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Van der Waals Interactions and Exciton Condensation

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ABSTRACT **It is shown that the van der Waals interaction can lead at low temperatures to a condensed state of excitons with properties in qualitative agreement with the observations of exciton droplets. Our calculation gives a binding energy of the correct sign and magnitude for the exciton condensate. In a dielectric medium, the strong enhancement of the exciton polarizability leads to a giant van der Waals interaction, and this interaction appears to make possible a condensed exciton phase.**

The interaction between excitons in semiconductors has received considerable interest since new lines were observed in the spectrum of recombination radiation of germanium and silicon below 10°K. Radiation peaks slightly below the energy of annihilation of a free exciton were first considered as evidence of the formation of biexcitons (1–4, 8), but recent experiments of great beauty make it clear that we have an electron–hole condensate (5–7, 8). Elegant studies of electrical fluctuations (9, 10) in p–n junctions at the temperature of liquid helium strongly suggest the presence of exciton droplets, with 10^7–10^{10} excitons in a droplet. The light-scattering experiments of Pokrovskii and Svistunova (11) give good determinations of the droplet size.

Biexcitons or excitonic molecules were predicted by Lampert (12), in analogy to the polyelectrons of electrons and positrons proposed by Wheeler (13). Sharma (14) calculated a binding energy with respect to separated excitons of 0.63 meV for biexcitons in silicon and approximately 0.04 meV in germanium. The condensate proposed first by Keldysh (15) is rather different; this metallized state is a degenerate electron–hole plasma with concentrations (6) of each particle type of approximately 3×10^{17} cm^{-3} in Ge and 3×10^{18} cm^{-3} in Si.

In this communication, we show that the van der Waals interaction between excitons, if properly taken into account, can lead to liquid droplets of excitons. Our simple model of exciton condensation yields condensation temperatures and and concentrations of the order of the experimental values. The model also allows estimates of the binding energy, nucleation processes, and the shifts of binding energy at high concentrations of impurities. We phrase the discussion in terms of interactions between excitons, but the general argument will apply also to a fluid of biexcitons. We do not treat here the conditions under which the ground-state model of Keldysh will apply; it may be possible under different conditions of stress and concentration to change from the metallized to the van der Waals state.

We follow the simple perturbation calculation of Eisenschitz and London (16)* to obtain the van der Waals interaction energy of two hydrogen atoms (or excitons) imbedded in a medium of dielectric constant ϵ separated by a distance R:

$$V(R) = -6.47\, e^2 a_0^5/\epsilon R^6;\ a_0 = \epsilon\hbar^2/\mu e^2. \qquad [1]$$

For excitons in semiconductors, ϵ will be the static, low wave-vector limit of the dielectric function $\epsilon(\omega,k)$. The Bohr radius a_0 is calculated with the reduced isotropic effective mass μ chosen to yield the experimental exciton-binding energies (4), E_0, of 2.7 meV in Ge and 15 meV in Si. We use $\mu = 0.051\ m_0$ for Ge and $0.16\ m_0$ for Si, where m_0 is the free-electron mass. The validity of Eq. [1] is restricted to $R \gg a_0$, because all overlap and exchange effects were neglected in its derivation. In the region $R < R_0$, we replace Eq. [1] by a hard-core potential, where $R_0 = 1.7\ a_0$. This choice fits the statistical average of the tabulated singlet and triplet interaction energies (17) between two hydrogen atoms in the ground state and leads to a slight underestimation of the interaction.

Thus, we obtain the exciton-pair potential $V = -C(R_0/R)^6$, with $C = 0.536\ E_0$ for $R \geq R_0$ and $V = \infty$ for $R < R_0$. We obtain the customary statistical results (18) for the semiclassical partition function for N excitons, and the corresponding free energies F, energies E, and the van der Waals equation of state:

$$F = -NkT[\ln(v-b) + 1] + \frac{3}{2}NkT\ln(2\pi\hbar^2/mKT) - Na/v; \qquad [2]$$

$$E = \frac{3}{2}NkT - N\frac{a}{v} - \left(\frac{3Nk}{2^{7/2}vQT^{1/2}}\right); \qquad [3]$$

$$p \equiv -\left(\frac{\partial F}{\partial V}\right)_T = \frac{kT}{v-b} - \frac{a}{v^2} - \left(\frac{k}{2^{5/2}v^2QT^{1/2}}\right). \qquad [4]$$

The usual first-order quantum correction applicable to the excitonic bose gas has been included in the last two equations. Here, $Q \equiv (mk/2\pi\hbar^2)^{3/2}$; $a = 2\pi R_0^3 C/3$; $b = 2\pi R_0^3/3$; and v is the volume per exciton. The quantum correction calculated in

* Another well-known expression for the van der Waals interaction involves the product of the polarizabilities of the two atoms. To retrieve the present result, notice that each polarizability scales as the fourth power of the dielectric constant of the medium: three powers from the scaling of the radius of the exciton and one further power from the weakening of the Coulomb interaction within the exciton. (It is curious, but correct, that the polarizability can thus be greater than the polarizability in a vacuum of a conducting sphere of equal radius.) The van der Waals interaction in this form involves a further ϵ^{-2} from the scaling of the energy-level separation and another ϵ^{-2} from the second order of the Coulomb interaction.

this way does not appear to be important at the critical temperature.

The van der Waals Eq. [4] allows a determination of the critical temperature, T_c, and the critical volume per exciton, v_c:

$$T_c = \frac{8}{27k}\frac{a}{b} = \frac{8C}{27k} = \frac{0.1588}{k}E_0; \quad [5]$$

$$v_c = 3b = 2\pi R_0^3 = 30.87\, a_0^3. \quad [6]$$

For germanium, these expressions give $T_c = 5.0°$ K and $n_c = v_c^{-1} = 7.1 \times 10^{15}$ cm^{-3}. For pure silicon, $T_c = 27.6°$K and $n_c = 5.19 \times 10^{17}$ cm^{-3}. The critical parameters predicted by Eqs. [5] and [6] are compatible with the experimental evidence for pure germanium and silicon.

At any temperature $T < T_c$, the equations

$$\ln(x_2 - 1) - \ln(x_1 - 1) + \gamma(2x_2^{-1} - 2x_1^{-1} - x_2^{-2} + x_1^{-2}) = 0; \quad [7]$$

$$\gamma(x_1^{-1} + x_2^{-1})(1 - x_1^{-1})(1 - x_2^{-1}) = 1, \quad [8]$$

with $\gamma \equiv a/kTb = C/kT$; $x_{1,2} \equiv v_{1,2}/b$, yield the volume of the condensed phase $v_1 < v_c$ and of the exciton vapor $v_2 > v_c$ on the phase equilibrium curve. Eq. [7] expresses the equality of the Gibbs potential in the two phases at equilibrium, and Eq. [8] is a consequence of the van der Waals equation.

Four final remarks are important: (*i*) The van der Waals equation of state is known to be imprecise in the condensed region, and a better approach is obtained by using the Dietrici equation (17) with the same parameters a and b. The results $v_c = 2b$ and $T_c = a/4bk$ are usually in better accord with experimantal values. (*ii*) Eqs. [5]–[8] are solutions of the minimum Gibbs potential that correspond to a system with constant exciton pressure and temperature. Although the actual experiments may not be stationary, the ideal case of a uniform semiconductor sample uniformly illuminated over its whole volume for a short time corresponds to the more realistic picture of an initial exciton population at constant temperature and volume. The temperature is quasiconstant because internal equilibrium is reached before cooling of the whole sample by the helium cryostat can occur (8). Constant-volume conditions with a significant proportion of condensed phase present require minimization of the free energy given by Eq. [2]. The function $F(v)$ loses its monotonous variation for $T < T_c'$, with $T_c' = a/4bk$ and $v_c' = 2b$. These conditions are more restrictive than those obtained by minimizing the Gibbs potential and they mark the transition from small condensed-phase formations around nucleation centers to large droplets of condensate that contain a significant fraction of the exciton population. This transition has been observed by Asnin *et al.* (9) as a second abrupt increase of the size of the electrical fluctuations. (*iii*) The thermal average binding energy of an exciton in the condensed phase steadily increases from zero when the temperature is lowered below T_c, with $E_b = a(v_2^{-1} - v_1^{-1})$. This explains qualitatively the shift of the condensed exciton maximum that has been observed experimentally (8). (*iiii*) The quantum corrections in Eqs. [3] and [4] illustrate the well-known tendency towards Bose condensation. An estimate of the relative magnitude of the correction term in Eq. [4] yields about 5% at the critical temperature for germanium; for silicon, the correction is much smaller. However, W. Brinkman has pointed out that the quantum correction to the excitonic solid may be much larger, so that the question of the quantum correction is an insecure point in our argument.

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1. Haynes, J. R., *Phys. Rev. Lett.*, **17**, 860 (1966).
2. Cuthbert, Y. D., *Phys. Rev. B*, **1**, 1552 (1970).
3. Benoît à la Guillaume, C., F. Salvan, and M. Voos, *Proc. Int. Conf. on Luminescence*, Newark, N.J., 1969, p. 315.
4. Hartman, A. R., and R. H. Rediker, *Proc. 10th Int. Conf. on Semiconductor Physics, Boston, Mass., 1970*, p. 202.
5. Bagaev, V. S., T. I. Galkina, and O. V. Gogolin, *Proc. 10th Int. Conf. on Semiconductor Physics, Boston, Mass., 1970*, p. 500.
6. Pokrovsky, Y., A. Kaminsky, and K. Svistunova, *Proc. 10th Int. Conf. on Semiconductor Physics, Boston, Mass., 1970*, p. 504.
7. Vavilov, V. S., V. A. Zayats, and V. N. Murzin, *Proc. 10th Int. Conf. on Semiconductor Physics, Boston, Mass., 1970*, p. 509.
8. Benoît à la Guillaume, C., F. Salvan, and M. Voos, *Proc. 10th Int. Conf. on Semiconductor Physics, Boston, Mass., 1970*, p. 516.
9. Asnin, V. M., A. A. Rogachev, and N. I. Sablina, *J. Exp. Theor. Phys. Lett.*, **11**, 99 (1970).
10. Benoît à la Guillaume, C., M. Voos, F. Salvan, L. Laurant, and A. Bonnot, *C. R. Acad. Sci. Paris, Ser. B*, **272**, 236 (1971).
11. Pokrovskii, V. E., and K. I. Svistunova, *J. Exp. Theor. Phys. Lett.*, **13**, 212 (1971).
12. Lampert, M. A., *Phys. Rev. Lett.*, **1**, 450 (1958).
13. Wheeler, J. A., *Ann. N.Y. Acad. Sci.*, **48**, 219 (1946).
14. Sharma, R. R., *Phys. Rev.*, **170**, 770 (1968).
15. Keldysh, L. V., *Proc. 9th Int. Conf. on Semiconductor Physics*, Moscow 1968, p. 1303.
16. Eisenschitz, E., and F. London, *Z. Phys.*, **60**, 491 (1930).
17. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, N.Y., 1954), pp. 1060 and 1063.
18. Mayer, J. E., and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, N.Y., 1940), chap. 12.