COMMENTS AND ADDENDA

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On the cloud of electron-hole droplets*

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In a recent experiment, Voos, Shaklee, and Worlock have shown that under a very high excitation, the electron-hole plasma of germanium forms a cloud of droplets of same size instead of one large drop. Various explanations are studied, but only one seems possible: drops are ejected from the boiling liquid formed near the laser spot, they are slowed by collisions with exciton and stop near the edge of the cloud. This process is strongly related to the excitation power. At lower excitation, exciton gas should be created first and drops should be nucleated from it.

The existence of a dense plasma of nonequilibrium electron-holes (e-h) in semiconductors like germanium and silicon was predicted by Keldysh and has been verified by several experiments.[1,2] The density and binding energy of such a plasma agree very well with theoretical calculations.[3]

The plasma condenses in small drops (radii usually reported are in the range 1–10 μm)[4]; however, little is understood about how the drops are formed, how they move, and what process fixes their radius. The radius seems to depend strongly on the experiment: under constraint, drops of 1 mm have been reported.[5] It is believed that excitons are created near the place where the laser is focused and diffuse in the sample. Drops are then nucleated from nucleation centers or by fluctuations of the exciton-gas density[6] and kept alive by the flow of excitons. This mechanism cannot be applied to the cloud of e-h droplets observed recently by Voos, Shaklee, and Worlock.[7]

A 100-mW beam is focused to a spot less than 50 μm diameter. By looking at the attenuation of a probe beam, they find that droplets are forming a cloud of radius $R \simeq 1$ mm, with a sharp edge. Light scattering shows that the radius of the drops is constant ($r = 2 \pm 0.5$ μm) inside the cloud. Upon increasing the excitation, R increases but r does not change appreciably.

In this paper, we want to study various possibilities for the formation of this cloud and finally to present the only one we have found compatible with its various properties: drops are ejected from the center of the cloud, are slowed by collisions with excitons, and stop near the edge of the cloud.

a. *First we will show that a constant radius inside the cloud implies that if the drops are in equilibrium with the excitons gas, there is no diffusion of excitons.* For that, let us suppose that the drops are kept alive by the flow of excitons and they do *not move*. If $N(x)$ is the number of e-h inside the drop which lies at the distance x from the center, its evolution within the time is given by

$$\dot{N}(x) = bN^{2/3}(x)\rho_{ex}(x) - N(x)/\tau - aT^2N^{2/3}(x)\,e^{-\varphi/kT}, \quad (1)$$

where $\rho_{ex}(x)$ is the exciton density and τ is the relaxation time which controls the recombination of e-h inside the drop. Taking into account the surface term, the binding energy of the plasma versus excitons is

$$\varphi = \varphi_\infty(1 - r_0/r)\,, \quad (2)$$

where r is the radius of the drop, φ_∞ is the binding energy for an infinite surface, and $r_0 = 2S/\varphi_\infty\rho$ ($\sim 10^{-2}$–10^{-3} μm), where S is the surface term and ρ is the density of the liquid. Calculation of back flow and Richardson's constant gives

$$b = 4\pi(3/4\pi\rho)^{2/3}\,(k_BT/2\pi m^*)^{1/2}\,, \quad (3)$$

$$a = 8\pi^2 m^* g\,(k_B^2/h^3)\,(3/4\pi\rho)^{2/3}\,, \quad (4)$$

m^* being the center-of-gravity mass of the exciton and g its degeneracy.[8] As all the drops are found to have the same radius, it must be constant in time so that $\dot{N}=0$ or

$$\rho_{ex}(x)=\rho_{ex}^{0}\, e^{\varphi_\infty r_0/k_B T r}+\alpha r\ , \tag{5}$$

where ρ_{ex}^0 is the thermodynamic density $\rho_{ex}^0=(a/b)T^2 \times e^{-\varphi_\infty/k_B T}$ and $\alpha=(\frac{4}{3}\pi\rho)^{1/3}/\tau b$. Because r is constant in the cloud, $\rho_{ex}(x)$ is constant too; consequently, diffusion of excitons cannot exist.

But recombination of e-h in the cloud has to be compensated in order to keep the steady state; so either the excitons have to diffuse or the drops have to move.

Before eliminating completely the possibility of e-h coming by diffusion of excitons alone—drops being fixed—let us see if it could be compatible with a small change in the drop radius. The equation of conservation of e-h is

$$-\operatorname{div} J(x)=[\rho_{ex}(x)/\tau_{ex}]+[\mathfrak{N}(x)/\tau]\tfrac{4}{3}\pi r^3\rho\ , \tag{6}$$

where $\mathfrak{N}(x)$ is the density of drops. If the flow of e-h is due to exciton diffusion, $J(x)=-D\operatorname{grad}\rho_{ex}(x)$. Neglecting the death of e-h in drops, one gets

$$\rho_{ex}^{min}(x)=\rho_{ex}(R)\,(R/x)\exp\left[(R-x)/(D\tau_{ex})^{1/2}\right], \tag{7}$$

which is a lower bound for the change of exciton density; using[1] $D=1500\ \text{cm}^2/\text{sec}$ and $\tau_{ex}=8\ \mu\text{sec}$, the exciton density between 0.1 and 1 mm changes by about a factor of 20, which will correspond to a drastic change in the steady-state radius [verifying (5)], incompatible with a drop radius observed to be almost constant in the cloud.

So the drops have to move.

b. *Let us still suppose that drops are nucleated from exciton gas.* Balslev and Hvam[9] have shown the possibility of a motion of drops due to the diffusion of excitons: The resulting pressure due to the variation of the exciton density on the two sides of a drop pushes it to low-density region. But with this model, the radius of drops depends on when they are nucleated and is far from constant. So this mechanism cannot explain the cloud.

c. *Another possibility is that drops are directly formed.* The laser is creating a very dense and hot liquid; temperature decreases when one goes far from the laser spot until the lattice temperature is reached. If the temperature-density trajectory touches the coexistence curve of the phase diagram on the gas side, a supersaturated exciton gas is first formed, and drops are nucleated from it. On the other hand, if the liquid side is reached first, bubbles of exciton gas are formed inside the liquid, and due to a high pressure of e-h, drops may be ejected from the boiling liquid. The initial speeds and radii of the drops are *a priori* different. If the laser spot is small, one can expect to have a ballistic regime. The first question which arises is what fixes the radius. The second one is what slows the drops in order to have a sharp edge in the cloud.

Let us follow a drop along a radial axis $\vec{x}$. After a short distance (~ 0.1 mm), the radius is observed to be constant. In Eq. (1), which governs the time variation of N, the back-flow term depends *a priori* on the speed v of the drops, but one can show that

$$b(v)=b(0)[1+O(m^*v^2/2kT)]\ , \tag{8}$$

so that, for $T=2\,^\circ\text{K}$, this correction can be neglected if $v\ll 10^4$ m/sec (the consistency of this assumption will be checked at the end). From Eq. (5), any radius above r_{min} with

$$r_{min}^2=\frac{12\pi}{h^3\rho^2}\, s\tau g m^* kT\exp\left[-\frac{\varphi_\infty}{kT}\left(1-\frac{r_0}{r_{min}}\right)\right] \tag{9}$$

can be stable, as illustrated in Fig. 1.[10] What fixes the radius? One could think that the flow P of electrons and holes can be distributed between gas and drops in order to minimize the total free energy F. Using Eq. (5) and the relations

$$F=\mathfrak{N}(-\tfrac{4}{3}\pi r^3\rho\varphi_\infty+4\pi r^2 s)$$
$$+\rho_{ex}(1-\tfrac{4}{3}\pi r^3\mathfrak{N})\,kT\ln(\rho_{ex}\lambda^3/e)\ , \tag{10}$$

$$P=(\rho_{ex}/\tau_{ex})(1-\tfrac{4}{3}\pi r^3\mathfrak{N})+(\rho/\tau)\tfrac{4}{3}\pi r^3\mathfrak{N}\ , \tag{11}$$

where λ^3 is defined as

$$\varphi_\infty=-kT\ln(\rho_{ex}^0\lambda^3)\ . \tag{12}$$

$\partial F/\partial r|_{r_F}=0$ leads to an implicit equation for r_F,

$$\alpha r_F^2=\frac{\varphi_\infty}{kT}\, r_0\left[\rho_{ex}^0\exp(\varphi_\infty r_0/kTr_F)+\frac{\frac{3}{2}(P-\rho_{ex}/\tau_{ex})[(\tau_{ex}\rho/\tau)-\rho_{ex}]}{((\rho/\tau)-P)[(1-\tau_{ex}/\tau)\varphi_\infty/kT]}\right]+(\tau_{ex}/\tau)\ln(\rho_{ex}/\rho_{ex}^0)-\tfrac{3}{2}(r_0/r_F)\,\varphi_\infty/kT]) \tag{13}$$

Without the second term of the large square bracket, (13) reduces to $r_F=r_{min}$. As this second term is positive, r_F is larger than r_{min}. Neglecting the fraction of volume $V=\frac{4}{3}\pi r^3\mathfrak{N}$ occupied by the drops, the second term of the large square bracket is approximately equal to $\frac{3}{2}\tau_{ex}\rho VkT/(\tau-\tau_{ex})\varphi_\infty$; the two terms in the large square bracket are of the same order of magnitude, and consequently, r_F is of order r_{min}. Numerically, Eq. (9) gives r_{min} between 0.1 and 2.5 μm (see Table I); thus, both r_F

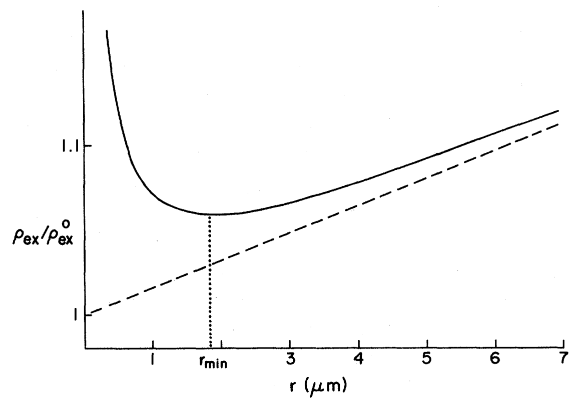

FIG. 1. Density of excitons ρ_{ex} in equilibrium with drops of radius r for $s=1.5\times10^{-7}$ J/m^2, $\tau=45$ μsec, $gm^*=11$, $\varphi_\infty=15$°K, $\rho=2\times10^{17}$ particles/cm^3, and $T=2$°K.

and r_{min} are compatible with the observed radius.

Another possibility is that the drops have the minimum radius. E-h recombination must be compensated in the cloud. When a drop has a radius $r>r_{min}$, it can shrink and evaporate excitons without trouble until it reaches r_{min}. The exciton gas tends to bring all the drops at the same radius via the back flow [Eq. (1)]. When all the drops have the minimum radius and one of them shrinks, it will inevitably die (a radius less than r_{min} is unstable). Many excitons will be created from that evaporation, which will compensate for e-h recombination in the neighborhood and keep the other drops alive at a $r=r_{min}$ radius.

d. *Let us now turn to the dynamics of the drops.* Because there is a sharp edge in the cloud, the drop has to stop somewhere near the edge (or at least arrive at the borderline of this steady-state region with a low speed so that a tail of dying drops with decreasing radius is not seen).

One can imagine different types of forces on the drops. There could be an electrostatic force between the charge of the drop and the charges of the other drops added to an eventual steady-state distribution of charge (the force between drops being an accelerative one which alone gives rise to a long tail for the cloud). As it is almost impossible to follow the establishment of the steady state, one can *a priori* imagine any distribution of charge (on the surface of the sample, near the center, on the borderline of the cloud, etc.), but it is *a priori* not very easy to obtain a solution which leads to spherical symmetry from hemispherical cloud (except with charges only on the center).

Another possibility[14] (which would have to be added to the preceding one if it exists) is the collision of the drop with the excitons. Let us suppose that the radius of the drop is exactly constant (no variation of mass). In the referential of the drop (with a radial velocity $\vec{v}$), each exciton with speed $\vec{u}$ going into the drop is dissociated and gives its impulse $m^*\vec{u}$ to the drop. The resulting force, supposing excitons to be at thermodynamic equilibrium, is

$$\vec{F}=-\rho_{ex}(m^*/2\pi kT)^{3/2}\iint d^3u\exp[-m^*(\vec{v}+\vec{u})^2/2kT] \times[\vec{u}\cdot d\vec{s}\,\theta(-\vec{u}\cdot d\vec{s})]\,m^*\vec{u}\,, \qquad (14)$$

where $d\vec{s}$ is normal to the surface of the drop. In the limit $m^*v^2/2kT\ll1$, $\vec{F}=-\alpha\vec{v}$, with $\alpha=\frac{8}{3}r^2\rho_{ex}\times(2\pi kTm^*)^{1/2}$. The drop is emitting excitons in all directions, so there is no resulting force from emission. Going back to the referential of the sample, the motion of the drop is then simply ruled by

$$M\,d\vec{v}/dt=-\alpha\vec{v}\,, \qquad (15)$$

where M is the mass of the drop. (M may be assumed to be $\frac{4}{3}\pi r^3\rho m^*$, but note that the combination of the various masses of the electrons and holes which enters into the exciton center-of-gravity mass m^* has no reason to be the same as for the plasma.) The solution of (15) is

$$v=(\alpha/M)(L-x)\,, \qquad (16)$$

where L is the distance where the drop with an initial speed $v_0=\alpha L/M$ stops. The term α/M, which varies as $m^*g/r\rho\,e^{\varphi_\infty/kT}$, has values between 10^4 and 3×10^5 sec^{-1}, according to the values of the parameters (see Table II). So a drop which reaches a point 1 mm away from the center had an initial speed between 10 and 300 m/sec. One can note that the combination of parameters which gives $r_{min}\simeq2$ μm, also gives a large initial speed; the most important consequence is that the equilibrium process due to exciton back flow which tends to bring all the drops to the same radius, is not short

TABLE I. Minimum radius r_{min} for various values of the parameters.

S (10^{-7} J/m^2)	τ (μsec)	gm^*	ρ (10^{17} particles/cm^3)	φ_∞ (°K)	r_{min} (μm)
0.8[a]	40	5.5	2.4	19	0.13
1.5[b]	50	5.5	2.0	15	1.41
2.5[c]	50	10.0	2.0	15	2.51

[a]Ref. 12. [b]Ref. 13. [c]Ref. 6.

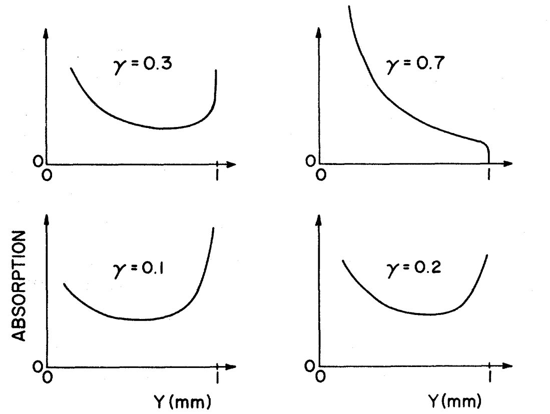

FIG. 2. Absorption in arbitrary units due to a cloud of drops with same initial radius and same initial speed for various values of γ.

enough for such speeds. One can look, for example, at the evolution with time of a drop with an initial radius r_i in a density of excitons which corresponds to drops of radius r^*; this is given by

$$r - r^* \simeq (r_i - r^*)\, e^{-t/3\tau} .$$

So a drop of 3 μm in the neighborhood of drops of 2 μm will take 80 μsec to reach 2.5 μm and would have traveled over 4 mm if its average speed was 50 m/sec. Finally, due to their large initial speed and long lifetime, the drops spend the larger part of their flight in the cloud with their initial radius (determined by the emission process and which has, *a priori*, nothing to do with $r_{\min}$).[11]

During its motion, the drop shrinks a little, but its mass can be assumed to be constant, and so Eq. (15) is still valid. One can now look at the distribution of the density of e-h in drops with such a speed inside the cloud. Neglecting the contribution of excitons to the current of e-h and supposing that e-h come only from drops, $J(x) = \overline{\mathfrak{N}}(x)\, v(x)$ with $\mathfrak{N}(x) = \mathfrak{N}(x)\frac{4}{3}\pi r^3 \rho$ (the variation of $\overline{\mathfrak{N}}$ coming from drops which shrink); the equation of conservation (6) leads to

$$\overline{\mathfrak{N}}(x) = \mathrm{const}/x^2 (L - x)^{1-\gamma} \tag{17}$$

if $\gamma = M/\alpha\tau$ (~ 0.1–2); the recombination of excitons is then neglected. Note that $\overline{\mathfrak{N}}(x)$ is not valid around $x = 0$, because a boiling liquid is supposed to exist

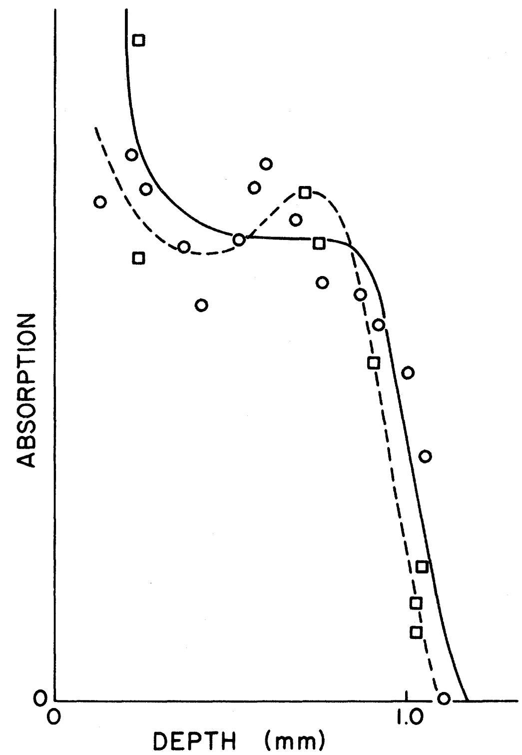

FIG. 3. Experimental data for the absorption of the e-h droplets cloud. The solid curve corresponds to $\gamma = 0.2$ and $b = 0.2$, and the dotted curve corresponds to $\gamma = 0.1$ and $b = 0.2$. (Note that the theory gives only the shape of the absorption curve, and so, the horizontal and vertical units are fitted to experimental data.)

in that region. For $\gamma < 1$, $\overline{\mathfrak{N}}(x)$ diverges for $x = L$, which corresponds to an accumulation of dying drops on the borderline of the cloud.

In order to compare that theory to experiment, one has to calculate the absorption of a probe beam parallel to the surface of the sample and at a distance y from it, due to a cloud with such a distribution of e-h. This absorption is given by

$$S(y) \propto \int_y^L [x dx/(x^2 - y^2)^{1/2}]\, \overline{\mathfrak{N}}(x) . \tag{18}$$

The shape of $S(y)$ for various values of γ is shown in Fig. 2. For $\gamma \geq \frac{1}{2}$, there is no divergence for $y \simeq L$, in agreement with the experimental absorption, but $S(y)$ is varying too much with y. In re-

TABLE II. Initial speed V_0 for various values of the parameters. r is taken from the experiment.

r (μm)	gm^*	ρ (10^{23} particles/cm^3)	φ_∞ (°K)	$\frac{\alpha}{M}$ (10^5 sec^{-1})	V_0 (m/sec)
2.0	10.0	2.0	16	1.20	120
2.5	5.5	2.4	19	0.10	10
1.5	10.0	2.0	15	2.70	270

gard to this point, curves for $\gamma = 0.2$ or $\gamma = 0.1$ would have been better. In fact, their divergences at $x \simeq L$ can be easily broadened by introducing a distribution of initial speed (which most probably exists) for the drops. (Note that a distribution of initial radius plays the same role.) Using, for example, a Gaussian distribution of speed with width b, a reasonable fit to the experimental curve is obtained for $\gamma = 0.2$ and $b = 0.2$, and also for $\gamma = 0.1$ and $b = 0.2$ (see Fig. 3).

The experimental sharp edge is found with this model, but the absorption would have to present a big increase when one approaches the center ($x \leq 0.1$ mm). The experimental data are not accurate enough to eliminate this possibility.

In conclusion, we have presented a possible model for the e-h droplets cloud. The most important points are that the drops are ejected with an initial speed, they are slowed during their motion in the cloud by collisions with excitions, and they stop near the edge. The radius of the drops seems to be linked to the emission process, and it is not understood why all the radii are the same. We hope to stimulate other experiments in order to confirm or destroy this model. They would really help to understand the formation of drops. We also would like to emphasize that we think this model may work probably only for a very powerful excitation, where a very high density of e-h are formed near the laser spot. At lower excitations, exciton gas may be created first and drops nucleated from it.

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[1] Y. Pokrovskii, Phys. Status Solidi A 11, 385 (1972).

[2] J. C. Hensel, T. G. Phillips, and T. M. Rice, Phys. Rev. Lett. 30, 227 (1973); C. Benoit à la Guillaume and M. Voos, Solid State Commun. 12, 1257 (1973); T. K. Lo, B. J. Feldman, and C. D. Jeffries, Phys. Rev. Lett. 31, 224 (1973).

[3] M. Combescot and P. Nozières, J. Phys. C 5, 2369 (1972); W. F. Brinkman and T. M. Rice, Phys. Rev. B 7, 1508 (1973); P. Vashista, P. Bhattacharyya, and K K. S. Singwi, Phys. Rev. Lett. 30, 1248 (1973).

[4] V. S. Bagaev, N. A. Penin, N. N. Sibel'din, and V. A. Tsuetkov, Fiz. Tverd. Tela 15, 3269 (1973) [Sov. Phys.-Solid State 15, 2179 (1974)].

[5] J. P. Wolfe, R. S. Markiewicz, C. Kittel, and C. D. Jeffries, Phys. Rev. Lett. 34, 275 (1975).

[6] T. K. Lo, B. J. Feldman, R. W. Westerveer, J. L. Staehli, and C. D. Jeffries, report (unpublished).

[7] M. Voos, K. L. Shaklee, and J. M. Worlock, Phys. Rev. Lett. 33, 1161 (1974).

[8] Due to the degeneracy of the valence band, $m^* g$ can be calculated easily from the band structure parameters only in two cases. Neglecting the light holes, one obtains, $g = 16$ and $m^* = [m_{e\parallel} + m_{hH})(m_{e\perp} + m_{hH})^2]^{1/3}$ so that $m^* g \simeq 10$. Assuming that the holes have the same mass, $m_h = 2[(1/m_{hH}) + (1/m_{hL})]^{-1}$, one obtains $m^* = [m_{e\parallel} + m_h) \times (m_{e\perp} + m_h)^2]^{1/3}$ and $g = 32$, so that $m^* g \simeq 11$. A recent experiment by Frova, Thomas, Miller, and Kane [Phys. Rev. Lett. 34, 1572 (1975)] indicates that $m^* g$ is more probably of order 5.5.

[9] I. Balslev and J. M. Hvam, Phys. Status Solidi B 65, 531 (1974).

[10] As also found by R. N. Silver, Phys. Rev. B 11, 1569 (1975).

[11] Note that, in that case, the drops are not necessarily in equilibrium with the exciton gas; so a constant radius does not imply a constant density of excitons. But the contribution of excitons to the e-h current is still probably negligible compared to the current due to the motion of drops.

[12] T. M. Rice, Phys. Rev. B 9, 1540 (1974).

[13] T. L. Reinecke and S. C. Ying, Solid State Commun. 14, 381 (1974).

[14] J. C. Hensel and T. M. Rice pointed out to me that phonon damping is actually larger than the one due to excitons.