Electron-hole liquid in the hexaborides

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We investigate the energetics of the electron-hole liquid in stoichiometric divalent metal hexaborides. The ground state energy of an electron-hole plasma is calculated using RPA and Hubbard schemes and compared to the binding energy of a single exciton. Intervalley scattering processes play an important role in increasing this binding energy and stabilizing a dilute Bose gas of excitons.

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The remarkable discovery of the high-temperature weak ferromagnetism in La-doped CaB$_6$, SrB$_6$, and BaB$_6$ has opened a new page in the physics of magnetism \[1\]. In our previous work \[2\] we attributed this effect to an unusual ground state of undoped divalent hexaborides. This so-called excitonic insulator is characterized by a condensation of bound electron-hole pairs (excitons). An excitonic instability in narrow gap semiconductors or semimetals was predicted \[3\] and studied theoretically in the mid-sixties \[4\]. However, its occurrence in any real compound is still controversial. Band structure calculations \[5,6\] predict a small direct overlap in divalent-metal hexaborides between a boron-derived valence band and a cation-derived conduction band at three equivalent points in the cubic Brillouin zone. This feature, together with absence of direct electric-dipole transitions between the two bands, is extremely favorable for electron-hole pairing and leads to the excitonic instability. Weak ferromagnetism develops, then, in a triplet excitonic insulator due to spontaneous time-reversal symmetry breaking under doping \[4\].

There are many open questions in the physics of the excitonic ferromagnetism. Some of them were raised recently in Refs. \[7,8\]. In the present work we, however, want to shift emphasis from the (un)doped excitonic state to general properties of electron-hole (e-h) liquids in the hexaborides. Charge conservation does not fix the number of e-h pairs, which in thermal equilibrium depends on the e-h chemical potential (band overlap). In the original theory of the excitonic insulator the band gap (overlap) $E_G > 0$ ($E_G < 0$) was considered to be a free parameter that changes continuously through the value $E_G = 0$. Subsequently, investigation of optically pumped electrons and holes in semiconductors showed \[9,10\], that a first order transition between two states, one with a substantial band gap and the other with a substantial band overlap, will occur and that smaller values of $|E_G|$ lie in the unphysical intermediate region. The details of such transition are very sensitive to the actual band degeneracies and anisotropies. Here, we study possible scenarios for the transition from a semiconducting state into a metallic e-h liquid in CaB$_6$, including the appearance of a free exciton gas. We find that a novel mechanism of intervalley scattering of excitons is important in stabilizing an intermediate gas phase.

Electrons and holes in CaB$_6$ have the following values of the effective masses measured in units of the bare electron mass \[2\]: $m_e^\perp = 0.504$, $m_e^\parallel = 0.212$ (conduction band) and $m_h^\perp = 2.17$, $m_h^\parallel = 0.206$ (valence band). These values agree with the early results using the muffin-tin approximation \[3\]. First, we retain only the dominant intravalley scattering processes shown in Fig. 1a, when an electron (hole) scatters between states near a single X-point. In the small-$q$ limit the scattering matrix element is given by a screened Coulomb potential $V_q = 4\pi e^2/\kappa q^2$ ($\kappa$ is a static dielectric constant). We define an e-h chemical potential as a sum of two individual potentials $\mu = \mu_e + \mu_h$. The relation to the band model is made by $\mu = -E_G$, i.e. the band gap is equivalent to the chemical potential. Natural units for energies and lengths are effective Rydberg $E_R$ and Bohr radius $a_B$: $E_x = m^*e^4/2\kappa^2 = e^2/2\kappa a_x$, where reduced mass $m^* = m_{oe}m_{oh}/(m_{oe} + m_{oh})$ is determined by optical masses: $3/m_{oe} = 2/m^\parallel + 1/m^\perp$. The e-h pair density $n$ is characterized by a dimensionless parameter, $r_s = (3/4\pi n a_x^3)^{1/3}$.

![FIG. 1. Electron-hole scattering processes in the hexaborides. Operators $a$ and $b$ correspond to conduction and valence bands, respectively. Figure (a) shows a dominant intravalley vertex. Figures (b) and (c) correspond to intervalley scattering.](image)

At high densities, small $r_s$, we use the random phase approximation (RPA) \[11\]. Strictly speaking, a dense metallic e-h liquid can transform into an excitonic insulator \[3\]. This assumption was a key starting point in our explanation of the high-temperature weak ferromagnetism in the hexaborides \[4\]. However, the ground
state energy correction from the excitonic instability in a semimetal is of order $\Delta^2/\varepsilon_F$ and is small ($\Delta \ll \varepsilon_F$), so we neglect it. The kinetic energy per $e$-$h$ pair is given by

$$E_K = \frac{3m^*}{5\alpha^2\nu^2/3} \left[ \frac{1}{(m_c^*m_e^*)^{1/3}} + \frac{1}{(m_h^*m_e^*)^{1/3}} \right],$$

(1)

where $\alpha = (4/9\pi)^{1/3}$ and $\nu = (3)$ is the number of valleys. The exchange energy for anisotropic bands is

$$E_{\text{exch}} = -\frac{3}{2\pi\alpha\nu/3} \left[ \frac{1}{(m_c^*m_h^*)^{1/3}} + \frac{1}{(m_h^*m_h^*)^{1/3}} \right],$$

(2)

The correlation energy describes the remaining contribution to $E_{\text{g.s.}}$.

$$E_c = \frac{i}{2} \int \frac{dq\,d\omega}{(2\pi)^4} \int_0^1 d\lambda \left[ \frac{V_q \Pi^*(q,\omega)}{1 - \lambda V_q \Pi^*(q,\omega)} - V_q \Pi^0(q,\omega) \right],$$

(3)

where $\Pi^*(q,\omega)$ is the irreducible polarization operator and $\Pi^0(q,\omega) = \sum_i \Pi^0_i(q,\omega)$ is a sum of (anisotropic) RPA-polarizabilities for each species of electrons or holes. Substitution $\Pi^*(q,\omega) = \Pi^0(q,\omega)$ in Eq. (3) gives the RPA-expression for $E_c$. An approximate way of treating the higher order exchange corrections was considered by Hubbard [3]. His expression generalized to the multicomponent plasma is

$$\Pi^*(q,\omega) = \sum_i \frac{\Pi^0_i(q,\omega)}{1 + f(q) V_q \Pi^0_i(q,\omega)} ,$$

(4)

with $f(q) = 0.5q^2/(q^2 + k_F^2)$. We also change an $\omega$-integration from real to imaginary axis, which avoids a difficulty related to a plasmon pole in $\Pi^0(q,\omega)$. Numerical results for the ground state energy are shown in Fig. 2. The band degeneracy improves substantially the accuracy of the RPA, because corrections to the RPA diagrams have extra smallness in $1/2\nu$. The minimum of the ground state energy is reached at $r_s = 0.92$ with a minimum value $E_{\text{g.s.}}^{\text{min}} = -1.55E_x(-1.51E_x)$ in the RPA (Hubbard) scheme. The use of RPA is justified by a small value of $r_s$ at the minimum, which corresponds to a dense plasma with strong screening and small corrections from multiple $e$-$h$ scattering. Such corrections become significant at $r_s \gtrsim 3$. The ground state energy is also known in the limit $r_s \to \infty$, where it approaches the binding energy of a single exciton $E_c$. (Here, we disregard possible formation of exciton molecules.)

The presence of a local minimum at metallic densities for $E_{\text{g.s.}}(r_s)$ has an important effect on transformation from a semiconductor to a semimetal [11,12]. The two possible scenarios are shown schematically in Fig. 3. In the first case, curve (a), the local minimum is also the absolute one: $E_{\text{g.s.}}(r_{sA}) < E_c$. The pair chemical potential is related to the ground state energy by:

$$\mu = E_{\text{g.s.}} + n \frac{\partial E_{\text{g.s.}}}{\partial n}.$$  

At the extremal point the second term is zero and $\mu = E_{\text{g.s.}}^{\text{min}}$. Therefore, when the band gap decreases to $E_G = |E_{\text{g.s.}}^{\text{min}}|$, a first-order metal-insulator transition takes place. The number of $e$-$h$ pairs jumps from zero to $n(r_{sA})$. Smaller densities with $r_s > r_{sA}$ correspond to unstable states. In optically pumped semiconductors, where a number of carriers is fixed instead of a chemical potential, this effect leads to $e$-$h$ droplet condensation [14]. In the second case, curve (b), the exciton energy lies below the metallic minimum. Semiconducting state becomes unstable at $E_G = |E_c|$ and transforms into a low-density exciton gas. If $E_G$ is further reduced, a first order transition of gas-liquid type takes place between two states $B_1$ and $B_2$, which have same pressure $P = n^* \frac{\partial E_{\text{g.s.}}^{\text{min}}}{\partial n}$. The case (b) is believed to be realized in isotropic one-component $e$-$h$ plasma, whereas in many semiconductors band degeneracies and anisotropies favor the case (a) bypassing a free exciton gas state [11,12].

![FIG. 2. The ground state energy per pair in units of $E_x$ for $e$-$h$ liquid in CaB$_2$. Solid line is the RPA and dashed line is the Hubbard result. Dot-dashed line is the RPA including correction from the intervalley scattering. Thin horizontal lines denote position of the $A_1$ exciton level in zeroth (upper) and first (lower) order approximations in the intervalley scattering. Self-consistent mechanism proposed in the text pushes the exciton energy further down below the local minimum.](image-url)

To check which of the two scenarios occurs in the hexaborides we now compare the above value of $E_{\text{g.s.}}^{\text{min}}$ to the binding energy of a single exciton. The simplest estimate for the exciton energy is $-E_x$. It is obtained by substituting an isotropic $1s$-type wave function into the Schrödinger equation. This estimate predicts the same binding energy for excitons formed by an electron and a hole from same or from different valleys. We improve this result by using a simple variational ansatz appropriate to the cylindrical symmetry of the bands near each of the $X$-points similar to the treatment of shallow impurity states [13]. The binding energy of an electron and a hole from the same valley is $E_c = -1.12E_x (|a_X|b_X) \neq 0)$, whereas an electron and a hole from different valleys have...
The dominant term approximation (Fig. 3a) used above leaves threefold degeneracy of the excitonic level corresponding to e-h pairing at three X-points. Coherence between different excitons is established by inter-valley scattering processes shown in Fig. 3b. Instead of a single hydrogenic equation, one must solve now a system of three coupled integral equations for a three-component excitonic wave function $\psi_\nu(r)$. The scattering matrix element $g_\nu$ includes a large momentum transfer on $Q = b/\sqrt{2}$, where $b$ is an elementary reciprocal lattice vector. Consequently, we can neglect its momentum dependence and estimate

$$
g \approx \sum_G \frac{4\pi e^2}{|Q + G|^2} F^{aa}_G(X, X') F^{bb}_{-G}(X', X). \quad (5)$$

Here, summation is over reciprocal lattice, $F^{aa}_G(X, X')$ is a form factor for two conduction band states at points $X$ and $X'$. The absence of the dielectric constant in the Fourier transform of the Coulomb potential reflects a lack of lattice screening for these processes. Another vertex, which has the same strength $g_\nu$ but does not contribute to the electron-hole pairing, is shown in Fig. 3b. Several other inter-valley vertices correspond to processes, when an electron transforms into a hole. However, they correspond to higher momentum transfers and we neglect them. Generally, the form factors in Eq. (5) reduce the matrix element compared to the amplitude of a Coulomb potential by a factor of $\sim 2-5$ and can also change the sign of $g_\nu$. Nevertheless, in the absence of necessary numerical band structure results we use a somewhat optimistic estimate $|g| \approx 4\pi e^2/Q^2$. Returning back to a spatial form of the Schrödinger equation we obtain a contact-like interaction of excitons in different valleys with a strength $g$.

Since the total momentum of excitons vanishes, eigenstates of the Schrödinger equation are classified according to the irreducible representations of the cubic point group $O_h$. Treating the inter-valley scattering perturbatively, we find $E_{x1} = E_e - 2\lambda$ for a nondegenerate exciton state with $A_1$ symmetry $\psi_r \sim \psi_B(r)(1,1,1)$ and $E_{x2} = E_e + \lambda$ for a degenerate doublet with $E$ symmetry: $\psi_B^{(1)} \sim \psi_B(r)(1,e^{2\pi i/3},e^{4\pi i/3})$ and $\psi_B^{(2)} \sim \psi_B(r)(1,e^{-2\pi i/3},e^{-4\pi i/3})$, where $\psi_B(r)$ is a $1s$ hydrogenic wave function. The coupling constant is $\lambda = g/\psi_B(0)^2$ and, therefore, choice of the lowest energy exciton depends on the sign of $g$. If interaction between excitons is attractive ($g > 0$) the symmetric $A_1$-state has lower energy. If it is repulsive, then the $E$-doublet is more stable. One can easily estimate $\lambda$ using unperturbed $\psi_B(r): \lambda = 0.15E_e$. We have also calculated the effect of inter-valley vertices Figs. 3a and 3b on the ground state energy of the metallic e-h liquid shown by dashed line in Fig. 3. This correction is much smaller than a change of the exciton energy and does not exceed 3%. Qualitatively, such a difference is explained by different orders of the two corrections: for the metallic plasma it is a second-order effect, while the shift of exciton energy is a first order effect. Another effect of lifting threefold degeneracy of excitons in different valleys is suppression of multi-exciton molecules.

As one can see from Fig. 3 the exciton energy is still above the ground state energy of the metallic phase, though the two energies move closer to each other. However, it appears that our estimate for the inter-valley scattering effect may be too conservative. The origin of extra enhancement is similar to a mechanism of anomalously large hyperfine splitting of donor states in Si proposed by Kohn and Luttinger [13]. The actual exciton energy is shifted below prediction of the effective mass theory because of both the inter-valley scattering effect and a so called central cell correction [10]. Contrary to a naive point of view, related changes in the amplitude $\psi(0)$ are determined by a long distance Schrödinger equation rather than by an exact short distance e-h Hamiltonian. Since the actual $E_e$ is not an eigenvalue of the effective mass equation, there is no solution for this energy which satisfies both boundary conditions at $r = 0, \infty$. Therefore, actual exponentially decaying wave-function develops a singularity at short distances. We find that for a moderate 20% shift of $E_e$ the probability to find electron near hole $|\psi(0)|^2$ is enhanced by a factor of 4 compared to $|\psi_B(0)|^2$. This effect significantly increases $\lambda$, espe-
cially for the $A_1$-singlet \cite{16}. As a result, the excitonic level in the hexaborides must lie well below the metallic minimum of $E_{g.s.}(r_s)$.

We have considered stability of different phases of the $e$-$h$ liquid in the hexaborides. They include a semiconducting state with no carriers, a dilute Bose gas of excitons and a dense electron-hole liquid. The latter can be clearly distinguished from the other two states in infrared optical conductivity by its large Drude peak. If an excitonic instability develops in a dense $e$-$h$ liquid, $\sigma(\omega)$ must also have an edge-type singularity at the excitonic gap. Semiconducting and free exciton gas states, on the other hand, have no significant features in $\sigma(\omega)$ because of the absence of direct optical transitions between the two bands. Which of the three states really occurs depends on the band gap parameter $E_G$. Note, that in the scenario (a), see Fig. 3, a first order transition between a semiconducting state and a dense plasma takes place at a positive $E_G$, which always corresponds to a semiconductor in a single electron picture. Small values of $|E_G| \sim E_x \approx 0.08$ eV found in the band structure calculations \cite{11,12} indicate that the hexaborides can be close to an instability of semiconducting state, which, as we argued for CaB$_6$, transforms into a dilute exciton gas. The other possible instability in the hexaborides, if $E_G$ is varied on experiment, is a gas-liquid transition between a dilute Bose gas of excitons and a dense $e$-$h$ plasma.

We suggest that some of the above phase transformations could be induced in the hexaborides by applying hydrostatic pressure, which changes the band gap $E_G$. Applied uniaxial stress can further lift the degeneracy between different valleys and, thus, reduce significantly an energy of the metallic phase \cite{11,12}. Our main result, stability of a dilute exciton gas in CaB$_6$ either at normal conditions or under pressure, provides a new way to look at the Bose condensation of excitons. Another intrinsic mechanism for gap variations can also come from impurity doping, in particular from La-substitution for a divalent element. Therefore, doped hexaborides can differ from undoped compounds not only because of unequal number of electrons and holes, but also in terms of an appropriate starting picture: a Bose gas of excitons or a dense $e$-$h$ liquid. In the latter case screening effects must be quite significant due to a high density restriction for $e$-$h$ plasma: $r_s \lesssim 1$.

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\bibitem{16} Central cell corrections to the exciton energy come in part because of a lack of lattice screening of $e$-$h$ interaction at distances smaller than lattice constant. We estimate this effect as $\Delta E_x \sim -0.2 E_x$ for the $A_1$-state. Note that similar shift is also present for the ground state energy of $e$-$h$ plasma with $r_s \sim 1$. Hence, central cell correction alone cannot explain stability of a dilute exciton gas. The $E$-states have vanishing probability to find an electron at a hole and central cell corrections are much smaller for them.
\end{thebibliography}