

## Electron-hole droplet condensation in semiconductors: CdS

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A noninteracting droplet fluctuation model for electron-hole droplet condensation in semiconductors is applied to describe the condensation phase diagram for CdS. Good agreement with recent experimental measurements is obtained by fitting the temperature dependence of the liquid side of the diagram. The model then also gives the gas side of the phase diagram, the critical density, and an estimate of a surface tension parameter.

### I. INTRODUCTION

The condensation of electron-hole droplets (EHD) from a high density of carriers at low temperatures in the elemental indirect-gap semiconductors Ge and Si has received much study recently both experimentally and theoretically.<sup>1</sup> Very recently experimental evidence has been obtained for droplet condensation in compound semiconductors including II-VI systems (CdS,<sup>2-4</sup> and<sup>3</sup> CdSe) and III-V systems (GaP,<sup>5</sup> and<sup>6</sup> GaAs). Droplet condensation in the compound semiconductors can differ in important ways from that in the Ge and Si because (i) the interactions between carriers can be influenced significantly by the carrier-phonon interaction<sup>7</sup> (especially so in the II-VI systems) and (ii) for direct-gap materials (e.g., CdS) the electron-hole recombination lifetime is several orders

of magnitude smaller than for indirect-gap materials.

The most complete experimental study of EHD condensation in a compound semiconductor has been made for CdS. Leheny and Shah<sup>4</sup> have measured the temperature dependence of the liquid side of the condensation phase diagram for densities down to nearly the critical density  $\rho_c$  (see Fig. 1), and they have obtained an estimate of the critical temperature  $T_c$ . The phase diagram gives a particularly full picture of the condensation; it is the boundary separating a region of dense electron-hole liquid (EHL) from a region consisting of a "gas" of free carriers and/or excitons and from a coexistence region of these two phases which is characterized by EHD.

In the following a noninteracting droplet fluctuation model for EHD condensation in semiconductors is applied to describe the condensation phase diagram for CdS. Good agreement is obtained by fitting measurements of the temperature dependence of the liquid side of the phase diagram. The model then gives the gas side of the phase diagram, the critical density, and an estimate of a surface tension parameter.

In Sec. II the necessary results from the droplet fluctuation model of EHD condensation are written down. In Sec. III the phase diagram for CdS is given and discussed. In the Appendix the region of temperature for which the finite electron-hole lifetime is expected to affect the shape of the phase diagram in CdS is discussed.

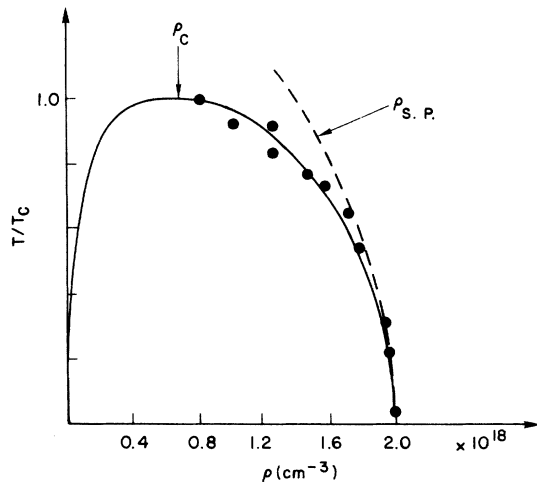


FIG. 1. Phase diagram for electron-hole droplet condensation in CdS. The circles are the experimental measurements from Ref. 4. The solid curve is the result of the model discussed in the text, and  $\rho_{s.p.}$  gives the temperature dependence of the liquid due to single-particle excitations.

### II. DROPLET FLUCTUATION MODEL FOR EHD CONDENSATION

The droplet fluctuation model for EHD condensation was developed by Reinecke and Ying<sup>8,9</sup> who applied it to Ge and Si in the region  $T \approx \frac{1}{2}T_c$ , a region which cannot be described by simpler approaches. It gives good agreement<sup>8</sup> with measurements<sup>10</sup> of the entire phase diagram for Ge. It is a simple, physically clear model which is a generalization of a

model discussed earlier by Fisher<sup>11</sup> and others for the classical liquid-gas transition.

In this model the gas phase is pictured as composed of noninteracting droplet fluctuations of EHL at constant chemical potential  $\mu$  and  $T$ . Its density is

$$\rho_G = q_0 \sum_{n=1}^{\infty} n \exp\left(-\frac{(F_B n + F_S a n^\sigma + k_B T \tau \ln n - \mu n)}{k_B T}\right). \quad (1)$$

The exponential factor gives the probability for a droplet fluctuation of  $n$  electron-hole pairs.<sup>12</sup> Here the free energy of a droplet is separated into a bulk term  $F_B n$ , a surface term  $F_S a n^\sigma$  where  $a n^\sigma$  is the surface area, and a higher-order term in  $\ln n$ ;  $q_0$  is an overall proportionality constant.

In this model the condensation point, which is indicated by the onset of a stable liquid phase, is given by the condition  $\mu(T) = F_B(T)$ ; this is seen from Eq. (1) by noting that for  $\mu > F_B$  the probability of very large droplets diverges and for  $\mu < F_B$ , it does not. In addition, as  $T$  approaches  $T_c$ , the surface tension  $F_S(T)$  decreases and fluctuations increase. At a temperature for which  $F_S(T)$  vanishes, stable droplet formation is not possible, and therefore  $F_S(T = T_c) = 0$  determines  $T_c$ .

In a similar manner the liquid phase is pictured as dense (temperature-dependent) EHL containing noninteracting "bubble" fluctuations of the "gas" phase. On the coexistence curve ( $\mu = F_B$ ), the liquid density is

$$\rho_{L, \text{coex}} = \rho_{\text{SP}}(T) - q_0 \sum_{n=1}^{\infty} n \exp\left(-\frac{(F_S a n^\sigma + k_B T \tau \ln n)}{k_B T}\right). \quad (2)$$

Here  $\rho_{\text{SP}}(T)$  gives the density variation of the electron and hole Fermi systems 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 which implies that the critical density is given by

$$\rho_c = \frac{1}{2} \rho_{\text{SP}}(T_c). \quad (3)$$

Equations (1) and (2) give the entire phase diagram in terms of  $\rho_{\text{SP}}(T)$  and  $F_S(T)$ , which are properties of the dense, homogeneous EHL alone. If  $T_c \ll T_{Fe}, T_{Fh}$ , the Fermi temperatures of the electrons and holes, then the EHL remains degenerate for temperatures of interest, and its properties can be expanded as

$$\rho_{\text{SP}}(T) \cong \rho(0) [1 - \delta_\rho T^2], \quad (4a)$$

$$F_S(T) \cong F_S(0) [1 - \delta_F T^2]. \quad (4b)$$

### III. PHASE DIAGRAM FOR EHD CONDENSATION IN CdS

The droplet fluctuation model of EHD condensation is now applied to describe the condensation phase diagram in CdS for  $T \geq \frac{1}{2} T_c$ . For CdS  $T_{Fe}, T_{Fh} \geq T_c$  ( $T_{Fe} \cong 327$  K,  $T_{Fh} \cong 50$  K), and therefore  $\rho_{\text{SP}}(T)$  and  $F_S(T)$  can be expanded as in Eq. (4). In order to make the most direct comparison with the available experimental results  $\rho(0)$ ,  $\delta_\rho$ , and  $\delta_F$  are chosen from the measurements of Leheny and Shah,<sup>4</sup> which are shown in Fig. 1.  $\rho(0)$  and  $\delta_\rho$  are estimated from the experimental  $\rho_{L, \text{coex}}$  for  $T \ll T_c$  to be  $\rho(0) = 2 \times 10^{18}$  cm<sup>-3</sup> and  $\delta_\rho = 0.00010$  K<sup>-2</sup>. Also the experimental value of  $T_c = (\delta_F^{-1/2}) = 55$  K is chosen. Then from Eq. (3) we obtain  $\rho_c = 0.70 \times 10^{18}$  cm<sup>-3</sup> as shown in Fig. 1. For spherical droplets  $\sigma = \frac{2}{3}$ , and

$$a(T) = 4\pi \{3/[4\pi\rho(0)]\}^{2/3} [1 + \frac{2}{3} \delta_\rho T^2].$$

$q_0 = \rho_c / \zeta(\tau - 1)$  where  $\zeta$  is the Riemann  $\zeta$  function, and  $\tau = 2.2$  is chosen.<sup>13</sup> Then only  $F_S(0)$  remains unspecified; the solid curve in Fig. 1 is obtained from Eqs. (1) and (2) using the above parameters and taking  $F_S(0) = 20 \times 10^{-4}$  erg/cm<sup>2</sup> to give the best fit to the measured temperature dependence of the liquid side of the phase diagram. Changes of about 30% in  $F_S(0)$  give noticeably poorer fits to experiment, and thus this variation is roughly the accuracy to which  $F_S(0)$  can be obtained from the present data.

The parameter  $F_S(0)$  plays the role of a surface energy in the present model, and the value for  $F_S(0)$  obtained above is the first experimental estimate of the EHD surface energy in a compound semiconductor. The interpretation of  $F_S(0)$  as a surface energy should be taken somewhat cautiously, however, because, except for  $T$  quite close to  $T_c$ , the sums in Eqs. (1) and (2) are dominated by relatively small droplets. For example, for  $T = 46$  and  $52$  K,  $n > 15$  and  $n > 40$ , respectively, contribute  $\sim 10\%$  of the sums. For such small drops the separation of the free energy into a bulk and a surface term is somewhat arbitrary. A more accurate value of the surface energy can be obtained by fitting the phase diagram within  $\sim 1$  K of  $T_c$ , but adequate experimental data is not presently available there. An alternative way to assess the accuracy of the present value of  $F_S(0)$  as the surface energy is to note that the corresponding value of  $F_S(0)$  obtained by fitting detailed measurements of the phase diagram for EHD condensation in Ge is  $1.0 \times 10^{-4}$  erg/cm<sup>2</sup>,<sup>8</sup> whereas later values of the surface energy from nucleation measurements<sup>14</sup> and from theoretical calculations<sup>15</sup> are about 2.5 times larger.

The fact that the value of  $F_S(0)$  obtained here for EHD in CdS is considerably larger than that in Ge is

consistent with what is expected on simple dimensional considerations. Dimensionally the surface energy is expected to scale as  $F_B(0)\rho(0)^{2/3}$  where  $F_B(0)$  is the condensation energy per pair. Using recent values of  $F_B(0)$  and  $\rho(0)$  for Ge,<sup>16</sup> and CdS,<sup>4</sup> this scaling implies that the surface energy of EHD in CdS should be  $\approx 25\frac{1}{2}$  times that in Ge. This is quantitatively consistent (within the experimental uncertainty) with the ratio of 20 for the values of  $F_S(0)$  obtained from fitting the phase diagrams for CdS and Ge.

Finally, consider the region of the EHD phase diagram for CdS in which the finite value ( $\sim 10^{-9}$  sec) of the electron-hole recombination time  $\tau_0$  may have significant effects on the shape of the phase diagram. Physically, at sufficiently low temperatures the value of  $\tau_0$  in the droplet becomes appreciable compared to the rates at which carriers are collected at or emitted from the droplets, and this results in a somewhat larger gas density required for condensation than that corresponding to  $\tau_0$  infinite. A model which treats the time dependences of these processes for  $T \ll T_c$  (Ref. 17) has been developed,<sup>14,18</sup> and in the Appendix results of this model and the best available estimates of the appropriate parameters are used to suggest that for CdS the finite value of  $\tau_0$  will probably not have significant effects on the phase diagram for  $T \gtrsim \frac{1}{2}T_c$ , which is the region that has been treated here with the droplet fluctuation model.

#### IV. CONCLUDING REMARKS

A noninteracting droplet fluctuation model has been applied to electron-hole droplet condensation in a compound semiconductor CdS. Good agreement is obtained by fitting the liquid side of the phase diagram, and the model then gives the gas-side of the diagram, the critical density, and an estimate of a surface tension parameter. Further measurements of the entire phase diagram and independent measurements of and calculations of the surface tension in CdS and other compound semiconductors would be very interesting.

#### APPENDIX

A rough estimate of the temperature below which the finite electron-hole recombination time  $\tau_0$  in CdS may have a significant effect on the EHD condensation phase curve is now given. In the case of Ge ( $T_c = 6.5$  K) significant deviations were obtained only for  $T \lesssim 2$  K.<sup>14,18</sup>

The difference between the phase curve for finite  $\tau_0$  and that for infinite  $\tau_0$  depends on  $\Delta\mu/k_B T$  (evaluated on the phase curve), where  $\Delta\mu$  is the difference between the chemical potential of the gas and that of the EHD for  $\tau_0$  infinite. We can thus make a

convenient estimate of the temperature below which deviations in the phase curve for CdS are expected by comparing the value of this ratio for CdS with that for Ge for which explicit numerical evaluations of the phase curve have been made based on a model which treats evaporation, collection, and recombination as random processes.<sup>14,18</sup> Silver<sup>18</sup> gives for a lower bound to this difference in chemical potentials<sup>19</sup> (evaluated on the gas side of the phase curve)

$$\frac{\mu_G - \mu_I}{k_B T} \geq \ln \left[ 1 + \left( \frac{2S}{3AT^3\tau_0 k_B} \right)^{1/2} e^{\phi/2k_B T} \right]. \quad (\text{A1})$$

Here  $S$  is the surface energy,  $A$  is the coefficient in the Richardson-Dushman expression for exciton evaporation from the droplet surface, and  $\phi$  is the bulk condensation energy [ $\equiv F_B(0)$  above]. As  $T$  decreases,  $\mu_G$  becomes increasingly greater than  $\mu_I$ .

Evaluating Eq. (A1) for Ge at the temperature ( $= 2$  K) above which appreciable deviations from the infinite  $\tau_0$  curve are not seen gives  $[(\mu_G - \mu_I)/k_B T]_{T=2K} = 0.55$ .<sup>20</sup> Then using the best estimates of the parameters available for CdS,<sup>21</sup> we find that the temperature at which  $(\mu_G - \mu_I)/k_B T$  has most nearly the same value ( $= 0.56$ ) to be  $T = 27$  K. This value is smaller for larger temperature and larger for smaller temperature. This suggests that significant deviations from the infinite  $\tau_0$  phase curve due to finite  $\tau_0$  are not expected in CdS for temperatures  $T \gtrsim \frac{1}{2}T_c$ , which is the region to which the droplet fluctuation model has been applied in the text.

The above evaluations of the difference  $\mu_G - \mu_I$  employ parameters which are not yet known well, especially for CdS. Its value depends strongly on  $\phi$  which is relatively well known, and it is far less sensitive to  $S$ ,  $A$ , and  $\tau_0$ , which are less well known. For example, in the case of CdS, if the value of the quantity  $S/A\tau_0$  were changed by a factor of 10, the resulting change in the value of  $T$  for which  $(\mu_G - \mu_I)/k_B T$  equals a fixed number (e.g., 0.55 above) is  $\lesssim 10$  K.

For Ge the parameters  $S$  and  $\tau_0$  are known quite well,<sup>14,15,22</sup> and for the present purposes  $A$  has been estimated from the decay kinetics study of Westervelt *et al.*<sup>22</sup> For CdS an estimate of  $\tau_0$  is given by Leheny and Shah,<sup>4</sup> and an estimate of  $S[\approx 2.5F_S(0)]$  is made from the results of fitting the phase curve as discussed above (this nearly equivalent to estimating  $S$  by dimensional scaling of the results for Ge—see Sec. III above). To the author's knowledge there is no experimental value of  $A$  for CdS, so we have made an estimate of it from the experimental value for Ge by appropriately changing the excitonic mass and degeneracy.

While there is some uncertainty in the parameters used above we believe that they are sufficiently accurate to support the suggestion that the phase diagram for CdS in the region  $T \geq \frac{1}{2}T_c$  is not expected to differ significantly from that for in-

finite  $\tau_0$ . More accurate experimental values for these parameters will provide a more accurate estimate of the size of the region in which finite  $\tau_0$  effects are important and of the magnitude of these effects.

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- <sup>1</sup>For reviews, see, Ya. Pokrovskii, *Phys. Status Solidi A* **11**, 385 (1972); C. D. Jeffries, *Science* **189**, 955 (1975); J. C. Hensel, T. G. Phillips, and G. A. Thomas, *Solid State Physics*, ed. F. Seitz, D. Turnbull, and H. Ehrenreich (to be published); T. M. Rice, *ibid.*
- <sup>2</sup>V. G. Lysenko, V. I. Revenko, T. G. Tratas and V. B. Timofeev, *Zh. Eksp. Teor. Fiz.* **68**, 335 (1975) [*Sov. Phys.-JETP* **41**, 163 (1975)].
- <sup>3</sup>R. F. Leheny and Jagdeep Shah, *Phys. Rev. Lett.* **37**, 871 (1976).
- <sup>4</sup>R. F. Leheny and Jagdeep Shah, *Phys. Rev. Lett.* **38**, 511 (1977).
- <sup>5</sup>Jagdeep Shah and R. F. Leheny, *Bull. Am. Phys. Soc.* **22**, 350 (1977).
- <sup>6</sup>O. Hildebrand and E. Göbel, in *Proceedings of the XIII International Conference on the Physics of Semiconductors, Rome, 1976*, edited by F. G. Fumi (Tipografia Marves, Rome, 1977), p. 942.
- <sup>7</sup>G. Beni and T. M. Rice, *Phys. Rev. Lett.* **37**, 874 (1976).
- <sup>8</sup>T. L. Reinecke and S. C. Ying, *Phys. Rev. Lett.* **35**, 311 (1975); **35**, 547(E) (1975).
- <sup>9</sup>T. L. Reinecke and S. C. Ying, *Phys. Rev. B* **13**, 1850 (1976).
- <sup>10</sup>G. A. Thomas, T. M. Rice, and J. C. Hensel, *Phys. Rev. Lett.* **31**, 386 (1973).
- <sup>11</sup>M. E. Fisher, *Physics (L. I. City N.Y.)* **3**, 255 (1967).
- <sup>12</sup>Charged droplet fluctuations (with unequal numbers of electrons and holes) make a small contribution (<10% up to 1 K of  $T_c$ ) to the sums in Eqs. (1) and (2) because of their electrostatic self-energy; see also Ref. 8.
- <sup>13</sup>See Refs. 8 and 11.
- <sup>14</sup>R. M. Westervelt, *Phys. Status Solidi B* **74**, 727 (1976); **76**, 31 (1976).
- <sup>15</sup>J. H. Rose and H. B. Shore (unpublished); see also P. Vashishta, R. K. Kalia, and K. S. Singwi, *Solid State Commun.* **19**, 935 (1976).
- <sup>16</sup>T. K. Lo, *Solid State Commun.* **15**, 1231 (1974).
- <sup>17</sup>Specifically for temperatures sufficiently low that the temperature dependence of the parameters can be ignored.
- <sup>18</sup>R. N. Silver, *Phys. Rev. B* **11**, 1569 (1975); **12**, 5689 (1975).
- <sup>19</sup>Note that an error in the power of  $T$  in Eq. (38) of Ref. 18 has been corrected here.<sup>†</sup>
- <sup>20</sup>The estimates of the values of the parameters used for Ge are  $S = 3 \times 10^{-4}$  ergs/cm<sup>2</sup> (Refs. 14 and 15),  $A = 8.2 \times 10^{20}$  sec<sup>-1</sup> cm<sup>-2</sup> K<sup>-2</sup> (see text and Ref. 21),  $\phi = 23$  K (Ref. 16), and  $\tau_0 = 40 \times 10^{-6}$  sec (Ref. 21); see also discussion in text.
- <sup>21</sup>R. M. Westervelt, T. K. Lo, J. L. Staehli, and C. D. Jeffries, *Phys. Rev. Lett.* **32**, 1051 (1974); **32**, 1331(E) (1974).
- <sup>22</sup>The estimates of the parameters used for CdS are  $S = 50 \times 10^{-4}$  ergs/cm<sup>2</sup> (see text),  $A = 5.9 \times 10^{20}$  sec<sup>-1</sup> cm<sup>-2</sup> K<sup>-2</sup> (see text),  $\phi = 13$  meV (Ref. 4), and  $\tau_0 = 10^{-9}$  sec (Ref. 4); see also discussion in text.