} line. In this case, for lower concentrations there are fewer clusters of the

proper size and character. Again it is possible that for lower concentrations the EHD are nucleating on other defects; some ultrapure crystals show an exciton no-phonon line but no EHL_{NP} line.

In conclusion, the measured EHL_{NP} hysteresis curves are consistent with Fishman's proposal that EHD in ultrapure Ge nucleate on fluctuations in the non-electrical impurity concentration. For a crystal with high electrical impurity concentration, our results are consistent with EHD nucleating on shallow neutral impurities as suggested by Westervelt.^{2,4}

Chapter IV, References

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CHAPTER V.

FREE EXCITON DIFFUSION AND DECAY IN ZERO STRESS Ge

An experimental study of free exciton (FE) diffusion can potentially lead to the determination of quantities of physical interest. If the dominant scattering mechanism for FE diffusion is FE-FE collisions, then the FE-FE collision cross section can be determined. If the dominant FE scattering mechanism involves collisions with phonons, then a FE-phonon scattering time τ_p can be determined. If the former case (self diffusion) is physically realizable, then the potential exists to study another type of diffusion. By reducing the FE density FE-FE collisions become less probable and other FE scattering mechanisms will become dominant. If self diffusion is not observed, then one can use the maximum attainable FE density to set limits on the FE-FE scattering cross section.

The value of the FE diffusion constant or diffusivity D_x can also be an important parameter in the study of other photoexcitations of interest. As an example, the measurement of the electron density at the site of a hole for the electron-hole liquid, was described in Chapter III. This correlation factor is of intense interest as a strict test of the validity of various many-body theory approximation schemes. The justification of the experimental procedure used to make this measurement requires the knowledge of D_x .

There are good reasons to be suspicious of the experiments claiming to measure D_x that have been published prior to this work.¹ The basic problem is that people have not been measuring what they have intended to measure: Diffusion has been measured with electron-hole liquid droplets (EHD) present. The EHD act as a FE source which seriously

perturbs the FE spatial distribution. Or the FE diffusion length L_x ($L_x = \sqrt{D_x \tau_x}$) is measured and D_x is calculated using a separate measurement of the FE lifetime τ_x . The FE lifetimes used for such calculations have been suspect, as I will explain later. Finally, care must be taken that the transport studied is diffusive transport and not forced transport. As an illustration, consider the related problem of EHD diffusion. The early experiments² purporting to measure the EHD diffusivity D_d yielded a spread of values from $0.1 \text{ cm}^2 \text{ s}^{-1}$ to $500 \text{ cm}^2 \text{ s}^{-1}$. Westervelt et al.,³ by cleverly making use of the optical hysteresis in the formation of EHD were able to monitor an essentially fixed set of EHD for periods of hours using low intensity photoexcitation. They found an upper limit $D_d \leq 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. The reason for the discrepancy between this result and earlier measurements lies in the use of intense photoexcitation sources in the earlier work. The transport observed was forced transport, not diffusive transport. Drops were propelled from the photoexcited region by forces, notably the phonon wind, due to the high excitation levels used.

The main portion of this experiment involves measuring spatial profiles of FE luminescence intensity I_x at various times after a GaAs laser photoexcites a Ge crystal. From these FE density profiles a FE diffusivity is deduced, surface recombination is characterized and an exciton lifetime, with surface effects excluded, is found. The diffusivity determined does not depend on any measurement of the FE lifetime.

The FE radiative lifetime in Ge is expected to be $\tau_{rx} \sim 500 \pm 200 \text{ } \mu\text{s}$. This estimate is based on the observation that the EHD lifetime measured for a variety of Ge crystals is $\tau_d = 40 \pm 5 \text{ } \mu\text{s}$. This lifetime is taken to be an intrinsic property of the electron-hole liquid (EHL) in zero

stress Ge. A further measurement⁴ has deduced the radiative efficiency of the EHL to be $e_{rl} = \tau_l/\tau_{rl} = 0.33$. Finally, Westervelt⁵ and Westervelt et al⁶ have measured $\tau_{rx}/\tau_{rl} = 4.1 \pm 1.8$. The above τ_{rl} then follows straightforwardly from $\tau_{rl} = (\tau_l/e_{rl})(\tau_{rx}/\tau_{rl})$. Actual measurements of FE lifetimes have varied from 1 to 20 μ s. The large non-radiative recombination rate is not yet completely understood. Impurities, dislocations and surfaces may act as recombination sites. To study FE decay in bulk Ge one needs to be aware of the relative importance of surface recombination. In this chapter I will evaluate the importance of surface recombination.

Experimental Details

The measurements in this chapter were made at 4.2K unless it is stated otherwise. The experimental geometry is illustrated in Fig. V.1. A single junction GaAs laser diode is pulsed (pulse width $\leq 2 \mu$ s, pulse rate ~ 4 kHz). The light ($\lambda \approx 0.865 \mu$ m) escaping from the length of its junction is focused as a stripe on the face of a Ge crystal. Luminescence leaving the crystal through a surface at right angles to the excitation surface is routed to a spectrometer. The spectrally resolved luminescence is then detected by a cooled Ge photodiode [see Fig. V.2]. Figure V.2 illustrates the basic experimental set-up. Spatial, spectral, and temporal measurements were automated. The results were stored in a multichannel scaler (MCS). A control box, made using simple TTL logic chips, coordinated the stepper motors translating the output lens (spatial scan) and rotating the spectrometer grating (spectral scans) with the channel advance of the MCS. For time-resolved measurements an A-B boxcar integrator was used. Such a boxcar measures the input voltage

EXPERIMENTAL GEOMETRY

Fig. V.1 Experimental geometry. A stripe of radiation from a GaAs laser diode's junction is pulsed onto an ultrapure $8 \times 8 \times 4 \text{ mm}^3$ Ge crystal at $T = 4.2\text{K}$. Luminescence leaving the side of the crystal is routed to the detection apparatus. Spatial scans of luminescence are made by translating the output lens.

EXPERIMENTAL SETUP

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Fig. V.2 Experimental set-up. A square wave generator triggers an A-B boxcar and a pulse generator for the GaAs laser. The GaAs laser photoexcites a Ge crystal immersed in liquid helium at 4.2K. A lens focuses luminescence on the slit plane of a 1/4 meter Jarrel Ash spectrometer with a 890 groove/mm grating blazed at 1 μm . A Ge photodiode detects the luminescence. An A-B boxcar is used for time resolved measurements. Spatially and spectrally resolved measurements are made by translating the output lens or rotating the spectrometer grating. These operations are automated by using stepper motors controlled by TTL logic circuitry. This circuitry also coordinates the channel advance for the multichannel scaler.

of a waveform within two intervals of time, called gates A and B. The boxcar output is proportional to the difference between the two signals measured in these two intervals. In this experiment gate B was always positioned before the laser pulse. Gate A was positioned afterward. Typical scans required from a minute to an hour. An A-B boxcar was necessary, as opposed to a single gate boxcar, to avoid the distortion of the data that would otherwise have occurred due to drifts in the dc level of the preamp output voltage. The gate A was kept stationary for spectral and spatial scans. For temporal measurements gate A was advanced for each channel advance of the MCS. The voltage-to-frequency (V/f) converter included in Fig. V.2 was used to convert the boxcar output voltage to a train of pulses whose frequency is proportional to that voltage. The MCS then counts these pulses for a preset time.

The detector used was an older version of the one discussed in Chapter I. The preamp [see Fig. V.3] was used with a 10 Megohm feedback resistor as shown. This resulted in a $\sim 2 \mu\text{s}$ preamp time response. For more details on this detector and preamp see Ref. V.7.

Because accurate imaging was a high priority, special care was taken to prepare flat highly polished crystal surfaces. The crystals used had dimensions $\sim 4 \times 8 \times 8 \text{ mm}^3$. A square face was photoexcited and luminescence leaving a rectangular face was collected. In cutting the samples out of larger pieces of Ge crystal, this rectangular face was optically polished before a cut was made for the excitation surface. This avoided the rounding of the viewing surface near the corner with the excitation surface that otherwise would have occurred during polishing.

Another concern was internally reflected luminescence escaping out the edges of the crystal. Because of germanium's large index of refraction

SENSITIVE CURRENT AMPLIFIER AND DETECTOR BIASING CIRCUIT

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Fig. V.3 Sensitive current amplifier and detector biasing current. With a 10 Megohm feedback resistor the preamp time response was $\sim 2\text{ }\mu\text{s}$.

($n \sim 4$) light is internally reflected for angles of incidence greater than $\sim 15^\circ$. On crystals that are normally prepared (etched surfaces) there are large "edge effects" on spatial scans of luminescence. To minimize these edge effects none of the crystal surfaces were etched. This leaves a distribution of angles covering all crystal surfaces. Thus a smaller fraction of the internally reflected light needs to reach an edge to escape and the "edge effects" are correspondingly reduced. Later in the experiment the excitation surface alone was etched in order to see the effect on the surface recombination of FE's.

The spatial resolution for the optics used was 0.2 mm for luminescence coming from the middle of the crystal where the laser stripe illuminated the crystal. The depth of field was 3 mm. Thus, the luminescence collected by the output lens that passes through the spectrometer slit and is detected came from a ~ 0.2 mm thick slice of the crystal. One reason for using stripe excitation was to minimize the spreading of the measured FE spatial distribution due to the finite depth of field.

Expectations

Qualitatively one expects to see the FE diffuse into the crystal away from the excitation surface. If the surface does not act as a recombination site for FE the slope of the FE distribution should be zero at the excitation surface. Since surface recombination is expected the distribution should be pulled downward toward the surface.

Self-Diffusion ?

To determine whether the self diffusion of FE at 4.2K is important for the FE densities n_x of this experiment, FE diffusion profiles were compared for a number of laser pulse energies. The diffusion profiles should depend on the laser pulse energy for self diffusion ($D_x \propto n_x^{-1}$ for self diffusion). Profiles corresponding to a fixed time delay from the laser pulse were observed to have the same shape and width for over a factor of ten variation in pulse energy. For the highest pulse energy used the maximum n_x was just below the n_x where EHD would still be present ($n_x \sim 10^{14} \text{ cm}^{-3}$). This indicates that the self diffusion of FE is not the dominant diffusion mechanism. Further evidence supporting this finding will be discussed in the "Results on Conclusions" section of this chapter. This finding greatly simplifies the treatment of experimental FE diffusion profiles.

A Simple Interpretation of FE Diffusion Profiles

The scattering mechanism responsible for the diffusion occurring in this experiment does not depend on the FE density n_x . This means that the diffusion of two FE distributions superimposed on one another proceeds identically to the sum of the ways each separate distribution would diffuse. Thus the diffusion profiles corresponding to one laser stripe should equal the diffusion profiles corresponding to a continuous distribution of laser stripes across the excitation surface. The solution to a one-dimensional diffusion equation should describe diffusion profiles measured in this work.

The one-dimensional diffusion equation is:

$$D_x \frac{\partial^2 n_x}{\partial y^2} + \frac{\partial n_x}{\partial t} = \frac{n_x}{\tau_x} \quad (V.1)$$

It will be assumed that τ_x is independent of n_x . A semi-infinite medium will be assumed. As a boundary condition for the excitation surface it will be assumed that the flux of FE into the surface is proportional to the FE concentration $n_x(0)$ at the surface:

$$J_{\text{into surface}} = D_x \left. \frac{dn_x}{dy} \right|_{y=0} = S n_x \Big|_{y=0} \quad (V.2)$$

Here y increases going into the crystal, and S is called the surface recombination velocity. For an isotropic velocity distribution simple kinetic and geometric arguments predict S can be no larger than one-fourth the average thermal velocity.

Equation (V.1) can be simplified by making the following substitution:

$$n_x(y,t) = n(y,t) e^{-t/\tau_x} \quad (V.3)$$

The resulting equation for $n(y,t)$ is:

$$D_x \frac{\partial^2 n}{\partial y^2} + \frac{\partial n}{\partial t} = 0 \quad (V.4)$$

Note that τ_x effects only the amplitude, not the shape, of the diffusion profiles. To solve this equation it is convenient to Laplace transform the time variable.

$$\tilde{n} = \int_0^{\infty} e^{-\beta t} n(y,t) dt \quad (V.5)$$

Equation (V.4) becomes

$$D_x \frac{\partial^2 \tilde{n}}{\partial y^2} = \tilde{\beta n} - n(y, t = 0^+) \quad . \quad (V.6)$$

For P δ -functions worth of FE inserted at $y=a$ ($a \sim 1 \mu m$) at $t=0$, Eq. (V.6) becomes

$$\frac{\partial^2 \tilde{n}}{\partial y^2} - \frac{\tilde{\beta n}}{L_x} = -\frac{P}{D_x} \delta(x-a) \quad . \quad (V.7)$$

The homogeneous equation solutions are $\exp[\pm y\sqrt{\beta/D_x}]$. The boundary conditions on this solution (a Green's function) follow from Eq. (V.2) for the excitation surface, and from $\tilde{n} \rightarrow 0$ as $y \rightarrow 0$, and from the requirement that $\tilde{n}$ be continuous at $y=a$, and finally from the specification of the discontinuity of the slope of $\tilde{n}$ at $y=a$ given by Eq. (V.7). Applying these boundary conditions to linear combinations of the homogeneous equation solutions, inverse Laplace transforming the result, and taking the limit as $a \rightarrow 0$ results in:

$$\begin{aligned} n_x(y, t) &= n(y, t) e^{-t/\tau_x} \\ &= P e^{-t/\tau_x} \left[\frac{e^{-y^2/4D_x t}}{\sqrt{\pi D_x t}} - \frac{S}{D_x} \exp\left(\frac{yS}{D_x} + \frac{S^2 t}{D_x}\right) \operatorname{erfc}\left(\frac{S\sqrt{t}}{D_x} + \frac{y}{\sqrt{4D_x t}}\right) \right] \end{aligned} \quad (V.8)$$

To assess the importance of surface recombination I integrate over the volume of the semi-infinite medium. Defining

$$N_x = \int_0^\infty n_x(y, t) dy \quad (V.9a)$$

and

$$N = \int_0^\infty n(y, t) dy \quad (V.9b)$$

the result is

$$N_x = e^{-t/\tau_x} N = P e^{-t/\tau_x} \left[e^{S^2 t/D_x} \operatorname{erfc} \left(\sqrt{\frac{S^2 t}{D_x}} \right) \right] \quad (\text{V.10})$$

The measured decay rate is given by

$$\begin{aligned} \frac{1}{\tau_{\text{apparent}}} &= - \frac{\frac{dN_x}{dt}}{N_x} = \frac{1}{\tau_x} + \left(- \frac{dN}{N} \right) \\ &= \left(\frac{1}{\tau_x} \right)_{\text{bulk}} + \left(\frac{1}{\tau_x} \right)_{\text{surface}} \end{aligned} \quad (\text{V.11})$$

Evaluating $(\tau_x)_{\text{surface}}$ using Eq. (V.10) yields

$$(\tau_x)_{\text{surface}} = \frac{D_x/S^2}{\left[\frac{e^{-S^2 t/D_x}}{\sqrt{\frac{S^2 t \pi}{D_x}} \operatorname{erfc} \left(\sqrt{\frac{S^2 t}{D_x}} \right)} - 1 \right]} \quad (\text{V.12})$$

The manner in which $(\tau_x)_{\text{surface}}$ varies in time is determined entirely by the ratio D_x/S^2 .

Data and Discussion

This experiment has been done for two crystals: 437D (dislocated, n-type) and 145M (dislocation free, p-type). See Table I.2 for further information. I will illustrate the general procedure with data measured using sample 145M.

The first step was to vary the laser pulse energy until an energy just able to create some electron-hole droplets (EHD) was found. Figure V.4 shows three spatial profiles of EHL luminescence for various times after the laser pulse. The EHL luminescence is seen to decay in place much faster than the 40 μ s lifetime of bulk EHL. This is due to the creation of many small EHD. Because of large surface-to-volume ratios, their decay is dominated by the surface evaporation of e-h pairs. The FE and EHD spatial profiles (d) and (c) indicate that FE's dominate the behavior of the system after a 12.5 μ s delay. This is especially clear when one recalls from the first paragraph of this chapter that the EHL radiative decay rate is four times the FE radiative decay rate. To plot the curves (a)-(d) such that a given amplitude corresponds to the same number of electron-hole (e-h) pairs, curve (d) would have to be multiplied by four. Also the rate at which the decaying EHD give off e-h pairs is not sufficient to have prevented the peak of the FE distribution from moving inside the crystal. Finally, I emphasize that the EHD are all decaying in place very close to the crystal surface. This is an indication of the low excitation powers used. The powers are low enough that the phonon wind is not strong enough to propel EHD. Arguments concerning whether the phonon wind need be considered for FE in this experiment are given in the "Results and Discussion" section of this chapter.

Figure V.5 shows the spatially integrated FE and EHL luminescence decay curves corresponding to the same laser pulse energy as Fig. V.4. The EHL luminescence decays much faster than the 40 μ s lifetime of the EHL. The EHL luminescence disappears into the noise 15 μ s after the laser pulse. The FE decay rate becomes continuously slower until about 30 μ s after the laser pulse. After 30 μ s the FE decay appears to be exponential with an

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Fig. V.4 Spatial scans of electron-hole droplet (EHD) luminescence intensity (a-c) at times up to 12 μ s after the laser pulse, when the first free exciton (FE) profile (d) is recorded. All profiles are to the same scale. Crystal 145M.

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Fig. V.5 Free exciton (FE) and electron-hole droplet (EHD) luminescence decay. The width of the tickmark at $t=0$ is the $2 \mu\text{s}$ pulse width of the exciting laser. Crystal 145M.

apparent lifetime $(\tau_x)_{\text{apparent}} = 27 \mu\text{s}$. Within the $15 \mu\text{s}$ span of time (no EHD) in which the FE decay rate changes, the spatially integrated FE luminescence intensity has dropped by almost half a decade. A larger initial FE decay rate is consistent with an initially larger FE decay at the crystal surface. As time progresses the FE distribution should move into the crystal and surface decay should become less dominant. I believe the FE decay is starting to become faster than exponential toward the end of the observable decay due to the shifting of the free carrier (FC) - FE equilibrium toward FC.

Free exciton spatial profiles, for times ranging from 13 to 30 μs after the laser pulse, are plotted in Fig. V.6. The FE are seen to move into the crystal away from the excitation surface on the right (indicated by arrows). The back face of the crystal is clearly indicated by the small peak. This peak is due to internally reflected light escaping through the corner of the crystal (edge effect). As was expected the FE distribution is pulled down near the excitation surface. By 30 μs after the laser pulse the peak of the FE distribution has moved $3/4 \text{ mm}$ into the crystal and FE are starting to reach the back surface of the crystal (which was not taken into account in the previous section). By 40 μs the back surface is starting to significantly effect the time evolution of the diffusion profiles and perhaps the FE decay. By 80 μs the distribution of FE between the crystal surfaces is becoming fairly symmetric. After 40 μs the effect of FE recombination at the excitation surface may be decreasing, but surface recombination at the back surface is increasing. If the increase in the back surface's decay rate balances out the decrease in the front surface's decay rate, then the lengthening of the apparent FE lifetime $(\tau_x)_{\text{apparent}}$ with time could be halted.

Fig. V.6 Free exciton (FE) luminescence is viewed through a surface at right angles to the photoexcited surface at various times after the end of the laser pulse. These data show the FE diffuse into the crystal from the excitation surface (indicated by the arrows on the right) toward the rear surface (indicated by the peak due to escaping internally reflected luminescence). The FE density near the surface is pulled down by surface recombination. Crystal 145M.

A mechanism such as this quite conceivably can have effected FE lifetime measurements made using small Ge crystals.

Analogous decay curves and diffusion profiles, measuring using a sample (437D) with approximately 350 dislocations/cm², are plotted respectively in Figs. V.7 and V.8. The apparent FE lifetime of 12 μ s suggests dislocations are active as recombination centers. This correlation has been independently verified by a Soviet group.^{8,9} The diffusion profiles exhibit the same features as those for sample 145M.

Results and Conclusions

The data were fit to Eq. (V.8), the solution for a δ -function excitation just inside the crystal surface. The fitting parameters were D_x , S , and the time in Eq. (V.8) corresponding to the first measured diffusion profile. These parameters were chosen to optimize the agreement between the position and width of the FE diffusion profiles as well as the slope at the excitation surface. The theoretical [Eq. (V.8)] diffusion profiles that result from fitting the diffusion profiles of Fig. V.6 are plotted in Fig. V.9.

It should be noted at this point that the above experiments were repeated on the same two crystals, but with the excitation surfaces etched. The resulting decay curves and diffusion profiles were identical to those measured using unetched surfaces. The main difference was that it took one-seventh as much laser pulse energy to reach the EHL threshold. This observation would seem to support an argument that the surface recombination velocity S is determined by the fact that there is a surface and not so much the detailed character of that surface (at least

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Fig. V.7 Free exciton (FE) and electron-hole droplet (EHD) luminescence decay. Crystal 437D.

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Fig. V.8 Time resolved free exciton (FE) spatial profiles in response to pulsed photoexcitation. Crystal 437D.

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Fig. V.9 Theoretically generated free exciton spatial profiles using the best fit parameters for the data of Fig. V.6.

for the surface preparations used here). Further, the effect that crystal damage at the surface has on the laser pulse energy necessary to create a given number of e-h pairs can be understood through absorption length effects: the excitation light incident on a polished surface that actually makes it through the damaged layer is attenuated by an amount determined by the absorption length of the radiation and the thickness of the layer. For the GaAs laser used here this corresponds to a 1 μm thick layer of damaged crystal (consistent with the grit sizes used for polishing).

The fit corresponding to Fig. V.9 used $D_x = 300 \text{ cm}^2/\text{s}$ and $S = 3000 \text{ cm/s}$. For the crystals studied here D_x is not dependent on impurity type or concentration, or on dislocation density. This behavior is consistent with diffusion mediated by LA phonons as given by Eq. (II.62) which predicts $D_x \propto T^{-1/2}$. This trend with temperature is qualitatively supported by separate measurements of the diffusion length L_x from FE spatial profiles produced by steady state surface excitation (small absorption length): The diffusion lengths were measured to increase with decreasing temperature. The FE lifetimes were not measured for the lower temperatures, but the trend holds as long as the FE lifetime doesn't increase with decreasing temperature. At 3K, assuming τ_x is the same as at 4.2K, the D_x that I determine from these measurements is about one-fourth of the value $D_x = 1500 \text{ cm}^2/\text{s}$ reported by Pokrovskii et al¹⁰ which I critically evaluated at the end of Chapter II. The D_x determined from the steady state L_x at 4.2K and the measured $\tau_x = 27 \mu\text{s}$ is consistent with the value $D_x = 300 \text{ cm}^2/\text{s}$ reported above. The steady state L_x was measured for FE densities an order of magnitude lower than were used in the pulsed experiment. This is further support for the contention that

self diffusion is negligible. This would also seem to indicate that forced transport (e.g. phonon wind) is not involved. That is, of course, barring the unlikely situation in which the opposing effects of phonon wind and self diffusion cancel or mask the effect of each other. These observations support the hypothesis that FE diffusion, for the conditions specified in this chapter, is mediated by LA phonons and furthermore that the $(\tau_x)_{\text{apparent}}$ measured in the exponential decay region is indeed the bulk Ge FE lifetime τ_x . The value of the FE-phonon scattering time implied by $D_x = 300 \text{ cm s}^{-1}$ is determined from Eq. (II.56) using the most recent spherical average FE translational mass^{7,11} ($m_x = 0.436 m_0$) to be $\tau_p = 2 \times 10^{10} \text{ s}$ at 4.2K.

The value of $S = 3000 \text{ cm s}^{-1}$ for FE at a crystal surface should be compared with $S \sim 10^2 \text{ cm s}^{-1}$ for free carriers (attributed to J.C.Hensel). The FE surface recombination velocity should be larger than that for free carriers, because carriers bound in FE bring their recombination partners with them to the surface. Further, S should be less than one-fourth the average FE velocity as required by simple kinetic and geometric arguments. Using the FE mass $m_x = 0.436 m_0$ this provides the upper bound $S \leq 5 \times 10^5 \text{ cm/s}$. The value of S reported here is consistent with the expected limits on its value.

Finally, within the accuracy of the values D_x and S and the accuracy of the FE decay data (Fig. V.5), there is agreement between the predicted $(\tau_x)_{\text{apparent}}$ from Eq. (V.12) and those measured from Fig. V.5.

In conclusion, the effects of surface recombination should be carefully considered when measuring FE decay rates. If the FE decay rate τ_x^{-1} in the bulk material is smaller than or comparable to the surface decay rates, then lifetimes significantly shorter than τ_x will

be measured. Lifetime measurements made using samples whose dimensions are comparable to the diffusion length or smaller can be dramatically effected. As an example, a lifetime measurement⁵ made using a thinner ($2 \times 8.5 \times 8.5 \text{ mm}^3$) piece of crystal 145 (cut from a position adjacent to sample 145M) yielded a value $\tau_x = 7.7 \text{ } \mu\text{s}$. For crystal 145M I measured $\tau_x = 27 \text{ } \mu\text{s}$. The decay of FE in a small sample can even look exponential and still be dramatically effected by surface recombination. All that is required for exponential FE decay is that the rate at which FE decay be proportional to the number of FE. If a symmetric diffusion profile is reached, it will decay maintaining its shape. Thus the concentration of FE at a surface becomes proportional to the total number of FE. Thus the rate of surface decay is proportional to the total number of FE and the measured exponential decay rate is given by the sum of the bulk and surface decay rates — both of which are constant.

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