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Electron-Hole Condensation in Semiconductors

Electrons and holes condense into freely moving liquid metallic droplets, a plasma phase with novel properties.

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Although semiconductors have been extensively studied for many years, it was only in 1967 to 1970 that it became established, by Soviet physicists (*1–10*), that electrons and holes (vacant electron states) in germanium and silicon could "condense" at low temperatures into an electron-hole plasma of constant density, which undergoes a phase separation from a gas of electron-hole pairs. This idea was first put forth by Keldysh (*2*). Electrons and holes, being oppositely charged, are attracted to one another: an electron-hole pair becomes bound together into a hydrogen-like particle, a free exciton. Just at the point of condensation the exciton gas begins to form observable macroscopic electron-hole droplets, which are electrically conducting. In 1970 many other investigators began studying the properties of the droplets, which highlighted the 1974 International Conference on the Physics of Semiconductors (*11*).

The phenomenon is roughly analogous to the condensation of water vapor into fog droplets. From diverse experiments with germanium, these characteristics are emerging: the droplets are usually a few micrometers in size and have a liquid metallic character and a lifetime of about 40 microseconds, decaying by emission of infrared light. The droplets have a definite surface energy. They can move freely through a pure crystal lattice and can be accelerated by crystal strain gradients. There is evidence that a stream of free excitons can push the droplets through the crystal. The droplet medium itself is described by plasma specialists as an anisotropic multicomponent cold dense plasma, of density $n = 2 \times 10^{17}$ electron-hole pairs per cubic centimeter. Stated simply, this means that the medium consists of 2×10^{17} electrons per cubic centimeter and an equal number of holes, thoroughly mixed and swarming about. The effective masses of the electrons and holes are only about one-tenth of the free electron mass and, in fact, depend somewhat on the direction of motion with respect to the crystal axes. The plasma exists only at low temperatures, say up to 20°K, and is much denser than typical hot gas plasmas being studied in thermonuclear fusion research. The droplet plasma has both classical and quantum properties and can be considered a novel state of matter.

Much larger drops, almost a millimeter in size, can be formed. Indeed, small crystals can be entirely filled with the plasma. Still, many experimental results are not yet fully understood and it is not surprising that some of the basic ideas reviewed in this article are as yet unsettled—for example, the mechanisms of drop nucleation, diffusion, and motion; the surface characteristics; properties of large drops; and the existence of biexcitons. Although the analogy is not exact, I point out that water vapor forms diffuse fog, cumulus clouds, raindrops, and even ice; similar meteorological complexities may occur, if we are lucky, in electron-hole condensation in semiconductors.

How and why are the droplets formed? What experimental methods are used to study their properties? Exactly what are their properties and how do they compare with those expected theoretically? In this article I will review the work in this field and try to answer these questions.

Formation of Excitons

Most studies have been made on single crystals of Ge, for which the pertinent bands of energy states $E(k)$ of an electron of momentum $\hbar k$ are shown in Fig. 1. At liquid helium temperatures ($T \approx 4$°K) the valence bands are completely filled and the conduction bands completely empty: a crystal of pure Ge is a perfect insulator. Incident photons of visible light are absorbed within about 1 μm of the crystal surface and excite electrons up into the conduction bands. These electrons rapidly relax to the indirect band gap edge at $E_g = 744$ millielectron volts. This process leaves holes in the valence band edge. If the intensity of the exciting light is increased the electrons and holes become more numerous and approach one another in their motion. Through Coulomb attraction an electron and a hole form a weakly bound hydrogenic species, the so-called Mott-Wannier exciton, with a binding energy $E_x \approx 4$ mev and a "Bohr radius" $a_x \approx 115$ angstroms. We can visualize the excitons as rather large prolate spheroids drifting through the crystal lattice. In fact, almost all the electrons and holes are bound into excitons within a few nanoseconds if the incident light flux is greater than a few milliwatts per square centimeter.

In normal semiconductors the electrons and holes are the carriers of electric current. The free excitons have the same high mobility as the free carriers and diffuse away from the surface a mean distance $L_x \approx 1$ mm in their lifetime $\tau_x \approx 7$ μsec. Being neutral, however, they do not conduct electric current. Excitons can decay by emitting characteristic electromagnetic radiation at 714 mev. This infrared luminescence, at 17,350 Å (*4*), is a most convenient signal from the free excitons in Ge, allowing one to probe their density N_x in space and time. (Actually, this luminescence is accompanied by a quantized lattice vibration, a longitudinal acoustic phonon at 27 mev, indicated in Fig. 1.)

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Condensation of Excitons

An exciton is the most fundamental many-particle excitation produced in semiconductors by optical excitation. That is, it is the simplest complex that can be made up of electrons and holes. What happens, or could happen, when the exciton density is increased by pumping still harder, and excitons become numerous enough to interact with each other? It has been postulated that they might form excitonic molecules like H_2, that is, biexcitons (*12*). There is theoretical evidence that at low temperatures they may condense by van der Waals interaction into a dielectric liquid like H_2 (*13*), or possibly undergo a Bose-Einstein condensation (*14*)—that is, form a superfluid.

None of these possibilities explains the peculiar phenomenon observed by Asnine *et al.* (*1*)—an abrupt increase in the low-temperature photoconductivity of Ge at exciton densities exceeding $N_x \approx 10^{16}$ cm^{-3}. Although they ascribed this "metallization" of excitons to a kind of insulator-metal transition, proposed earlier by Mott (*15*), Keldysh (*2*) gave a novel interpretation, apparently from insight: like most gases at sufficient density the exciton gas can condense into a constant density liquid, but instead of being a molecular excitonic liquid like H_2 the liquid in Ge must be conducting. That is, each hole is no longer tightly bound to an electron, but both are free to move—the liquid is an electron-hole plasma. Asnine and Rogachev (*3*) reported that certain band edge absorption data could be explained by the assumption of a phase separation into "drops" of constant density.

However, the crucial experiments were those of Pokrovskii and Svistunova (*4, 5*), who discovered a new luminescence line at 709 mev whose intensity increased two orders of magnitude when the temperature was lowered from 2.5° to 2.2°K. They interpreted this as a first-order phase transition to an electron-hole condensed phase, shown very approximately in Fig. 1 as a partially filled band of energy states at an energy E_B below the conduction band edge. Since electrons must obey Fermi-Dirac statistics, only one electron can occupy each accessible state. To accommodate a finite number of electrons, one must fill all the states up to the so-called electron Fermi energy. The same is true for holes. Actually the electrons and holes occur in separate bands, but in Fig. 1 we schematically represent the electron-hole liquid as a single band where $E_F \approx 6$ mev is the sum of the electron and hole Fermi energies. The condensation energy $\phi \approx 2$ mev is the energy released by an exciton upon condensation on the surface of a drop. Pokrovskii and Svistunova found that the line shape of the 709-mev line could be explained by a mathematical folding of Fermi-Dirac distribution functions for holes and electrons; this is just what one expects for a metallic medium. Since E_F is proportional to $n^{2/3}$, from the measured luminescence line width they found the value $n_0 = 2 \times 10^{17}$ cm^{-3} for the electron-hole density in the drops. Pokrovskii and Svistunova (*9*) next scattered infrared light on optically excited Ge: coincident with the onset of the 709-mev luminescence they observed Rayleigh-Gans scattering whose angular distribution determined the drop size. Assuming spherical shape, they observed radii from 4 to 9 μm—about the same size as fog droplets of water. Additional droplet properties were found by Bagaev *et al.* (*7*), who measured the luminescence energy in stressed crystals and discovered that drops could be accelerated remarkably by stress gradients, up to the velocity of sound, 10^5 cm sec^{-1}.

Although the results are not really known in such graphic detail, Fig. 2 is a rough visual display of droplet phenomena. Exciting light incident on a pure crystal is absorbed near the surface, generating free electrons and holes; these quickly form excitons, which diffuse up to a millimeter or so away from the surface. A drop-

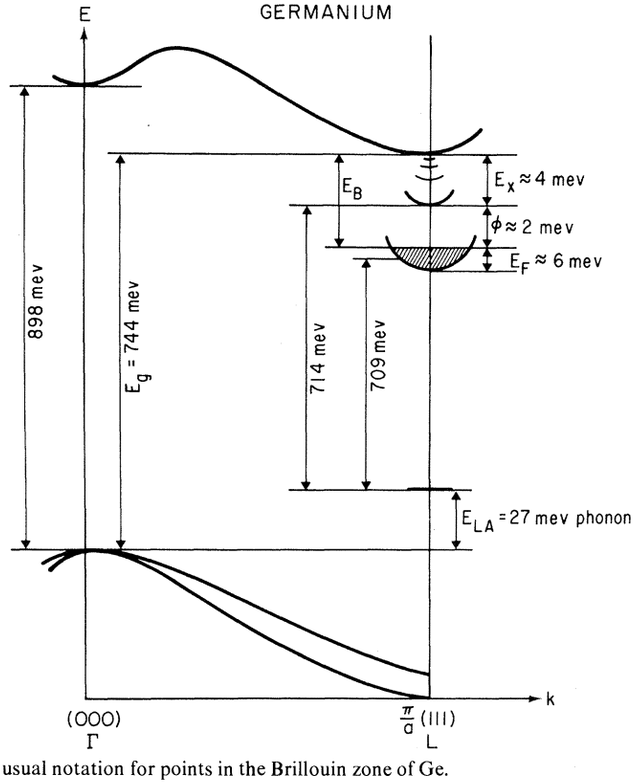


Fig. 1. Energy bands $E(k)$ for electrons in Ge versus wave vector k in the ⟨111⟩ direction. The two lower lines are valence band edges, the upper is the conduction band edge. An electron-hole pair bind into an exciton with an energy $E_x \approx 4$ mev below the band edge; they decay by luminescence at 714 mev. In a drop the electrons and holes are shown schematically as a partially filled "band" at $E_B \approx 6$ mev below the band edge; drops luminesce at 709 mev. The Fermi energy $E_F \approx 6$ mev corresponds to an electron-hole density of $n_0 \approx 2 \times 10^{17}$ cm^{-3}. Actually the drop "band" lies higher than shown by $\frac{2}{5}E_F$, but this energy is lost by relaxation and does not appear in the luminescence spectrum. Symbols Γ and L are the usual notation for points in the Brillouin zone of Ge.

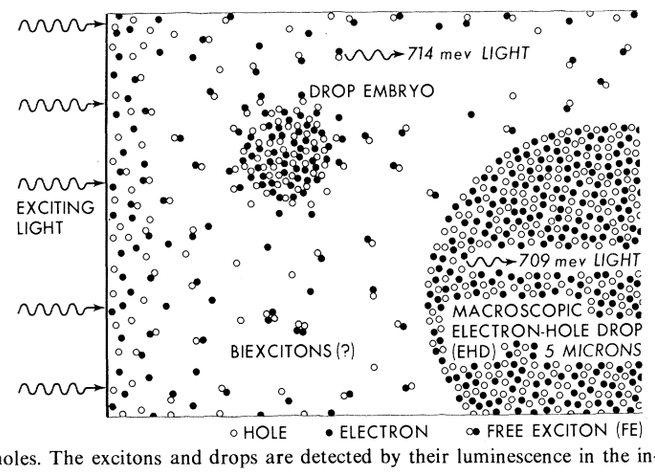
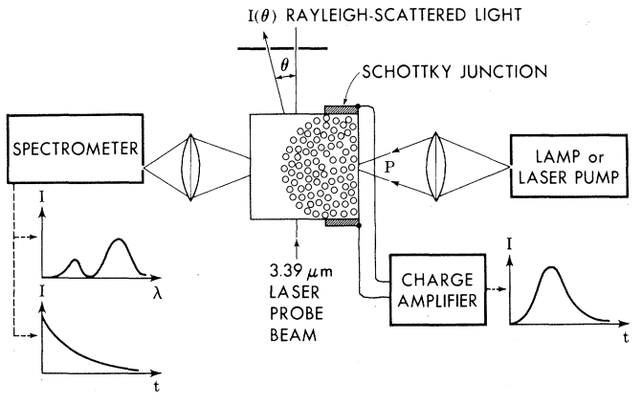


Fig. 2. Simplistic picture of processes inside a Ge crystal pumped by visible light flux: free electrons and holes are produced near the surface; they combine into free excitons, which diffuse away from the surface. Crystal imperfections or local supersaturation of the exciton density nucleates aggregates of excitons—that is, droplet embryos—which can grow to macroscopic metallic liquid drops containing equal numbers of electrons and holes. The excitons and drops are detected by their luminescence in the infrared at 17,350 and 17,482 Å, respectively.



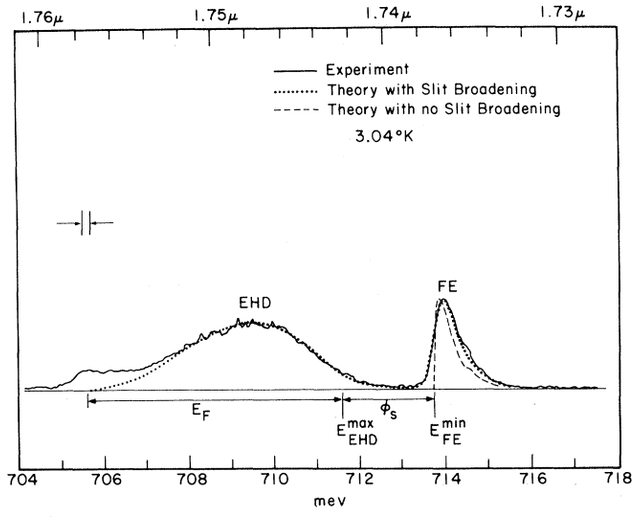


Fig. 3 (left). Composite diagram of some experimental methods used to study drops. The central cube represents a Ge crystal in a liquid helium Dewar with transparent windows, being excited by a pump lamp of power *P*. The drops formed may be studied by their luminescence spectra $I(\lambda)$, giving information on the binding energy, threshold condensation phenomena, and phase diagram. System kinetics are deduced from luminescence decay $I(t)$ following pulsed excitation. Rayleigh scattering gives information on drop size and density. Drops can also be detected by charge pulses arising from their breakup in junctions on the crystal. Fig. 4 (right). Luminescence spectrum of free excitons (*FE*) and electron-hole drops (*EHD*) in Ge at an optical excitation just above threshold for the formation of the drop phase. The line shapes are in reasonable agreement with theory, including corrections for broadening due to the finite spectrometer slit. [From Lo (*31*)]

let embryo may be formed either from a statistical fluctuation in the exciton density in a perfect crystal, or else on crystal defects or impurity atoms acting as nucleation centers. If the droplet embryo exceeds a critical radius, of the order of 0.05 μm for Ge, it is able to rapidly grow to a macroscopic drop, typically 5 μm in radius. A drop is maintained by a constant condensation of excitons onto its surface. At higher temperatures evaporation of electron-hole pairs from its surface become important, analogous to the Richardson-Dushman thermionic emission of electrons from metallic surfaces. If the light is switched off the drop decays with a characteristic volume decay time $\tau_0 \approx 40$ μsec at low temperatures (< 2°K); at higher temperatures it decays much faster by surface evaporation.

Under optimum experimental conditions each incident photon produces an electron-hole pair which is ultimately condensed onto a droplet. In the drop the probability of electron-hole radiative recombination is high: the quantum efficiency of the 709-mev luminescence is roughly 50 percent. An alternative mode of decay is by nonradiative Auger processes, whereby a pair is dissociated into carriers and the energy is given up as kinetic energy to other electrons or holes.

The simple events of Fig. 2 may be drastically changed by intense excitation, crystal strains, or significant doping of the crystal with impurity atoms. It is possible that electrons and holes may even condense directly into the drop without the exciton as a definite intermediate phase.

A typical 5-μm drop contains 10^8 electron-hole pairs. If it diffuses into the electric field gradient of a *p-n* junction on the crystal it will quickly break up into free electrons and holes, which will be collected by the junction terminals as a sizable charge pulse $\Delta Q \approx 10^{-11}$ coulombs. This phenomenon, first observed by Asnine *et al.* (*8*) and by Benoit à la Guillaume *et al.* (*16*), is strong and simple evidence for the existence of macroscopic drops.

Experimental Methods

Figure 3 is a composite diagram illustrating the experimental arrangements thus far described. A single crystal of Ge in a helium Dewar with transparent windows is illuminated with pump light from an incandescent lamp, arc lamp, or laser. The light may be focused or diffuse, continuous or pulsed, depending on the experiment. The free excitons and droplets so formed are studied most simply by collecting the 714-mev and 709-mev luminescence, focusing it onto the slit of a spectrometer, and recording the spectrum, the intensity *I* versus the wavelength λ. The time dependence $I(t)$ of the luminescence is observed in kinetic studies. For Rayleigh-Gans scattering a narrow laser probe beam of wavelength 3.39 μm is passed through the drop-infested region, and the scattered intensity $I(\theta)$ is recorded; this directly determines the drop size. The total number of electron-hole pairs per unit volume can be inferred from the absorption of the probe beam. In addition, the crystal may have ohmic contacts for conductivity measurements, or it may have junctions at the surfaces, either alloyed *p-n* junctions or metal-semiconductor (Schottky) junctions. The charge pulses produced by drop breakup are subjected to pulse height analysis.

For the technically sophisticated reader I list in this paragraph a number of other powerful experimental methods. Far-infrared absorption near the plasma frequency $\omega_p = [4\pi n_0 e^2/m^*]^{1/2}$ was first observed by Vavilov *et al.* (*6*), confirming the droplet metallic character and the density $n_0 = 2 \times 10^{17}$ cm^{-3}. The free Auger electrons from drop decay are observed with high sensitivity by cyclotron resonance (*17*). Since the drop consists of a neutral plasma it can propagate Alfvén waves in a magnetic field (*18*); large drops have been observed to display Alfvén wave resonances at microwave frequencies (*19*). In another type of experiment, microwave breakdown is observed in the exciton-free carrier-droplet system, giving information on droplet density, size, and lifetime (*20*). Oscillatory magnetoresistance (*21*) and magnetoluminescence (*22*) confirm the Fermi character of the drop. An enlarged image of a cloud of drops (*23, 24*) can be scanned past the slit of the luminescence spectrometer, giving spatial information. High-resolution time-resolved image scanning has been developed to a degree where the spatial distribution in time of a single drop 30 to 300 μm in size can be studied (*25*); this gives, in effect, a high speed movie of drop behavior. In addition to optical injection, droplets in Ge and Si can be formed from electrons and holes electrically injected into the crystal in *p-n* junctions (*26, 27*).

The existence of drops in Si similar to those in Ge was inferred by Kaminskii and Pokrovskii (*10*), who observed the free exciton luminescence at 1.097 mev and a new drop luminescence line at 1.081 mev, with a characteristic Fermi line shape corresponding to a density $n_0 = 3 \times 10^{18}$ elec-

tron-hole pairs per cubic centimeter. Actually the line at 1.081 mev had been observed by Haynes (*28*), who attributed it to the decay of a biexciton. In fact, a similar interpretation has sometimes been given for the 709-mev line in Ge (*29*); in my opinion this is not justified. Although the existence of free biexcitons in Si and Ge has not been established, there is tentative evidence for the existence of multiexciton complexes bound to impurity atoms (*30*). It is even possible that these complexes grow to become droplets, eventually breaking free from the impurities.

Figure 4 is an example of the luminescence spectra of free excitons and droplets in Ge, showing the sharp line shape characteristic of a gas of free excitons and the wide line characteristic of the metallic drops (*31*). Detailed analysis yields the Fermi energy $E_F \approx 6.5$ mev and the condensation energy $\phi_s \approx 2$ mev. From direct measurements of the exciton energy $E_x \approx 4$ mev (*32*), one finds $E_B = E_x + \phi_s \approx 6$ mev for the binding energy of an electron-hole pair in the drop, relative to the band edges. This is in acceptable agreement with the theoretical calculations of Brinkman and co-workers (*33*), Combescott and Noziéres (*34*), and Vashishta and co-workers (*35*). Both Ge and Si are indirect band gap semiconductors; that is, electron-hole radiative recombination must be accompanied by the generation of a lattice vibration, a phonon. This reduces the transition probability and gives longer exciton lifetimes, which is favorable for drop production. The anisotropy and degeneracy of the band structure also favor drop stability, as discussed below.

Threshold Phenomena

In many ways the formation of electron-hole drops in semiconductors is akin to the formation of fog and raindrops in the atmosphere. As the pump light level on the crystal (and thus the density of excitons) is increased, there is a threshold level marking the onset of condensation into drops. It is this threshold behavior which is the characteristic signature of the droplet condensation phenomena. As an example, the results of Lo and Westervelt (*27*) in Fig. 5 show both the drop luminescence intensity I_{709} and the maximum junction charge simultaneously collected from a Ge crystal as the pump light flux P is increased. The luminescence, initially zero, dramatically and abruptly rises as P crosses a threshold value, which is higher for higher temperatures. At this same threshold the junction pulse height V_{max} makes a sudden jump to a magnitude corresponding to $\Delta Q = 4 \times 10^{-11}$ coulomb, or 10^8 electron-hole pairs, corresponding to a drop with a radius of about 7 μm. The simultaneity of the I_{709} and giant pulse thresholds is clear evidence that the 709-mev line is indeed due to drops and not to biexcitons (*36*).

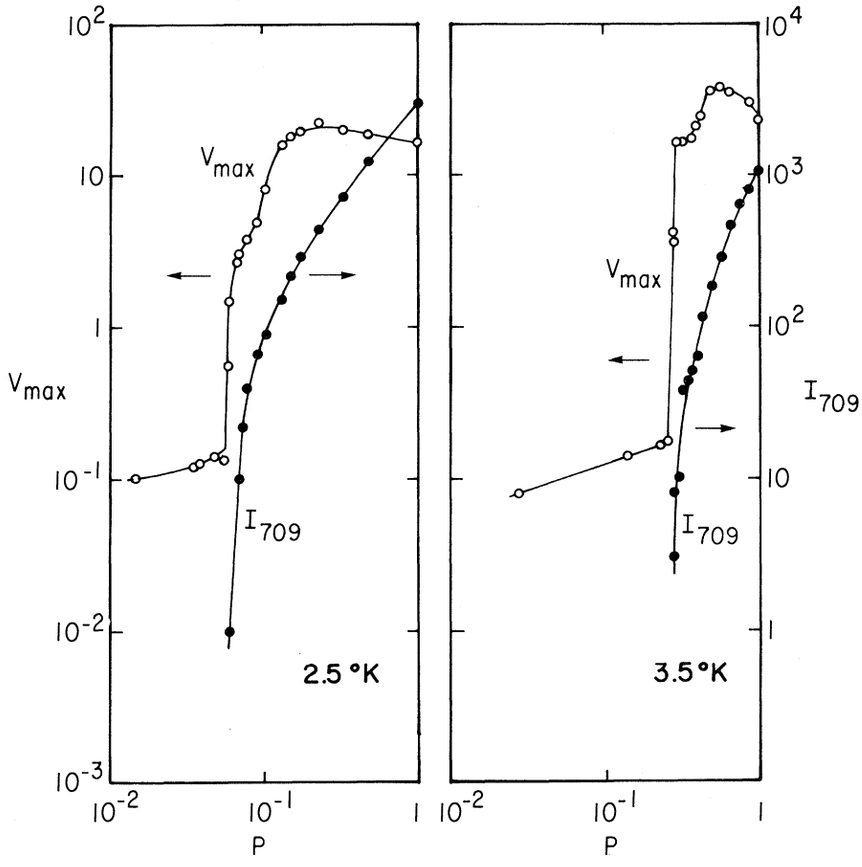


Fig. 5. Observed drop luminescence intensity I_{709} in Ge as a function of light pump flux ($P = 1$ corresponds to 60 milliwatts absorbed by the crystal in a spot 0.5 mm in diameter). Also shown is V_{max}, a voltage proportional to the maximum charge collected, from a pulse height analysis of droplet breakup in a junction on the same crystal (see Fig. 3). This experiment proves that the 709-mev luminescence arises from drops and not from biexcitons. [From Lo and Westervelt (*27*)]

Measurements of the threshold excitation P_{th} and the corresponding exciton density N_x at various temperatures give the gas-liquid coexistence curve for the exciton-drop system. Careful luminescence measurements by Lo *et al.* (*37*) show that P_{th} depends on whether one is increasing or decreasing the pump light intensity: the threshold P^i_{th} for monotonically increasing the pumping light is considerably larger than the threshold P^d_{th} for monotonically decreasing the light. This hysteresis is clearly shown in Fig. 6, which also shows the hysteresis of the free excitons, which is smaller and of opposite sense. This behavior is just what is expected if the drop has a surface energy: the exciton gas must be considerably supersaturated in order to nucleate droplets. Preliminary relative threshold measurements at other temperatures yield the two branches of the coexistence curve, Fig. 7. The solid lines are the upgoing and downgoing branches for the exciton threshold density calculated from a nucleation model by Westervelt and coworkers (*38*). For comparison, the dashed line in Fig. 7 is a theoretical coexistence curve obtained simply by equating the condensation energy ϕ to the chemical potential of an ideal exciton gas (thereby neglecting hysteresis and surface energy effects); the resulting "saturated" exciton density is

$$^sN_x = g(m^*_x kT/2\pi\hbar^2)^{3/2}\exp(-\phi/kT) \quad (1)$$

where m^*_x is the effective exciton mass and g the degeneracy.

Silver (*39*) also has proposed a nucleation model, but without hysteresis effects. The point of departure of nucleation models is the classical theory of homogeneous vapor condensation (*40*); one then adds the effects of finite lifetime and nucleation by impurities. In very pure crystals exciton density fluctuations can nucleate embryonic droplets; otherwise impurities will provide nucleation. Embryos smaller than a critical radius R_c are unstable because the surface tension is large enough to shrink them to zero size. Embryos with radius $R < R_c$ quickly vanish, while those with $R > R_c$ quickly grow to macroscopic size.

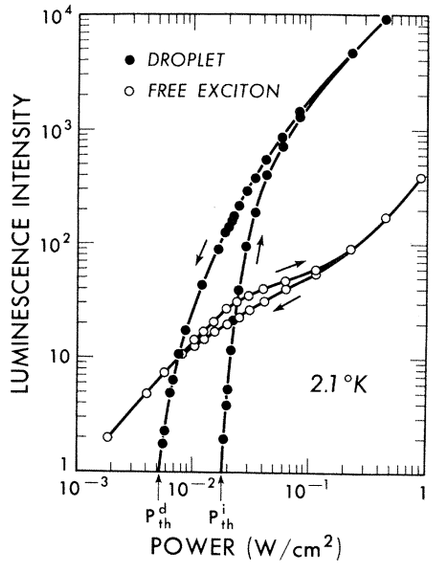


Fig. 6. Luminescence intensity of drops and free excitons in ultrapure Ge ($N_D = 3 \times 10^9$ cm^{-3} as a function of the power of the pumping light uniformly incident on the sample area. Data for monotonically increasing and decreasing the power show a large and reproducible hysteresis arising from the surface energy w of the drop. These data yield $w = 2.5$ erg cm^{-2}. [From Westervelt and co-workers (*38*)]

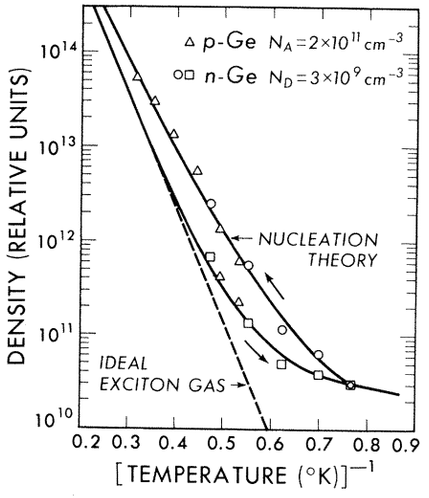
Kelvin showed that $R_c = [2w/n_0kTx]$, where w is the surface energy per unit area, n_0 is the particle density in the drop, and $x = \ln(N_x/{}^sN_x)$ is the degree of gas supersaturation. The central result of nucleation theory is that the frequency of formation of critical droplets is proportional to $\exp(-16\pi w^3/3k^3T^3n_0{}^2x^2)$ and thus extremely sensitive to the degree of supersaturation. This is measured, as in Fig. 6, from the difference between the upgoing and downgoing thresholds, which experimentally determines the surface energy w. It is possible that in the samples used to date nucleation preferentially occurs by binding on an impurity rather than by pure vapor density fluctuations. However, the evidence is that this binding energy is not greater than perhaps 10 mev (*30*), and this does not change the predicted curves of Fig. 7 by more than 20 percent. The data are best fit by $w \approx 2.5 \times 10^{-4}$ erg cm^{-2} and $\phi \approx 2$ mev. The magnitude of the hysteresis determines w; the slope determines ϕ. The surface energy has been theoretically estimated to be $w \approx 10^{-4}$ erg cm^{-2} (*41–43*); refined calculations of Vashishta and coworkers (*44*) predict $w \approx 3 \times 10^{-4}$ erg cm^{-2}. Light scattering experiments give a preliminary value of comparable magnitude (*45*).

The nucleation models (*38, 39*) also predict that the steady state drop size is limited by the finite lifetime τ_0 of the electron-hole pairs in the drop; otherwise a drop would grow indefinitely. In the model for hysteresis developed by Westervelt and coworkers (*38*), as the pump light is increased the drop size remains approximately constant, while the number of drops increases; going down, the number remains approximately fixed and the drop size decreases until threshold is approached. In general, the drop size and density depend on the pumping history, that is, on the time dependence of the pump power $P(t)$. The optical hysteresis clearly shows the existence of metastable states, which can actually be maintained for hours under stable experimental conditions.

The value $\phi \approx 2$ mev from Fig. 7 is close to the average spectroscopic value $\phi_s = 1.9$ mev (*23, 31, 46, 47*) obtained from luminescence line shapes. There are several other threshold measurements of ϕ: cyclotron resonance of Auger electrons from drops [Hensel *et al.* (*17*)]; drop luminescence threshold [Pokrovskii (*48*) and Lo *et al.* (*37*)]; and junction charge noise threshold [McGroddy *et al.* (*49*)]. The average value from these measurements is $\phi_t = 1.4$ mev, significantly smaller than ϕ_s. Since surface energy and hysteresis were not taken into account in these threshold experiments, the difference between ϕ_s and ϕ_t can be partly reconciled by nucleation theory. The value $\phi = 2.3 \pm 0.2$ mev of Martin and Pilkuhn (*50*), obtained by thermal activation and not by threshold, is in agreement with the spectroscopic value.

Theory; Phase Diagram

Before the discovery of drops no theory had been published predicting their existence—in particular, that the energy per electron-hole pair in the plasma is lower than that of the free exciton. It turns out that the binding energy E_B per pair has a well-defined minimum as a function of pair density n in the plasma for Ge and Si. There are three contributions to E_B: a positive term, the kinetic energy, proportional to the Fermi energy $E_F = \hbar^2/2m^*)(3\pi^2n)^{2/3}$; a negative term, the exchange energy $E_{ex} \propto n^{1/3}$, arising from Pauli repulsion between like particles; and the negative correlation energy E_c, weakly dependent on n, which arises from the attraction between electrons and holes and causes them to be correlated in space. The sum of these three terms has been calculated by several groups (*33, 35*) using various approximations. For Ge and Si there is a clear minimum when energy E_B is plotted against density n. The most accurate treatment of the correlation energy is by the fully self-consistent method of Vashishta and co-workers (*35*). Nature fortunately conspires to reduce the effective density in the Fermi term by the fourfold or sixfold conduction band degeneracy in Ge and in Si, respectively. The large anisotropy of the effective mass m^* further reduces the Fermi term: these band structures definitely favor a stable plasma state.



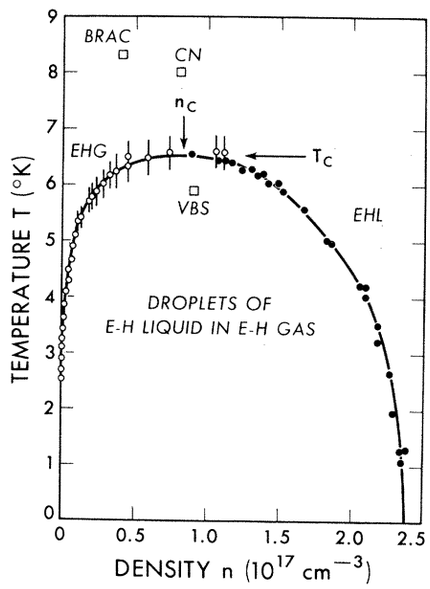


Fig. 7 (left). Preliminary relative exciton density versus T^{-1} for drop threshold in Ge, observed by increasing and by decreasing pump power. The coexistence curve has two branches because of the surface energy and the finite lifetime of the drops. The density is assumed to be proportional to the power, and the magnitude is scaled to fit the solid theoretical lines, derived from a nucleation model including surface energy $w = 2.5 \times 10^{-4}$ erg cm^{-2} and condensation energy $\phi = 2$ mev. The dashed line is the saturated exciton density per cubic centimeter from Eq. 1, which neglects surface and hysteresis effects. [From Westervelt and coworkers (*38*)] Fig. 8 (right). Phase diagram in temperature and density for electrons and holes in pure Ge. The solid data points were measured from the Fermi linewidth of the drop luminescence line. The open data points are scaled from threshold measurements of the liquid-gas coexistence curve. The solid line is the scaled law of corresponding states for classical fluids. Various theoretical predictions for T_c and n_c are shown: *BRAC* (*33*), *CN* (*34*), and *VBS* (*35*). [From Thomas *et al.* (*52*)]

Even for highly strained Ge and Si where all degeneracy is removed, Vashishta and co-workers predict a stable drop phase, although much less strongly bound. Experiments show the existence of drops in Ge with stress up to 25 kg mm^{-2}, the highest for which data have been reported (*51*).

An important characteristic of an electron-hole drop is that it is electrically conducting: it is a metallic liquid. At finite temperatures the Landau theory of Fermi liquids may be used to expand the free energy per pair $F(n,T) = E_B(n,0) - \frac{1}{2}\gamma(n)T^2$, where the second term corresponds to the contribution characteristic of a metal. This leads to temperature dependences of the Fermi energy and density. These have been observed in Ge by careful measurements of the 709-mev line width (*27, 31, 47*): $E_F(T) = 6.5(1 - 0.007T^2)$ mev; $n(T) = 2.4 \times 10^{17}(1 - 0.01T^2)$ cm^{-3}. Even a small temperature dependence of the chemical potential (the high energy edge of the luminescence line) has been observed by Thomas *et al.* (*47*). This provides direct evidence of the metallic nature of the electron-hole liquid, in addition to the line shape. From this measurement one can also obtain a temperature correction to the condensation energy: $\phi(T) = [\phi(0) + 0.015T^2]$ mev. These temperature dependences are in reasonable agreement with theory (*35*).

As in any gas-liquid system, one expects a critical temperature T_c for the exciton-drop system. This has been experimentally determined by Thomas *et al.* (*52*), whose phase diagram is shown in Fig. 8. They find the critical point at $T_c = 6.5 \pm 0.1$°K and $n_c = 8 \times 10^{16}$ cm^{-3}. The solid line is the scaled law of corresponding states (*53*), known to be valid for simple classical fluids near the critical point. At low densities, $N_x < 10^{14}$ cm^{-3}, the exciton gas luminescence line is sharp and quite distinguishable from the drop luminescence (see Fig. 4). However, at higher densities the gas behaves increasingly like an uncorrelated electron-hole gas, and at n_c it becomes indistinguishable from the electron-hole liquid phase.

Although most experiments have been performed with pure crystals, Halliwell and Parsons (*54*) found some interesting results with Si doped with impurity atoms beyond the Mott density (3×10^{18} cm^{-3}) where the donors become degenerate. They conclude that drops can be formed even in these metallic Si samples. Martin and Sauer (*55*) have studied drop formation in Ge doped with 6×10^{16} cm^{-3} indium acceptor atoms. The impurity atoms act strongly as condensation centers; as the pump power is increased the droplets grow and merge into a single "drop" 300 μm in size, with a density $n \approx 5 \times 10^{17}$ cm^{-3}. In doped Si there are more complicated effects due to the formation of bound multiexciton complexes (*30*), which may possibly become bound metallic drops.

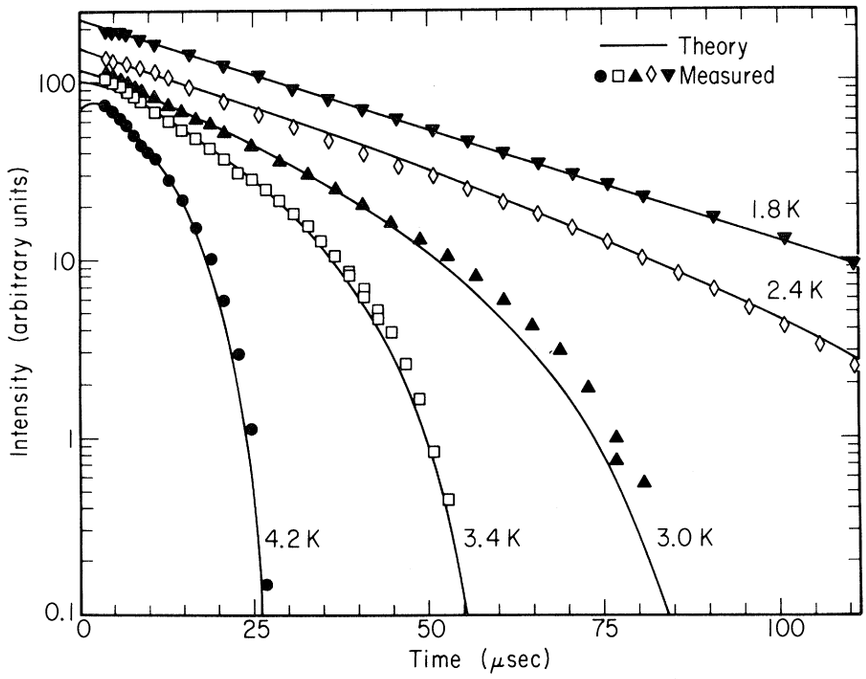


Fig. 9. Intensity of the drop luminescence line in Ge following a laser pulse. At low temperatures the drop decay is exponential, corresponding to the volume decay rate τ_0^{-1} (Eq. 2) due to electron-hole recombination. As the temperature is raised there is a transition to nonexponential decay by thermionic emission. The smooth lines represent the predicted behavior computed from Eqs. 2 to 4. [From Westervelt *et al.* (*56*)]

Kinetics

A number of experimenters have studied the decay of drops after the exciting light is switched off. A short pulse of light produces excitons and drops, and their decaying luminescence is observed with a fast detector (*29, 56, 57*). Auger electrons ejected from the drop are observed by cyclotron resonance (*17*), or the transient conductivity is observed (*58*). It is possible to understand most of these results semiquantitatively by a rather simple rate equation model originally introduced by Pokrovskii and Svistunova (*5*) and embellished by others. Other kinetic experiments, dominated by spatial effects, are not explicable by this simple model.

The actual situation is rather complex: in the crystal there is a spatial and a temporal distribution of free carrier density N_{eh}; free exciton density N_x; drop density n_d; and ν, the average number of pairs per drop. In the simplest cases it is an experimental fact that after a given excitation the drop size distribution is sharply peaked about ν, and furthermore the drop density N_d appears to remain constant during decay (*17, 56*). The exact problem is so intractable that one is tempted as a first approximation to take a local model in which no significant spatial variation occurs within the effective volume. The coupled rate equations for decay then become (*5, 17, 56, 59*)

$$\frac{d\nu}{dt} = -\frac{\nu}{\tau_0} + (\beta N_x - \alpha)\nu^{2/3} \quad (2)$$

$$\frac{dN_x}{dt} = -\frac{N_x}{\tau_x} - N_d(\beta N_x - \alpha)\nu^{2/3} + CN^2_{eh} \quad (3)$$

$$\frac{dN_{eh}}{dt} = G - CN^2_{eh} + \frac{\nu N_d}{\tau_{0A}} \quad (4)$$

In these equations τ_0^{-1} is the total volume decay rate of the drop due to direct recombination τ_{0r}^{-1} (luminescence) and to nonradiative recombination τ_{0A}^{-1} with ejection of carriers from the drop. The term $\alpha\nu^{2/3}$ represents evaporation of pairs from the droplet surface and may be estimated by the Richardson-Dushman equation $\alpha = 4\pi R^2\nu^{-2/3}AT^2\exp(-\phi/kT)$ sec^{-1}, where R is the drop radius, ϕ is the work function for evaporation of particles, and $A = 2g\pi m^*k^2/h^3$ is the Richardson constant for particles of effective mass m^* and degeneracy g. Since the experimental results are consistent with $\phi \approx 1.5$ mev, which is approximately the condensation energy of excitons, one presumes that electron-hole pairs are evaporating; this is energetically much more favorable than evaporation of free electrons or free holes. The exciton gas backflow onto the drop is represented by $\beta N_x\nu^{2/3}$, which is proportional to the exciton velocity. In Eq. 3, τ_x^{-1} is the total exciton decay rate due to direct recombina-

tion τ_{xr}^{-1} (luminescence) and nonradiative decay τ_{xA}^{-1}. The excitons condense on and evaporate from the drops and also are formed directly from the carriers at a rate CN_{eh}^2. The carriers themselves are generated in the first instance from optical injection at rate G, and later from Auger decay of drops and excitons.

If these details seem a bit heavy, I might assuage the reader by remarking that the model is quite similar to those in chemical or biological cases where one deals with the rate of change of abundance of several interacting species. The drop is like a giant molecule, decaying into simpler parts, all with finite lifetimes. Although complicated, kinetic studies provide several tests of such models.

There are two simple approximate solutions of these equations. At low temperatures, where evaporation is negligible and the excitation is well above threshold, the drop luminescence decays exponentially: $I_{709} \propto \nu = \nu(0)\exp(-t/\tau_0)$. At higher temperatures ($T > 4$°K), where evaporation dominates, the luminescence decays as $\nu \propto (1 - t/t_c)^3$, where the cutoff time $t_c \approx [R(0)n_0/AT^2\exp(-\phi/kT)]$ depends linearly on the initial drop radius $R(0)$. Both of these cases are seen in Fig. 9, from the work of Westervelt *et al.* (*56*): at $T = 1.8$°K the decay is exponential with a drop decay time $\tau_0 = 41$ μsec; at 4.2°K the decay is very nonexponential and displays a cutoff time $t_c = 25$ μsec due to evaporation. For both drops and free excitons the data are in good agreement with the computed behavior from the local model, Eqs. 2 to 4, which is reasonably successful in explaining time dependence over a dynamic range of 100 in the temperature range $1.8° < T < 4.2$°K. Benoit à la Guillaume *et al.* (*57*) have also studied luminescence decay of drops.

Drop Motion and Spatial Distribution

Forces can be exerted on drops by crystal strain gradients (*7, 61*), exciton density gradients (*62*), and possibly electric fields (*63*). These spatial effects add interesting complexities to the homogeneous model and can be discussed in elementary mechanical terms. Figure 10 shows the energy displacement of the drop luminescence as a function of uniform uniaxial stress along three crystal directions (*51*). At high stress the exciton luminescence shift is found to parallel that of the drop; both shifts are in fact due to the decrease in band gap. Figure 10 shows that in a nonuniform strain a drop will feel a force proportional to the strain gradient and will tend to move toward a region of maximum strain, thereby minimizing its energy.

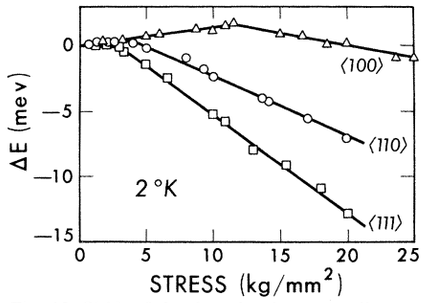


Fig. 10. Shift of the drop luminescence line under uniform uniaxal stress in three crystal directions in Ge. In a nonuniform stress the drops will move to points of maximum stress with a force proportional to the downward slope of the lines. [From Benoit à la Guillaume *et al.* (*51*)]

Strains also modify the electron-hole density in the drop and the decay time. The band structure of Ge is such that there are four equivalent energy ellipsoids for conduction electrons oriented along the four ⟨111⟩ axes, and two valence bands corresponding to heavy and light holes. In a drop these are all equally populated at zero stress. But a stress applied, say, along ⟨111⟩ induces a splitting such that only one electron band and ultimately only one hole band is populated. The overall effect is to reduce the pair density n in the drop phase, as well as the binding energy E_B and the condensation energy ϕ. The most refined theoretical predictions are those of Vashishta and co-workers (*35*): $n = 2.2 \times 10^{17}$, $n = 0.65 \times 10^{17}$, and $n = 0.11 \times 10^{17}$ cm^{-3} at stresses $p = 0$, 300, and 1500 kg cm^{-2}, respectively. Although these lowered densities have not yet been well verified experimentally, it has been observed (*51, 61*) that strain gives a decreased drop luminescence line width proportional to E_F and thus to $n^{2/3}$. Ohyama *et al.* (*64*) have observed a 30 percent decrease in ϕ in Ge strained along ⟨111⟩.

Shortly after drops were discovered, Bagaev *et al.* (*7*) showed that they were easily accelerated by stress gradients. Drops were observed to move by as much as a centimeter to reach a maximum stress point produced by needle pressure on the face of a crystal. In a stress gradient of 400 kg cm^{-2} drops were observed to move with velocity 3×10^5 cm sec^{-1}, with momentum relaxation time 2×10^{-8} second (*45, 61*). The drop luminescence may be greatly reduced in stressed crystals. This has been shown (*58*) to be due to heating of the moving drops by collision with phonons and to surface recombination. At a lattice temperature of 2°K and a stress gradient of 8×10^3 kg cm^{-2} the drop temperature rose to 6°K and the evaporation cutoff time dropped from 60 to 2 μsec. This limits the distance through which the drops can be moved.

Pokrovskii and Svistunova (*63*) have reported that a cloud of drops can be displaced by an electric field; their interpretation is that a typical 5-μm drop at 2°K has a net negative charge $Q \approx 100$ electrons. To understand this one notes that the binding energy of holes is about 1 mev smaller than that of electrons, because of the difference in Fermi energies. Thus, thermionic emission will preferentially eject holes until at equilibrium a "sufficient" net negative charge Q accumulates on the drop. Rice (*41*) has theoretically estimated that Q lies in the range 18 to 540 electrons, depending on the assumed excitation conditions and the temperature. However theory and experiment cannot yet be considered in satisfactory agreement. Another possible mechanism for charging drops is through the Auger decay of a pair in which the third particle escapes from the drop.

Since photons are absorbed close to the crystal surface, the exciton spatial distribution will be nonuniform, decaying exponentially away from the surface with a diffusion length of about a millimeter. Balslev and Hvam (*62*) have shown that in such a density gradient, excitons condense preferentially on one side of a drop, giving a net force toward regions of lower exciton density. This force and the frictional drag lead to a drift velocity V_d proportional to the drop radius and the fractional exciton density gradient $N_x^{-1}(dN_x/dx)$. For typical values $R = 5$ μm and $N_x^{-1}(dN_x/dx) = 10$ cm^{-1}, the drift velocity $V_d = 10^3$ cm sec^{-1}. The qualitative conclusion is that this drift motion will usually exceed that due to free diffusion of drops and will play a significant role in the overall spatial distribution of drops. Various experimental values of the free diffusion constant of drops have been reported, ranging from $D \approx 150$ cm^2 sec^{-1} (*65*), to $D \approx 1$ cm^2 sec^{-1} (*48*), to $D \leq 0.1$ cm^2 sec^{-1} (*60*). I believe the latter value to be the most reliable. Using microwave probing of the electric susceptibility of a pumped Ge crystal, Hensel and Phillips (*60*) also showed that near threshold drops formed and remained within about 50 μm of the surface.

At higher excitation the data on drop spatial distribution show a variety of phenomena, not yet fully understood. (i) Worlock *et al.* (*66*), using Rayleigh-Gans light scattering, observed an approximately exponential distribution of drop density $N_d(x) = N_d(0)\exp(-x/x_0)$ of uniform size drops; this seems to arise from diffuse or stripe excitation. (ii) Voos *et al.* (*67*), using light scattering, found a roughly hemispherical distribution of drops of constant density $N_d \approx 10^8$ cm^{-3} and uniform size $R \approx 3$ μm; the distribution had a reasonably well defined surface of radius r dependent on pump power. Similar results are

inferred from direct imaging of the drop luminescence (*23, 24*). This type of distribution seems to arise from point-focused laser excitation: for 100 milliwatts the cloud radius $r \approx 1$ mm. (iii) Small and thin Ge crystals under high excitation can be almost entirely filled with a slab of the electron-hole liquid (*68, 69*). Gurnee *et al.* (*68*) measured the conductivity $\sigma \approx 10^4$ (ohm cm)$^{-1}$ for the liquid under these conditions at 2°K. By sufficient pumping it appears that the liquid can be compressed to higher densities (*69*). (iv) In stressed Ge large, long-lived drops have been observed (*19*), as discussed in the following section.

The groups at the Lebedev Institute in Moscow have also been actively studying drop distributions: Alekseev *et al.* (*45*) have used light scattering to measure the drop radius R and density N_d as a function of temperature, pump power, and strain. Further experiments, as well as theoretical treatments, are needed to understand the variety of spatial distributions.

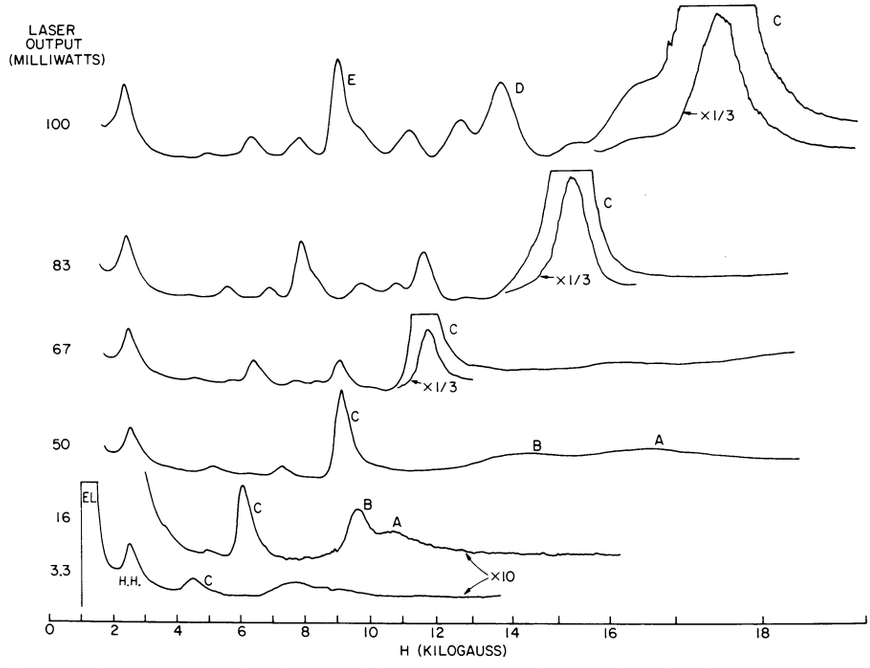


Fig. 11. Microwave absorption in stressed Ge at $\omega = 1.6 \times 10^{11}$ sec^{-1} plotted against magnetic field for various laser pump powers at $T = 1.6$°K. The cyclotron resonance of free electrons and heavy holes outside the drop are labeled *EL* and *H.H.* The absorption lines that shift with pump power are Alfvén standing wave resonances in a large, long-lived electron-hole drop. [From Wolfe *et al.* (*19*)]

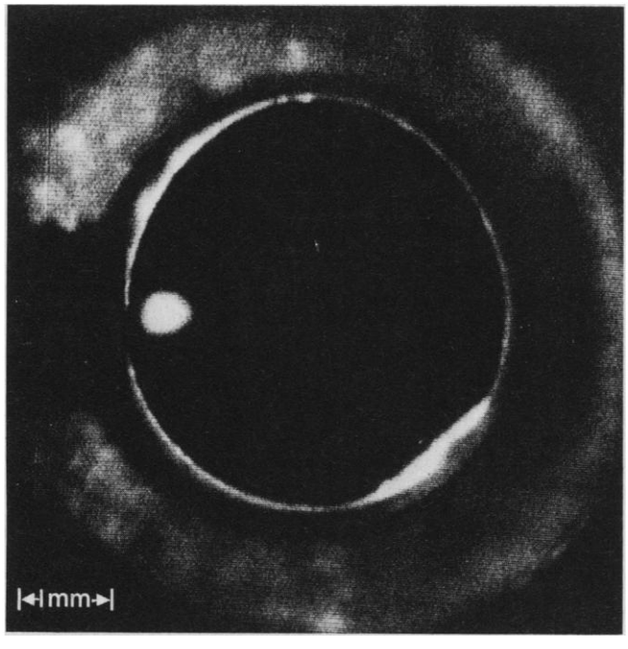


Fig. 12. Infrared photograph of a large, long-lived drop in a 4-mm disk of Ge. The sample is mounted in a dielectric holder (gray ring) and stressed by a screw (discernible on the left). The drop is the intense white spot adjacent to the screw, and is stabilized by a strain potential well. The bright ring is drop luminescence light scattered from the sample boundary. [From Wolfe *et al.* (*73*)]

Large, Long-Lived Drops; Alfvén Waves

It is of interest to study significant volumes of the electron-hole liquid, here viewed as a degenerate neutral plasma of constant density. Except for very high excitation levels, the usual drop size in the steady state is $R \leq 10$ μm, limited in part by the lifetime $\tau_0 = 40$ μsec. Although this size has not yet been satisfactorily explained, one expects $R \propto \tau_0$ from nucleation models (*38, 39*). In stressed Ge the density n is considerably lowered; since the radiative lifetime τ_{0r} varies as n^{-1} and the nonradiative lifetime τ_{0A} varies as n^{-2} or n^{-3} this suggests that an order of magnitude increase in τ_0 and in R would be observed in stressed Ge. Some earlier experiments (*51, 61*) showed a decreased drop lifetime, possibly arising from droplet motion to surface traps in unavoidable strain gradients.

In a quite different experiment Wolfe, Markiewicz, and co-workers (*19*) discovered large drops ($R \approx 100$ μm) with increased lifetimes, of the order of 500 μsec in stressed Ge. The drops were directly detected by their microwave resonance absorption at frequency $\omega = 1.6 \times 10^{11}$ sec^{-1}. Crystals of pure Ge are mounted without metallic contacts in a stressed plastic holder that does not mar the Ge surface. The holder is installed in a microwave cavity in a variable magnetic field H, and the sample is pumped with a laser beam at the point of maximum stress. The apparatus is similar to that used for paramagnetic resonance and cyclotron resonance of free carriers in semiconductors. Since the plasma frequency $\omega_p = 2 \times 10^{13}$ sec^{-1} for the electron-hole liquid is much higher than ω, electromagnetic waves will not normally propagate. However, Alfvén (*18*) showed that in a field $H > H_c \equiv m^* c\omega/e$ a special kind of wave is propagated at the velocity $V_A = H[4\pi n(m_e + m_H)]^{-1/2}$. In a field $H = 20$ kilogauss, $V_A = 6.2 \times 10^8$ cm sec^{-1} for Alfvén waves in the electron-hole plasma in Ge, corresponding to a wavelength $\lambda_A = 2\pi V_A/\omega = 240$ μm. Since this is comparable in magnitude to the size of a large drop, one expects a dimensional resonance corresponding to standing Alfvén waves in a drop of radius $R \approx \lambda_A/2 \approx 120$ μm. There are other higher modes: the general resonance condition for an isotopic medium is of the form $2\pi R/\lambda_A = \gamma(ij)$, where $\gamma(ij)$ are roots of a spherical Bessel function, leading to resonance fields $H(ij) \propto R/\gamma(ij)$. This problem is closely related to the microwave dimensional resonances observed in small semiconducting spheres by Cardona and Rosenblum (*70*).

The results of Wolfe, Markiewicz *et al.*

(*19*) are given in Fig. 11, which shows the microwave absorption plotted against H for a single drop, for various laser pump powers; increasing the power increases R and $H(ij)$, as expected. The exact theory of Alfvén resonances in Ge, including the full anisotropy, has yet to be solved. However, Markiewicz (*71*) has obtained an approximate solution by extending the method of Ford and Werner (*72*) for a single component plasma. The positions and intensities of the principal lines in Fig. 11 are approximately understood, the lack of perfect agreement indicating that the drop is not quite spherical. These microwave resonances are fully correlated with the drop luminescence observed simultaneously. When the laser power is switched off the drop radius $R(t)$ decays with a lifetime three times the volume decay time of the luminescence.

These large, long-lived drops have also been studied directly by luminescence and by image scanning (*25*) using a variable nonuniform stress along ⟨110⟩. The drop is formed in the region of maximum stress, with size $R \approx 30$ to 300 μm, depending on the exciting laser power. The results show an approximately spherical droplet whose radius exponentially decreases after laser switch-off with the same long time constant of the Alfvén wave resonance. The drop luminescence indicates a lowered density $n \approx 0.7 \times 10^{17}$ cm^{-3} as evidenced by a decrease in the Fermi line width. The static Alfvén wave resonance and the static luminescence image scan are consistent, as are the time-resolved resonance and the time-resolved luminescence image scan. We conclude that the drop corresponds to a low-density phase of the liquid with one or two electron ellipsoids occupied. The stress geometry used in these experiments creates a point of maximum strain and a minimum drop energy within the crystal. A large, stable drop can form in the strain potential well. This has recently been confirmed by a photograph of such an electron-hole drop, Fig. 12, by Wolfe *et al.* (*73*). The image in Fig. 12 was obtained by focusing the 709-mev drop luminescence onto the surface of an infrared-sensitive vidicon image tube. The drop was produced by optical injection from an 80-milliwatt Ar-ion laser beam focused on the back of the crystal, which was immersed in superfluid helium. Wolfe *et al.* found the photographed image to be almost independent of laser beam position, showing that small droplets, wherever they are produced, rapidly move into the potential well and coalesce into a large drop. In other stress geometries multiple potential wells and multiple drops can be produced because of the elastic anisotropy of Ge.

Summary

In Ge and Si, and also in Ge-Si alloys (*74*), there is extensive evidence for the stable binding of electrons and holes into a cold plasma of constant density, which undergoes a phase separation. Liquid metallic drops 1 to 300 μm in size are formed, with lifetimes ranging from 0.1 to 600 μsec. For Ge a surprising amount is known: the phase diagram, the surface energy, the work function, the decay kinetics. Much less is known for Si. There is good agreement between theoretical and experimental values of the liquid density, the critical density, the critical temperature, and the binding energy. The stability of the liquid phase is strikingly dependent on band structure. The multivalley structure and mass anisotropy of Si, Ge, and Ge-Si, together with their indirect band gap, are no doubt responsible for the observed stability in these crystals. In the similar semiconductor gallium phosphide, drops have not yet been observed, most likely because the high impurity content traps the excitons. In gallium arsenide the existence of drops is controversial (*75*). Undoubtedly drops will be found to exist in other semiconductors, perhaps at even higher temperatures. This is an exciting field for the experimentalist; new phenomena are being rapidly discovered, usually before they are predicted. For the theorist, the electron-hole drop is of high intrinsic interest. It represents the first example of a quantum liquid of constant density in a periodic crystal lattice. A number of challenging experimental and theoretical problems remain.

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Immunoglobulin-Receptors Revisited

A model for the differentiation of bone marrow–derived lymphocytes is described.

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The concept of an immunoglobulin (Ig) receptor for antigen on precursors of antibody secreting cells was first clearly enunciated by Ehrlich (*1*). Burnet, in his clonal selection theory, postulated that each cell was unipotential: that is, all the antibody receptor molecules on a given cell have a similar specificity (*2*). During the last two decades, considerable information, stimulated primarily by the introduction of immunofluorescent techniques by Coons (*3*), has accumulated concerning such receptors on lymphocytes. The purpose of this article is to evaluate past studies of Ig receptors for antigen on lymphocytes, to discuss new information regarding cell surface immunoglobulin D (IgD), and to propose a model of B cell (bone marrow–derived lymphocyte) differentiation and "triggering." The major reason for formulating the model was to accommodate the recent findings regarding receptor IgD. However, in developing the model, it became apparent that current concepts of B cell differentiation and triggering could be simplified by the inclusion of several additional concepts regarding the function of Ig receptors for antigen: these include a mechanism for induction of tolerance, absence of certain receptor isotypes (that is, immunoglobulin classes as defined by the H chain) on B cells, and a molecular mechanism underlying their stimulation.

The major concepts that have emerged from past studies are as follows: (i) Each clone of B lymphocytes has a single homogeneous immunoglobulin on the surface of its cells, which acts as antigen-specific receptor; these cells can differentiate into plasma cells that will secrete an immunoglobulin of identical specificity (*4*). (ii) Immunoglobulin M (IgM) is the class of receptor on immunocompetent virgin B lymphocytes (*5–7*). (iii) Binding of ligand to receptor is usually insufficient for stimulation; a second signal is needed from an accessory cell such as the T cell (*8*). (iv) After stimulation of B lymphocytes by antigen and T cell (thymus-derived lymphocyte) signals, they "switch" from the synthesis of IgM to either IgG, IgA, or IgE (*9*), and these isotypes are the antigen-specific receptors on memory B cells. These memory cells are the precursors of the plasma cells secreting immunoglobulin of the same isotype and specificity (*9*). (v) In many species, such as man and guinea pig, IgG-bearing lymphocytes represent the major type of circulating B lymphocyte in adults (*10*). (vi) IgA-bearing lymphocytes and IgA-secreting plasma cells are the predominant ones in Peyer's patches and lamina propria of the intestines (*11–13*). (vii) IgD is a cell surface immunoglobulin in humans that appears earlier in ontogeny than IgM and therefore may be the primordial cell surface Ig (*14*).

The above concepts are not universally accepted, however. For example, Sercarz and co-workers (*15*) argue that murine B lymphocytes are multipotential, that is, a large proportion of single cells from unimmunized mice can bind two unrelated protein antigens. If verified, this finding would challenge the clonal selection hypothesis. There is also controversy concerning the aforementioned arguments that large populations of B cells have surface IgG or IgA (*4*). Finally, there is contention concerning the antigen dependence of the presumed switch from synthesis of IgM to other classes of immunoglobulin in lymphocytes. Thus, Cooper and his co-workers suggest that such a switch can occur in germ-free animals (*9*) and in mouse fetal liver cultured in vitro (*16*).

In evaluating these conflicting data, two important obstacles to studies of cell surface immunoglobulins should be mentioned. (i) Specificity of antiserum to immunoglobulins. Clearly, specificity is critical to the interpretation of all data. Immunologists are aware of this problem, and the manipulations to obtain monospecific antiserums have become increasingly sophisticated. The magnitude of the problem is not fully appreciated, however. Not only are there natural antibodies to cell surface structures in the majority of, if not all, heterologous serums, which are not easily eliminated by conventional absorption, but there may be unexpected cross reactivities; for example, a rabbit antiserum prepared against purified mouse γ chain reacts with a portion of mouse δ and μ chains even af-

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