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Droplet Model of Electron-Hole Liquid Condensation in Semiconductors*

T. L. Reinecke†
Naval Research Laboratory, Washington, D. C. 20375

and

S. C. Ying‡§
Laboratoire de Physique des Solides, Université Paris-Sud, Orsay, France

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A model based on noninteracting droplet fluctuations is used to describe the phase diagram for electron-hole liquid condensation in semiconductors. All liquid and gas densities are related to the liquid density at low T. Good agreement is obtained by fitting recent detailed measurements of the phase diagram for Ge, and an experimental estimate of droplet surface tension ($\sim 1.0\times 10^{-4}$ erg/cm^2) is obtained. Theoretical values of the critical temperature and density for Ge are given. A theoretical phase diagram for Si is presented.

The condensation of high-density nonequilibrium carriers into electron-hole–liquid (EHL) droplets in Ge and Si at low temperatures has been studied extensively both experimentally[1-3] and theoretically.[4,5] The liquid-gas phase diagram provides an especially full picture of the condensation (see Fig. 1): It is the boundary (in density-temperature) separating a "gas" of excitons, electrons, and holes from the high-density "metallic-liquid" phase and a coexistence region (characterized by droplets of EHL). The most detailed experimental studies have been made for Ge. Thomas *et al.*[6] have recently measured the entire phase diagram for Ge, especially the region near the critical temperature, T_c. Their results are given in Fig. 1.

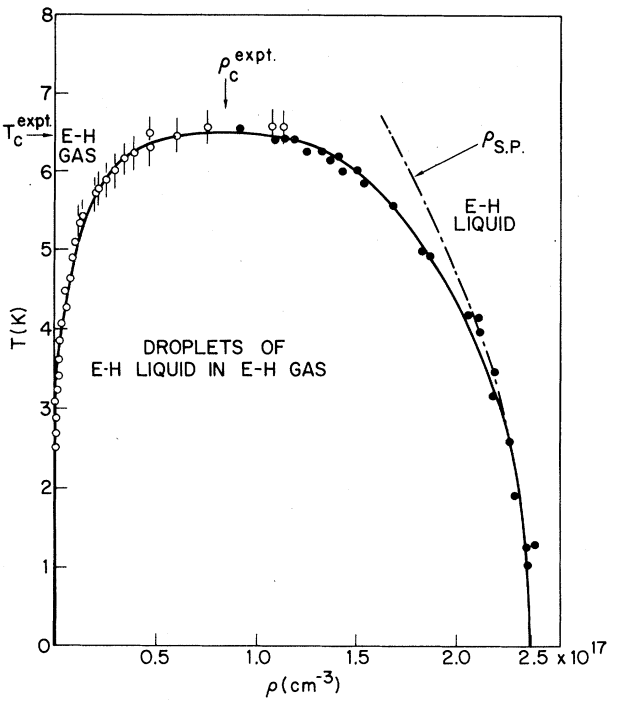

FIG. 1. Phase diagram in temperature and density of electrons and holes in Ge. The experimental points are from Ref. 6; the solid curve is obtained from the droplet model using parameters given in text; $\rho_{s.p.}$ gives the temperature dependence of the liquid density due to single-particle excitations, and is obtained from the experimental results.

In this Letter we present a model of the condensation based on a picture of EHL droplet fluctuations in the gas and use it to give the first detailed account of the experimental measurements of the phase diagram for Ge for $T \gtrsim \frac{1}{2}T_c$. It relates the shape of the phase diagram in this region to the surface properties of the liquid, and an estimate of the droplet surface tension is obtained from the data. Using theoretical parameters, it gives a complete phase curve for Si for which detailed measurements have not been made.

The shape of both sides of the phase diagram is reasonably well understood for $T \lesssim \frac{1}{2}T_c$, but less well understood for higher T (which spans two decades in density for Ge). With reference to the case for Ge, on the gas side for $T \lesssim 4$ K ($\rho_{G,\mathrm{coex}} < 2\times 10^{15}$ cm^{-3}), the exponential dependence of density on T is understood by thermal equilibrium between a low-density, classical gas and the liquid phase.[2] On the liquid side for $T \lesssim 4$ K, the T^2 dependence of density [$\rho_{L,\mathrm{coex}} = (2.1-2.4)\times 10^{17}$ cm^{-3}] can be understood with a simple picture of a noninteracting degenerate Fermi system.[3] For $T \gtrsim 4$ K these simple descriptions fail as can be seen in the flattening of the top of the phase diagram.

Previous attempts to treat the higher-T region include (i) the exact solution of a model with only Hartree-Fock interactions between particles,[7] and (ii) treating the system in the immediate vicinity of T_c as a dense plasma.[5,8] The interactions in this system are significantly more complex than those in the first approach. The second approach is useful in estimating T_c, but it cannot be used to describe *either* the liquid or gas curve away from T_c (for $T \gtrsim \frac{1}{2}T_c$) because to do so requires a knowledge of the chemical potential as a function of density in *both* phases and the use of a Maxwell construction between them; the plasma model does not adequately describe the chemical potential in the low-density part of this region (see Rice[9]).

To describe the liquid-gas phase diagram, we propose a simple, physically clear model which is an extension of a droplet fluctuation model discussed by Fisher[10] and others in the theory of phase transitions. Following his approach, we write the density of the gas phase as a sum of noninteracting droplet fluctuations of EHL at constant chemical potential μ and T:

$$\rho_G = q_0 \sum_{n=1}^{\infty} \exp\{-[F_B n + F_S a n^{\sigma} + k_B T \tau \ln(n) - \mu n]/k_B T\} . \tag{1}$$

Here the free energy of a droplet of n electron-hole pairs is separated into a bulk term $F_B n$, a surface term $F_S a n^{\sigma}$, where $a n^{\sigma}$ is the droplet surface area, and a higher-order term in $\ln(n)$; q_0 is an overall proportionality constant.

In this model the gas phase contains dropletlike fluctuations of liquid, and condensation is indicated by the onset of a stable liquid phase (see Ref. 10). For $\mu > F_B$ the probability of very large droplet fluctuations diverges, and for $\mu < F_B$ it does not; thus $\mu(T) = F_B$ gives the condensation point at a given T. Further, the number and size of the fluctuations is controlled by the surface tension of the liquid droplets $F_S(T)$. As T approaches T_c, $F_S(T)$ decreases, and fluctuations increase. Finally at a temperature for which $F_S(T)$ vanishes, stable droplet formation is no longer possible; thus the condition $F_S(T = T_c) = 0$ determines T_c.

In a manner similar to (1), we describe the liquid phase as dense EHL containing noninteracting bubble fluctuations. On the coexistence curve ($\mu = F_B$), the liquid density is written

$$\rho_{L,\mathrm{coex}} = \rho_{\mathrm{s.p.}}(T) - q_0 \sum_{n=1}^{\infty} \exp\{-[F_S a n^{\sigma} + k_B T \tau \ln(n)]/k_B T\} . \tag{2}$$

Here $\rho_{\mathrm{s.p.}}(T)$ gives the density variation of the electron-hole Fermi system due to single-particle excitations, and the second term gives the variation due to bubbles.

Complete symmetry between droplet and bubble fluctuations has been assumed. It then follows from (1) and (2) that

$$\rho_{G,\mathrm{coex}}(T) + \rho_{L,\mathrm{coex}}(T) = \rho_{\mathrm{s.p.}}(T) , \tag{3a}$$

$$\rho_c = \tfrac{1}{2}\rho_{\mathrm{s.p.}}(T_c) . \tag{3b}$$

Equations (1) and (2) give the liquid-gas phase diagram in terms of $\rho_{\mathrm{s.p.}}(T)$ and $F_S(T)$ which are properties of the liquid alone. For $T \lesssim T_c$, the liquid is a degenerate Fermi system ($T \ll T_F$; T_F equals 45 K for holes and 29 K for electrons in Ge), and its properties can be expanded as[11]

$$\rho_{\mathrm{s.p.}}(T) \cong \rho(0)(1 - \delta_\rho T^2) , \tag{4a}$$

$$F_S(T) \cong F_S(0)(1 - \delta_F T^2) . \tag{4b}$$

First we consider the phase diagram for Ge using theoretical values of $\rho_{s.p.}(T)$ and $F_S(T)$. $\rho(0)$ and δ_ρ have been calculated by several groups,[3-5] and their results are in good agreement with measurements of the low-T liquid side of the phase diagram where bubble fluctuations are negligible. The present authors have developed a method for calculating $F_S(T)$ based on the energy-density functional method.[12] For Ge we obtain[13]

$$F_S(T) = [(2.70\ \mathrm{K})/a_B^2][1 - (T/5.0)^2]\ . \qquad (5)$$

This yields $T_c = 5$ K. Using this T_c in (3b) with the theoretical values $\rho(0) = 2.2\times10^{17}$ cm^{-3} and $\delta_\rho = 0.0092$ K^{-2} from Ref. 5 gives $\rho_c = 0.845\times10^{17}$ cm^{-3}. These values of ρ_c and T_c compare favorably with the measurements of Thomas *et al.*[6] who give $\rho_c = (0.8\pm0.2)\times10^{17}$ cm^{-3} and $T_c = 6.5$ K. We note further that this theoretical $\rho_{s.p.}(T)$ satisfies (3b) for the sum $\rho_{G,\mathrm{coex}}(T) + \rho_{L,\mathrm{coex}}(T)$ from experiment (Fig. 1) to within 5% over the whole phase diagram.

The shape of the phase diagram is now discussed. For $T \lesssim \frac{1}{2}T_c$, (1) and (2) reduce to the simpler descriptions discussed above, so we will be concerned primarily with $T \gtrsim \frac{1}{2}T_c$. To make the most direct comparison with experiment, $\rho(0)$ and δ_ρ are chosen from the experimental $\rho_{L,\mathrm{coex}}$ for $T \ll T_c$ ($\rho_{s.p.}$ in Fig. 1): $\rho(0) = 2.38\times10^{17}$ cm^{-3}, $\delta_\rho = 0.0072$ K^{-2}. Also, the experimental value[6] $T_c(=\delta_F^{1/2}) = 6.5$ K is chosen. From geometry, $a = 4\pi[3/4\pi\rho(0)]^{2/3} = 4.5a_B^2$, $\sigma = \frac{2}{3}$ (for spherical droplets), and $\tau = 2.2$[14]; then $q_0 = \rho_c/\zeta(\tau)$, with ζ the Riemann zeta function. Then only $F_S(0)$ is unspecified; the solid curve in Fig. 1 is obtained by choosing $F_S(0) = (2.4\ \mathrm{K})/a_B^2$ to give a good overall fit. The agreement with experiment is very good on both sides. This value of $F_S(0)$ (1.0×10^{-4} erg/cm^2) provides an experimental estimate of droplet surface energy; it falls within the range of theoretical estimates[15] [(1.9–4.2 K)/a_B^2] and is in reasonably good agreement with experimental estimates, (3.9 K)/a_B^2[16] and (2.9 K)/a_B^2[17] from supersaturation measurements.

The interpretation of $F_S(0)$ as the surface energy should be taken somewhat cautiously. Except quite close to T_c, (1) and (2) are dominated by relatively small droplets (bubbles). For example, for $T = 5.5$ and 6.4 K, $n > 15$ and $n > 35$, respectively, contribute $\lesssim 15\%$ of the sums. For small droplets the separation of the free energy into surface and bulk terms is somewhat arbitrary. A more accurate value of the surface energy could be obtained by fitting within a few tenths of a degree of T_c, but experimental results there are not yet sufficiently accurate. Nonetheless the good overall fit to experiment (Fig. 1) indicates that this $F_S(0)$ provides a useful experimental estimate of the surface energy. It should be carefully noted that the droplets in (1) and (2) are fluctuations and are not the much larger equilibrium liquid-phase drops seen in the two-phase region.

The sums in (1) and (2) include only neutral fluctuations. Charged fluctuations (with unequal numbers of electrons and holes) also make a contribution, but it is small (less than 12% of the sums up to 0.1 K of T_c) because of their electrostatic self-energy. Charged fluctuations have been included by modifying (1) and (2) to account for the droplet electrostatic self-energy[18]; the best fit to experiment is then obtained by choosing $F_S(0) = (2.5\ \mathrm{K})/a_B^2$. This fit is slightly better than that in Fig. 1 by up to 5%.

We have described the gas phase of the system as a gas of electrons and holes plus droplet fluctuations of dense EHL. At very low density and temperature, however, the gas consists primarily of bound excitons plus droplet fluctuations. Estimates of the density at which this transformation of electron-hole gas to excitons occurs suggest that it is below $T = 4$ K on the condensation curve[4,6,9]; therefore, the description of the gas phase used here is considered appropriate for the higher-temperature region which we have treated.

No detailed measurements of the phase diagram are presently available for Si. Calculations of $\rho_{s.p.}(T)$ at low T give $\rho_{s.p.}(T) = 3.20\times10^{18}(1 - 0.000\,74T^2)$ cm^{-3}.[5] We have performed a calculation of $F_S(T)$ for Si similar to that for Ge yielding $F_S(T) = (5.20\ \mathrm{K})(1 - 0.002\,14T^2)/a_B^2$. Using the droplet model, these values give $T_c = 21.6$ K and $\rho_c = 1.04\times10^{18}$ cm^{-3} which are in good agreement with theoretical estimates based on quite different models.[5,8] The phase diagram with these parameters is given in Fig. 2. Detailed measurements of the phase diagram for Si would be very interesting.

The droplet model provides an alternative to the plasma approach[5,8] as a method of obtaining the critical parameters ρ_c and T_c from first-principles calculations. These approaches employ two different approximate treatments of the system at its critical point: In the plasma approach,[5,8] the chemical potential of the system is calculated neglecting density fluctuations (by using an entropy appropriate to a noninteracting

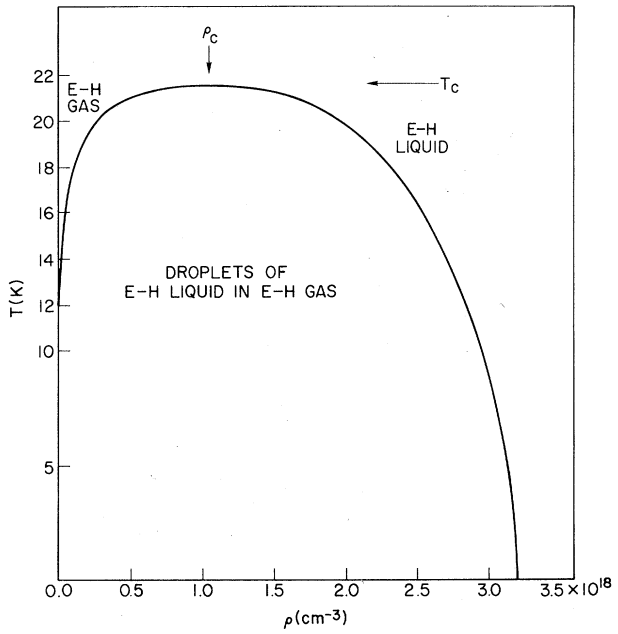

FIG. 2. Droplet-model phase diagram for Si using theoretical parameters.

system); in the droplet model, on the other hand, the fluctuations are included in an approximate way. The nature of the approximations involved in the two cases is different, and the accuracy of each approach is difficult to estimate; thus it does not appear that one can distinguish *a priori* which approach provides the best method to calculate ρ_c and T_c. It should be emphasized, however, that the droplet model provides a unified treatment of the entire phase curve, which is not done by the plasma approach.

In summary, the droplet model of EHL condensation proposed here provides a simple, physically clear picture of the condensation. It relates the shape of the phase diagram to the surface properties of the liquid, and it provides the first detailed description of the phase curve for $T \gtrsim \frac{1}{2}T_c$, which is in good agreement with measurements for Ge. By using theoretical parameters, the phase diagram for Si, which has not yet been measured in detail, has been constructed.

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†National Academy of Sciences–Naval Research Laboratory Resident Research Associate.

‡Permanent address: Department of Physics, Brown University, Providence, R. I. 02912.

§A. P. Sloan Foundation Research Fellow. Work supported in part by the National Science Foundation.

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[11]Combescot (Ref. 8) and Vashishta *et al.* (Ref. 5) have successfully employed an expansion of the density to order T^2 in treating the degenerate Fermi liquid for temperatures up to T_c. Further, Combescot points out that the inclusion of a T^4 term has little effect even at $T=T_c$. The surface tension $F_s(T)$ involves a density distribution about 80% of which is degenerate; using an interpolation procedure, we have also put the small contribution from the remainder in the form (4b). See, T. L. Reinecke, F. Crowne, and S. C. Ying, in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974*, edited by M. H. Pilkuhn (B. G. Teubner, Stuttgart, Germany, 1974), p. 61; T. L. Reinecke and S. C. Ying, to be published.

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[18]We neglect the interaction between charged droplets. This is believed to be small (except possibly very near T_c) because the charge screening length is less than the average interparticle spacing over the entire phase curve.

COMMENTS

Equivalence of a One-Dimensional Fermion Model and the Two-Dimensional Coulomb Gas

S.-T. Chui and P. A. Lee
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 9 January 1975)

We show that the one-dimensional Luttinger model generalized to include spin and backward scattering is equivalent to a two-dimensional Coulomb gas. Scaling equations are derived and correlation functions are given simple physical interpretation in terms of the Coulomb gas; e.g., existence of an energy gap can be understood in terms of Debye screening. We conclude that an energy gap exists for $U_{\parallel} < |U_{\perp}|$ so that triplet excitations are nondivergent, and we provide physical arguments to support the exponents proposed by Luther and Emery for singlet excitations for general coupling constant.

There has been considerable recent interest in an extension of the Luttinger model[1] to include spin as well as scattering from $+k_F$ to $-k_F$. The Hamiltonian is written as $H = H_S + H_L$, where H_S is the usual Luttinger-model Hamiltonian

$$H_S = v_F \sum_{k,s} k(a_{k,s}^{\dagger} a_{k,s} - b_{k,s}^{\dagger} b_{k,s}) + 2L^{-1} \sum_{k} V \rho_1(k) \rho_2(-k), \tag{1}$$

with $a_{k,s}$ ($b_{k,s}$) describing spin-$\frac{1}{2}$ fermions with momentum k ($-k$), and $\rho_1(k)$ and $\rho_2(k)$ density operators,

$$\rho_1(k) = 2^{-1/2} \sum_{p,s} a_{p+k,s}^{\dagger} a_{p,s}, \quad \rho_2(k) = 2^{-1/2} \sum_{p,s} b_{p+k,s}^{\dagger} b_{p,s}.$$

The large-momentum-transfer terms are described by

$$H_L = \sum_{s,s'} \int dx \, \Psi_{1,s}^{\dagger}(x) \Psi_{2,s'}^{\dagger}(x) \Psi_{1,s'}(x) \Psi_{2,s}(x) (U_{\parallel} \delta_{s,s'} + U_{\perp} \delta_{s,-s}), \tag{2}$$

where $\Psi_{1s}(x) = L^{-1/2} \sum_k \exp(ikx) a_{k,s}$ and $\Psi_{2s}(x) = L^{-1/2} \sum_k \exp(ikx) b_{k,s}$. Luther and Emery[2] (LE) have pointed out the similarity of this problem to the Kondo problem and have produced an exact solution of this model for a particular coupling constant $U_{\parallel}(2\pi v_F)^{-1} = -\frac{3}{5}$. They found an energy gap in the spin degrees of freedom and calculated exponents for the charge-density-wave response χ_S and singlet pairing response P_S. Their result on the spin-density-wave response χ_T and triplet pairing response P_T was found to be in error by one of us[3] who concluded that these triplet excitations are in fact nondivergent. This result is consistent with an exponentially activated uniform magnetic susceptibility χ_0. LE also argued on the basis of scaling that the gap exists for all $U_{\parallel} < 0$ and suggested exponents for arbitrary coupling constants. In this work we further exploit the similarity to the Kondo problem and show for general $U_{\perp}$ and $U_{\parallel}$ that the interacting-fermion problem at $T = 0$ is equivalent to a two-dimensional Coulomb gas at finite temperature. This problem has been studied in connection with the theory of melting in two dimensions[4] as well as the two-dimensional X-Y model.[5] On the basis of this equiv-