EFFECT OF THE SURFACE ENERGY ON THE ELECTRON-HOLE DROP LUMINESCENCE IN Ge

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ABSTRACT

The effect of surface energy on the luminescence line shape of electron hole droplets is considered theoretically. A shift $2\sigma/rn_o$ of the high energy cut off of the line is predicted, and two contributions to the variation of the line width are discussed. A differential method is described which allows the measurements of these effects. The radius of EHD near threshold can be fitted by a simple model which takes into account the surface energy and the internal EHD recombination.

I. INTRODUCTION

Bulk properties of electron hole drops (EHD) in germanium are now well understood.[1)] Several authors have published recently theoretical calculation of the surface energy of the electron hole liquid.[2)] In this paper we investigate the dependence of the EHD luminescence on their radius r, through the effect of surface energy. We show how small changes of luminescence line shape can be detected and used to measure EHD radius near the threshold of EHD condensation[3)] and thus obtain a deeper insight into the nucleation processes.

II. THEORETICAL MODEL

We consider a droplet of radius r containing N electron hole pairs. We restrict our consideration to T = 0 for simplicity. The total energy of the drop is the sum of the volume and surface energy:

$$\xi = NE(n) + 4\pi r^2 \sigma(n) \qquad (1)$$

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where $\sigma(n)$ is the EHD surface energy and $E(n)$ is the mean energy per pair as a function of the density n, which has a minimum value μ_∞ at $n = n_o$. Near n_o we use the development $E(n) = \mu_\infty + a\,(n-n_o)^2$. We can minimize ξ by a small change of n (and r). The condition $d\xi/dn = 0$ gives:[4)]

$$n - n_o = \frac{1}{r}\,\frac{\sigma(n_o) - 3/2\; n_o (d\sigma/dn)_{n\,=\,n_o}}{a\, n_o^2} . \tag{2}$$

which is the change of the density caused by the pressure due to surface tension.

The corrected value of ξ is now

$$\xi = N\mu_\infty + 4\,\pi\, r^2\, \sigma(n_o) - \frac{N}{r^2}\,\frac{[\sigma(n_o) - 3/2\;\, n(d\sigma/dn)_{n\,=\,n_o}]^2}{a\, n_o^4} . \tag{3}$$

Then, one can obtain the chemical potential

$$\mu = \frac{d\xi}{dN} = \frac{1}{4\,\pi\, r^2\, n}\,\frac{d\xi}{dr}$$

$$\mu(r) = \mu_\infty + \frac{2\sigma}{rn_o} + \frac{1}{3r^2}\,\frac{[\,\sigma - 3/2\; n(d\sigma/dn)_{n\,=\,n_o}\,]^2}{a\, n_o^4} . \tag{4}$$

In fact, we will use only the first order contribution to $\mu(r)$, *i.e.* $\frac{2\sigma}{rn_o}$.

We consider now the effect on the luminescence line of the droplet of radius r. The high energy cut-off of the line corresponds to a transition of a droplet with N pairs to a droplet with (N-1) pairs, both in their ground state: This is just the definition of $\mu(r)$. As shown in figure 1, the high energy cut-off of the luminescence line depends now on r through the high energy shift $2\sigma/r\,n_o$. This shift is small, since its value is 6×10^{-3} meV at $r = 1\ \mu m$ if one takes $\sigma = 10^{-4}$ erg/cm^2.[2)] The next step is to see if there is a change of the width $\Delta(r)$ of the luminescence line, which for $r \to \infty$ is equal, in the crudest

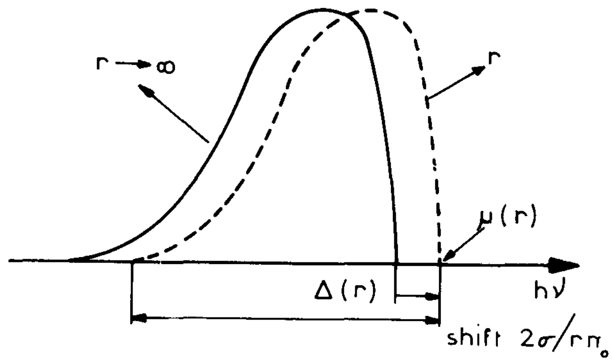


Fig.1. Recombination radiation line shape for a droplet of radius r. The solid line corresponds to $r \to \infty$ and the dashed line to r finite.

approximation, to $E_F(n_o)$ the sum of the Fermi energy of the electrons and the holes. Since there is no possibility to push the development $\xi(r)$ in eq.(3) to the term of order r^{-1}, we try to evaluate the difference $\Delta(r) = \xi^*(n^*) - \xi(n_r)$ between the energy of a droplet containing N pairs in its ground state and in an excited state with one pair excited from the bottom of the bands to the Fermi levels. On can write:

$$\xi^*(n) = \xi(n) + E_F(n) + 4\pi r^2 \Delta\sigma(n)$$

where $\Delta\sigma(n) = \sigma^*(n) - \sigma(n)$.

Here $\sigma^*(n)$ is the surface energy in the excited state. $\xi^*(n)$ should be in principle minimized by allowing a small change of n to n^*, but (n^*-n) turns out to be like r^{-3}, and such a change can be neglected. Using the value of n in eq.(2), one gets:

$$\Delta(r) = E_F(n_o)\left[1 + \frac{2}{3r}\,\frac{\sigma(n_o) - 3/2\, n_o (d\sigma/dn)_{n = n_o}}{a\, n_o^{3}}\right] + 4\pi r^2 \Delta\sigma. \quad (5)$$

There are two causes of change to $\Delta(r)$; the second term in eq.(5) corresponds to the compression (eq.2) and the third one gives also a r^{-1}

contribution if $\Delta\sigma$ is like r^{-3}.

We need now some evaluation of $d\sigma/dn$ and $\Delta\sigma$. In the most usual way of computing σ,[2] one minimizes the quantity:

$$S = \int_{-\infty}^{+\infty} \left[m\, E(m) + \frac{\alpha}{m} \left(\frac{dm}{dx}\right)^2 \right] dx \qquad (6)$$

where $m(x)$ is the density profile in a direction x perpendicular to the surface, which is supposed to be the same for electrons and holes (no dipole layer). A further simplification is to assume that $m(x)$ varies according to a given function with just one parameter d, the thickness of the surface layer. With scaling arguments, S can be transformed to:

$$S = A(n)\, \frac{d}{n} + B(n)\, \frac{n}{d} .$$

Then, σ is obtained by minimizing S with respect to d:

$$\sigma(n) = 2 \sqrt{A(n)B(n)}$$

$d\sigma/dn$ is probably small, because if one takes for $m(x)$ a linear function of x, then $(dA/dn)_{n_o} = 0$ and if one takes $m(x) = n\, (1+\exp(-x/d))^{-1}$ then $dB/dn = 0$. So we assume that $d\sigma/dn$ can be neglected in eq.(5).

In an attempt to obtain $\sigma^*(n)$ in eq.(6) we can modify the first term in the integrand

$$m\, E(m) \rightarrow m\, E(m) + m/nV\, [E_F(m) - E_F(n)]$$

but, we do not know how to modify the second one. Then, taking $m(x)$ as a linear function of x in the interval (0,d) one can compute $A^*(n)$

$$A^*(n) = \int_0^n m\, E(m)\, dm + \frac{1}{nV} \int_0^n m\, [E_F(m) - E_F(n)]\, dm$$

$$A^*(n) = A - \frac{1}{8}\, \frac{n}{V}\, E_F(n).$$

In this approximation, B is unchanged. Thus

$$\Delta\sigma = \sigma \frac{\Delta A}{2A} = - \frac{\sigma n\ E_F}{16\ AV} .$$

The contribution to the width $\Delta(r)$ (last term of eq.(5)) is:

$$4\pi r^2\ \Delta\sigma = - \frac{3}{2} \frac{\sigma n\ E_F}{16A} = - \frac{3}{8} \frac{d}{r} E_F \qquad (7)$$

since $A = \frac{\sigma}{2} \frac{n}{d}$.

Taking $d = 60$ Å, this contribution (7) is $- 23\ E_F/r$(r in Å) which has to be compared to $E_F(n)-E_F(n_o) = \frac{40}{r} E_F$, taking $\sigma = 10^{-4}$ erg/cm^2 and $a = 1.2\times10^{-35}$ meV cm^{-6}. With the same units

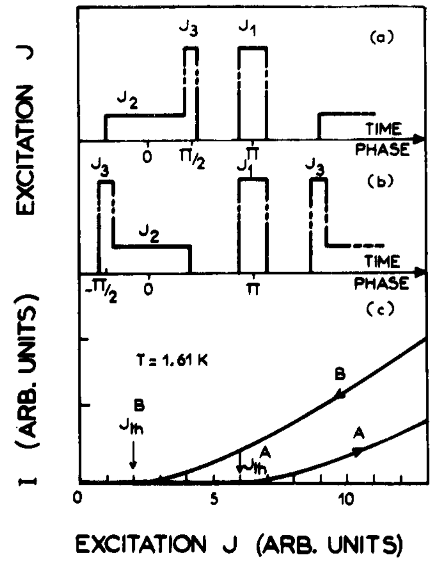
$$\mu_r - \mu_\infty = + \frac{10}{r} E_F \quad .$$

We must emphasize that this evaluation of $\Delta\sigma$ is a rough approximation. It proves that $\Delta\sigma$ is like r^{-3}. We hope that the negative sign in (7) is correct, but we cannot have any confidence in the order of magnitude. However, one can take it as an indication that a rather strong compensation occurs between the two r^{-1} contribution to $\Delta(r)$ in eq.(5).

III. EXPERIMENTAL SET UP

The idea is to measure, near the threshold of EHD condensation, the shift of the luminescence line of EHD when their size changes.[3] As shown below, EHD size depends on the pump level and also because of hysteresis,[5] on the pump level history. A pure Ge sample ($N_A-N_D \sim 2\times10^{10}$ cm^{-3}) is immersed in liquid He and excited by a very stable tungsten halogen lamp monitored by a special chopper, as shown in Fig. 2, so that both levels of pump J_1 and J_2 ($J_1 \sim 10\ J_2$) have opposite phases. The corresponding luminescence signals, analyzed through a grating spectrometer followed by a cooled PbS cell is sent to a lock in amplifier. The duration of J_1 is adjusted in order to get zero at the maximum of the EHD line. The resulting signal is proportional to the

Fig.2. (a)(b) - Time and phase dependence of the excitation in the differential experiment. The chopping frequency is 75 Hz.
(c) - Luminescence signal of the 709 meV EHD line versus excitation J_1 when J is continuously increased from zero to 1000 (off scale) and back to zero ($J_{th\ B} \sim 2$ mW/cm^2).



difference between the line shapes for excitation levels J_1 and J_2. This differential method allows a great amplification of small changes in line shape. Besides, adding just before J_2 and excitation J_3 equal to J_1, and in phase quadrature with J_1 and J_2 (see Fig. 2(b)), we can make measurements on the descending branch (curve B in Fig. 2(c)) of the optical hysteresis. The excitation scheme of Fig. 2(a) gives data on the rising branch (curve A); here J_3 is not functional, but is left for convenience. One can switch from A to B just by changing the rotation of the chopper from clockwise to counter clockwise. Fig. 3 gives typical data obtained on branch B at $J_2 \sim 10\ J_{th\ B}$. The peaks at 713,6 meV and 705.2 meV are due to free excitons.

In the region of the LA phonon assisted emission of EHD (~ 709 meV) one can see a signal resembling the derivative of the EHD line. The differential signal can be analyzed as follows. If f ($h\nu$) is the line shape at J_1, we suppose that the change at J_2 can involve a shift δ and a dilatation of the line ε giving $f\left[(1 + \varepsilon)h\nu + \delta\right]$. Then the differential signal is:

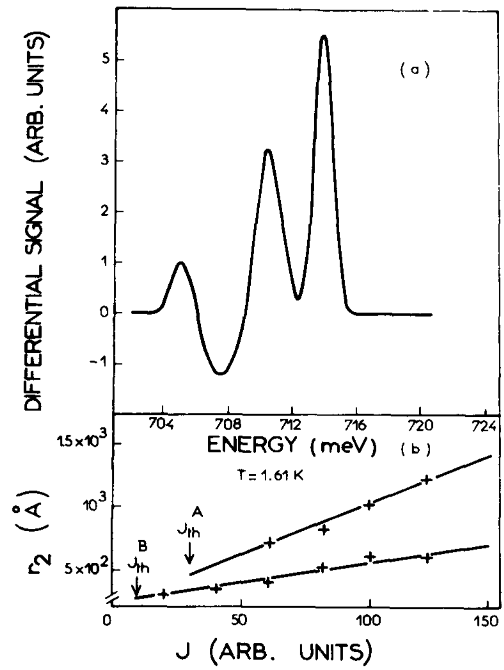


Fig.3. (a) - Typical differential luminescence signal at 1.61K for $J_2 \sim 10\ J_{th\ B}$.
(b) - Variation with the excitation of the radius of droplets on branch A and B of Fig. 2(c).

$$\Delta f = (\delta + \varepsilon h\nu)\ df/dh\nu \qquad (8)$$

Here, if $h\nu = 0$ at the high energy cut-off of the line, then the shift of the high and low energy cut-off are respectively δ and $(\delta - \varepsilon E_F)$.

IV. DISCUSSION OF THE EXPERIMENTAL RESULTS

a) Line Shape

Within the experimental uncertainties, the shape of the differential signal (Fig. 3(a)) is quite insensitive to the experimental conditions. This is consistent with the assumption that both δ and ε are like r^{-1}. Using the analysis sketched at the end of Chapter III, one obtains $\varepsilon E_F = 0.3\ \delta$. In fact, if r_1 and r_2 are the radii of EHD corresponding to J_1 and J_2, all variations are indeed like $(r_2^{-1} - r_1^{-1})$.

$\delta = 2\sigma/n_o \ (r_2^{-1} - r_1^{-1})$ and $\varepsilon E_F = \Delta(r_2) - \Delta(r_1)$.

As shown at the end of chapter II, if the only contribution to ε was the change of Fermi energy caused by the drop contraction, then εE_F would be equal to about $4\ \delta$. This experimental result, $\varepsilon E_F = 0.3\ \delta$, shows that indeed a strong compensation occurs between the two contributions considered in eq.(5).

b) Measurement of Droplet Radius Near Threshold

When $J_1 = 10\ J_2$, the r_1^{-1} term can be neglected because r is a rather rapid function of J as shown in figure 3(b), which gives the value of r as a function of excitation along the two branches A and B of Fig. 2(c). These data are of great importance for the study of nucleation since from the data of Figs. 2(c) and 3(b) one can deduce the variation of the density of droplets. In the remaining of this paper, we want just to compare the value of r obtained on branch B at the threshold with a simple theory.[3)]

Taking into account the surface energy, the EHD work function is now[6)] $\phi(r) = \phi_\infty - 2\sigma/rn_o$. Therefore, the well known Pokrovskii eq.(1) relating the density in the exciton gas n_{ex} to the drop radius r becomes:

$$n_{ex} = \alpha r + n_{ex,o} \exp(2\sigma/rn_o kT) \qquad (9)$$

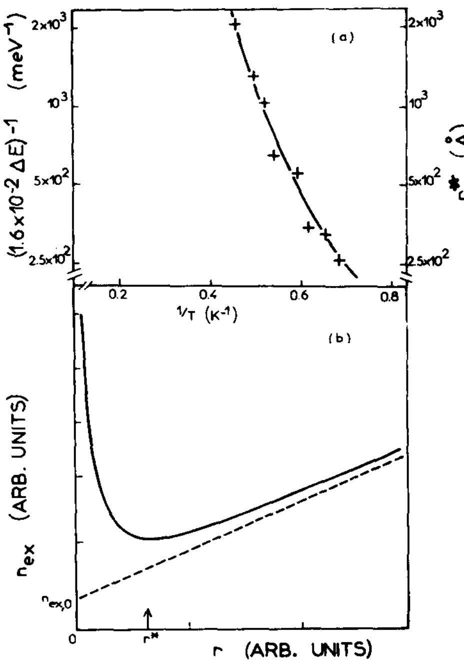
where $\alpha = 4\ n_o/3\ v_{ex}\tau_o$ (v_{ex} thermal velocity of excitons, τ_o EHD life-time) and

$$n_{ex,o} = g(2\pi\ m^*\ kT/h^2)^{3/2}\ \exp(-\phi_\infty/kT)$$

(g and m^*: degeneracy and mass of exciton).

Relation (9) is shown in Fig. 4(b). There is now a value r^* which is the radius of the smallest stable droplet.

Fig.4. (a) - Experimental temperature dependence of ΔE near threshold $J_{th\ B}$. On the right scale, the corresponding values of r^* have been plotted taking $\sigma = 10^{-4}$ erg/cm^{-2}. The solid line is a fit using eq.(10) as explained in in the text.
(b) - The free exciton density n_{ex} as a function of droplets radius r. The dashed line corresponds to Pokrovskii's model, and the solid line to the results obtained when the effect of surface energy is added.



$$r^* = \beta(A\sigma T)^{1/2} \exp(-\phi_\infty/2kT) \exp(\sigma/r^* n\ kT) \tag{10}$$

with $\beta^2 = 2\tau_o(3/4\ \pi)^{1/3}/k\ n_o^{4/3}$ and A is the coefficient of the Richardson law for thermal emission; r^* is identified with the value of r obtained at the threshold of branch B. The fit of experimental data with eq.(10) is shown in Fig. 4(a). This fit depends in fact on two parameters, ϕ_∞ and A/σ since what is measured primarily is the quantity $\Delta E^* = 2\sigma/r^* n_o$; This is clear if eq.(10) is written:

$$\frac{1}{\Delta E} \exp(-\ \Delta E/2kT) = \frac{\beta n_o}{2} \left(\frac{A}{\sigma}\right)^{1/2} T^{1/2} \exp(-\phi_\infty/2kT) .$$

Fig. 4(a) shows that a good fit is obtained taking $\phi_\infty/k = 23^oK$ and $A/\sigma = 1.6\times10^{14}\ s^{-1}K^{-2}erg^{-1}cm^2$. This value of A/σ is close to the calculated value, taking $A = 3.2\times10^{10}sec^{-1}K^{-2}$ (with $g = 16$ and $m^* = 0.33\ m_o$) and $\sigma = 10^{-4}erg/cm^2$. If $\phi_\infty/k = 16^oK$ is used, A/σ is reduced by a factor of 120, a result which seems unreasonable. One can remark that the result

$\phi_\infty/k = 16^oK$ has always been obtained through the analysis of threshold data related to branch A[1,7] and that these data should be reanalyzed taking into account supersaturation effects.[8]

To conclude, let us recall the importance of these measurement of droplets radius and density near the threshold of condensation for a detailed study of the nucleation processes.

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4) An explicit dependence of σ upon r could be added. Then the term $\frac{1}{n}\frac{d\sigma}{dn}$ in eq.(2) would be changed into $(\frac{1}{n}\frac{\partial\sigma}{\partial n} + \frac{1}{r}\frac{\partial\sigma}{\partial r})$.

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