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VAN DER WAALS INTERACTIONS AND EXCITON CONDENSATION

P. H. Handel and C. Kittel

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Van der Waals Interactions and Exciton Condensation

P. H. Handel*† and C. Kittel**

Department of Physics, University of California

and

Inorganic Materials Research Division, Lawrence Radiation Laboratory

Berkeley, California 94720

Abstract

We show 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 by Benoît à la Guillaume and others. Our calculation is the first to give "binding energy of the correct sign and magnitude for the exciton condensate.

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The interaction between excitons in semiconductors has received considerable interest since anomalies 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 have been considered as evidence either for the formation of biexcitons,[1-4] or for the apparition of an electron-hole condensate[5-7] or for both.[8] Elegant studies of electrical fluctuations[9,10] in p-n junctions at liquid helium temperatures strongly suggest the presence of exciton droplets, with perhaps 10^7 excitons in a droplet. We might even imagine a crystalline exciton phase at lower temperatures. Blatt[11] has earlier suggested that excitons may have an Einstein condensation. Naturally, it is first necessary to have a condensation in real space.

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 Ge. The condensate proposed by Keldysh[15] is rather different; it is a degenerate electron-hole plasma with concentrations[6] of each particle type of approximately 3×10^{17} cm^{-3} in germanium and 3×10^{18} cm^{-3} in silicon.

In this communication we show that the van der Waals interaction between excitons, if taken into account properly, can lead to a condensed state in real space. Our simple model of exciton condensation yields condensation temperatures 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 might in some respects resemble metallic hydrogen.

Following the simple perturbation calculus of Eisenschitz and London[16,17] we obtain the vdW interaction energy of two hydrogen atoms (or excitons) separated by a distance R imbedded in a medium of dielectric constant ϵ:

$$V(R) = -6.47\frac{e^2 a_0^5}{\epsilon R^6} \; ; \quad a_0 \equiv \frac{\epsilon\hbar^2}{\mu e^2} \; . \tag{1}$$

For excitons in semiconductors, ϵ will be the static, low wavevector limit of the dielectric function $\epsilon(\omega,\underset{\sim}{k})$. 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[18] 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 $C \equiv 0.536\ E_0$ for $R \geq R_0$ and $V = \infty$ for $R < R_0$. We use now the

customary statistical methods[19] to obtain the semiclassical partition function for N excitons, and the corresponding free energies F, energies E, and the vdW equation of state:

$$F = -NkT[\ln(v-b) + 1] + \frac{3}{2}NkT \ln\frac{2\pi\hbar^2 e^{5/3}}{mkT} - N\frac{a}{v} ; \tag{2}$$

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

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

In the last two equations the first order quantum correction applicable to the excitonic bose gas has been included in parentheses a posteriori for the sake of comparison; $Q \equiv (mk/2\pi\hbar^2)^{3/2}$; $a \equiv 2\pi R_0^3 C/3$; $b \equiv 2\pi R_0^3/3$; and V is the volume per exciton.

The vdW equation (4) allows a determination of the critical temperatur T_c and the critical volume per exciton v_c:

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

$$v_c = 3b = 2\pi R_0^3 = 30.86\, a_0^3 ; \tag{6}$$

For germanium these expressions give $T_c = 5.0$ K and $n_c = v_c^{-1} = 7.0 \times 10^{15}$ cm^{-3}. For pure silicon, $T_c = 27$K and $n_c = 5.08 \times 10^{17}$ cm^{-3}.

At any temperature $T < T_c$ the equations

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

$$\gamma(x_1^{-1} + x_2^{-1})(1 - x_1^{-1})(1 - x_2^{-1}) = 1 \; , \qquad (8)$$

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 vdW equation. The critical parameters predicted by Eqs. (5) and (6) are compatible with the experimental evidence for pure germanium.

Four final remarks are of importance: (1) Since the vdW equation of state is known to be imprecise in the condensed region, a better approach is obtained by using the Dietrici equation[18] with the same parameters a and b. The results $v_c = 2b$ and $T_c = a/4bk$ are usually in better accord with the experiment. (2) Eqs. (5) - (8) are solutions of the minimum Gibbs potential which correspond to a system with controlled 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 $v' = 2b$. 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 which 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. (3) 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 which has been observed experimentally.[8] (4) 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 approximately 5 percent at the critical temperature for germanium; for silicon the correction is much smaller.

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17. 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

the
of/Coulomb interaction within the exciton. It is curious, but correct, that the polarizability can thus be greater than the polarizability of a conducting sphere of equal radius. Further the vdW interaction in this form involves ϵ^{-2} from the scaling of the energy level separation and another ϵ^{-2} from the second order of the interexcitonic Coulomb interaction.

18. See J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular theory of gases and liquids, Wiley, 1954; see p. 1060 and 1063.

19. J. E. Mayer and M. G. Mayer, Statistical mechanics, Wiley, 1940, Chap. 12.

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