Excitonic ferromagnetism in the hexaborides

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(April 16, 1999)

A ferromagnet with a small spontaneous moment but with a high Curie temperature can be obtained by doping an excitonic insulator made from a spin triplet exciton condensate. Such a condensate can occur in a semimetal with a small overlap or a semiconductor with a small bandgap. We propose that it is responsible for the unexpected ferromagnetism in the doped hexaboride material Ca$_{1-x}$La$_x$B$_6$.

In a recent letter to Nature Young et al. reported ferromagnetism in Ca$_{1-x}$La$_x$B$_6$ — a material with no partially filled $d$- or $f$-orbitals. Three features are noteworthy: the narrow concentration range of doping ($0 \lesssim x \lesssim 0.01$), the small magnetic moment ($\lesssim 0.07\mu_B$/La), and the high Curie temperature ($T_C \approx 600$ K). The parent compound CaB$_6$ is a poor conductor which shows a small overlap $E_G (< 0)$ between a boron-derived valence band and a calcium-derived conduction band at the X-point in the Brillouin zone. The valence and conduction bands belong to different irreducible representations ($X_3^\prime$ and $X_3$, respectively) such that the interband dipole matrix element vanishes at the X-point. As a result the dielectric constant ($\kappa$) and the effective masses ($m_h$ and $m_e$) remain finite as $E_G \to 0$, which, as pointed out by Halperin and Rice, favors formation of an excitonic condensate.

An excitonic instability for a semimetal or a semiconductor with small values of $E_G$ was first proposed by Keldysh and Kopaev and later examined in detail by a number of authors in the mid-sixties. The effective mass Hamiltonian for a gas of electrons and holes, attracting each other through a Coulomb interaction screened by the background dielectric constant $\kappa$, is treated in the Hartree-Fock approximation.

The characteristic energy scale is set by the excitonic binding energy $E_{\text{ex}} = \mu^*\kappa^{-2}\text{Ry}$, where $\mu^*$ is the reduced mass ($\mu^* = m_h^{-1} + m_e^{-1}$) in electron mass units. In CaB$_6$ typical values for the effective mass tensors are $m_h^\parallel = 2.17$, $m_h^\perp = 0.206$ (valence band) and $m_e^\parallel = 0.504$, $m_e^\perp = 0.212$ (conduction band) from our band structure calculations and $\kappa \approx 5$ from optical measurements (L. Degiorgi, private communication) giving $E_{\text{ex}} \approx 0.08$ eV. A triplet exciton condensate is favored over a singlet one by the Coulomb interaction. In the present case of a direct gap the broken symmetry will give rise to a local spin polarization in each unit cell but no net magnetization at stoichiometry. As first shown by Volkov et al. extra electrons doped into the system are distributed asymmetrically between two spin projections in order to keep most favorable pairing conditions for at least one spin species of exciton. As a result, the excitonic insulator becomes ferromagnetic with the Curie temperature set by the energy scale of the primary excitonic order parameter.

The theory of a Bose condensate of loosely bound electron-hole pairs has a close formal resemblance to the description of Cooper pairs in superconductors. We consider a valence band maximum and a conduction band minimum both situated at $k = 0$. In the normal phase, without excitonic condensate, the electrons states are classified by their wavevectors and band numbers with creation operators $a_{k\alpha}^\dagger$ and $b_{k\sigma}^\dagger$ for valence and conduction bands, respectively. The band quantum number ceases to exist in the excitonic phase because of the formation of electron-hole pairs. This change in the ground-state is reflected in a new Hartree-Fock average $\langle a_{k\sigma}^\dagger b_{k\sigma^\prime}^\dagger \rangle$, which becomes the primary order parameter of the excitonic phase. Quasiparticles in two new bands are related to the old Bloch states via a canonical transformation

$$
\begin{align*}
\alpha_{k\sigma} &= u_k a_{k\sigma} + v_k M_{\sigma\sigma'} b_{k\sigma'} \\
\beta_{k\sigma} &= -v_k a_{k\sigma} + u_k M_{\sigma\sigma'} b_{k\sigma'}
\end{align*}
$$

where the unitary matrix $M_{\sigma\sigma'}$ describes a spin symmetry of the excitonic condensate. The singlet state of excitons corresponds to $M_{\sigma\sigma'} = \delta_{\sigma\sigma'}$, whereas a triplet exciton condensate has $M_{\sigma\sigma'} = \sum_i n_i \sigma_{\sigma'}$, $\sigma^\dagger$ being the Pauli matrices.

![FIG. 1. The structure of energy spectrum in a semimetal (left) and in an excitonic insulator (right) for one spin polarization. States in shaded volumes are occupied by doped electrons.](image)

We keep only the intraband exchange part of the Coulomb potential between electrons and holes, $V(k)$, which has smallest momentum transfer and is responsible for electron-hole binding. The formation of excitons opens a gap in the quasiparticle spectrum $\Delta_{k\sigma} = \sum_i V(k - q)(a_{k\sigma}^\dagger b_{k\sigma}^\dagger)\rho_i$ and the system transforms into an excitonic insulator see Fig. 1. Two new bands have energy dispersions given by $E^{\alpha, \beta}_{k\sigma} = \eta_k \mp \sqrt{\xi_k^2 + \Delta_{k\sigma}^2}$.
with \( \eta_k = \frac{1}{2}(\varepsilon_k^\uparrow + \varepsilon_k^\downarrow) \) and \( \xi_k = \frac{1}{2}(\varepsilon_k^\uparrow - \varepsilon_k^\downarrow) \). The gap is determined from the equation

\[
\Delta_{k\sigma} = \sum_q V(k-q) \frac{\Delta_{q\sigma}}{2\sqrt{\xi_q^2 + \Delta_{q\sigma}^2}}(n^\alpha_{q\sigma} - n^\beta_{q\sigma}) ,
\]

where \( n^\alpha_{q\sigma} = \langle \sigma^\dagger_k \sigma_{q\sigma} \rangle \) and \( n^\beta_{q\sigma} = \langle \sigma^\dagger_k \sigma_{q\sigma} \rangle \) are occupation numbers for \( \alpha \)- and \( \beta \)-branches of spectrum. The neglected Coulomb terms with a large momentum transfer select the triplet state with an arbitrary orientation of polarization vector \( \mathbf{n} \).

We start with the simplest weak-coupling variant: isotropic bands with masses \( m_h = m_e = m \) so that \( \varepsilon_k^\alpha = -\varepsilon_k^\beta = \varepsilon_0 - \frac{k^2}{2m} - \mu, \varepsilon_0 = -E_G/2 \). In the stoichiometric case the number of electrons equals the number of holes and \( \mu = 0 \). For a significant overlap there is a strong screening of the Coulomb interaction by free carriers and we can set \( V(k) \approx V_0 \) and, hence, neglect a momentum dependence of the excitonic gap. At zero temperature the lower band is occupied (\( n^\alpha_k \equiv 1 \)), while the upper band is empty (\( n^\beta_k \equiv 0 \)). Then, the spin-independent solution of the gap equation is \( \Delta_0 = 2\varepsilon_c \exp[-(V_0 N_0)^{-1}], \) where \( \varepsilon_c \) is a cut-off around the Fermi surface and \( N_0 = mk_F/(2\pi^2) \). The energy gain of the excitonic condensate over the normal phase per spin direction is \( E[0] = -\frac{1}{2}N_0 \Delta_0^2 \).

Electron-hole asymmetry created by doping leads to partial occupation of the upper \( \beta \)-band (Fig. 1), which according to Eq. (2) gradually destroys the excitonic condensate. We relate the number of doped carries \( n_d \) with a change of the chemical potential in the normal state: \( n_d = 4N_0 \mu_d \). Then, the zero temperature excitonic gap in the unpolarized state is

\[
\Delta_0^2 = \Delta_0(\Delta_0 - 2|\mu_d|) .
\]

The excitonic condensate becomes energetically unfavorable for \( \mu_d > \Delta_0/2 \). The ground state energy per spin direction (relative to the stoichiometric normal state) is

\[
E[\mu_d] = N_0 \mu_d^2 - \frac{1}{2}N_0(\Delta_0 - 2|\mu_d|)^2 .
\]

Polarization is included in this picture by allowing different chemical potentials for spin-up and spin-down quasiparticles: \( \mu_d(1 + p) \) and \( \mu_d(1 - p) \). A quick check shows that the energy of a polarized excitonic insulator \( E[\mu_d(1 + p)] + E[\mu_d(1 - p)] \) has a minimum value for \( p = 1 \), i.e. for complete polarization. All doped electrons have parallel spins leaving stoichiometric conditions for carriers with opposite spins. This gains pairing energy relative to the unpolarized state value \( 2E[\mu_d] \) and compensates for an increase in kinetic energy. The two gaps are nonzero in the following doping ranges

\[
\Delta_u = \sqrt{\Delta_0(\Delta_0 - 4\mu_d)} \quad \text{for} \quad 0 < \mu_d < \Delta_0/4 ;
\]

\[
\Delta_f = \Delta_0 \quad \text{for} \quad 0 < \mu_d < \Delta_0/2 .
\]

Note, that at intermediate concentrations electrons and holes are paired only for one spin direction. At the critical point \( \mu_d^c = \Delta_0/2 \) the ground state energy becomes degenerate with respect to the degree of polarization \( p \) and after a jump the system returns back to the normal unpolarized state.

In the case of CaB₆ the excitonic gap, as estimated from \( T_C \) is of the same order of magnitude or even larger than the overlap \( E_G = 2\varepsilon_0 \). Under this circumstances the weak-coupling approach does not work quantitatively. In addition there is a significant mass anisotropy in both bands. We, therefore, have solved the gap equation (2) numerically using effective masses from our band structure calculations and the gap value \( \Delta_0 = 0.07 \text{ eV} \) as suggested by optical measurements on the 5%-doped compound (L. Degiorgi, private communication). The band overlap remains a largely unknown parameter, which we take to be \( E_G = -0.2 \text{ eV} \). In addition, we again neglect momentum dependences of \( \Delta_k \) and \( V(k) \), i.e. assume a strong screening with a cut-off energy \( \varepsilon_c = |E_G|/2 \). The variation of the two gaps under doping is shown in Fig. 2. For small donor concentrations the excitonic insulator is again completely polarized. The major difference with the isotropic weak-coupling model is a new concentration range, where the upper gap gradually decreases and doped electrons are only partially polarized. Note, that ferromagnetic polarization disappears before the transition to the normal metallic state.

![FIG. 2. The doping variation of the gaps for spin-up and spin-down quasiparticles (dashed lines) and of the saturated ferromagnetic magnetization \( M^z \) (solid line) in Ca₁₋ₓLaₓB₆ at \( T = 0 \).](image)
to invoke extra Coulomb terms. The principal role in lifting this degeneracy is played by a direct Hartree contribution, which is written in terms of the Fourier harmonics of the charge density $\rho_{\mathbf{G}}$ as $V_{\text{dir}} = \frac{1}{2} \sum_{\mathbf{G},\mathbf{G}'} U_{\mathbf{G},\mathbf{G}'}(0) \rho_{\mathbf{G}}^{\alpha} \rho_{\mathbf{G}'}^{\alpha}$. In the case of weak doping, we obtain from (6) the following expression

$$\rho_{\mathbf{G}} = \sum_{\mathbf{k}\sigma} F_{\mathbf{G},\mathbf{k}}(\mathbf{k},\mathbf{k}) u_{\mathbf{k}\sigma} v_{\mathbf{k}\sigma} (M_{\sigma\sigma} + M_{\sigma\sigma}')(n_{\mathbf{k}\sigma}^\alpha - n_{\mathbf{k}\sigma}^\beta), \quad (6)$$

where $F_{\mathbf{G},\mathbf{k}}(\mathbf{k},\mathbf{k})$ are the form-factors defined in Ref. 1. In order to minimize the direct Coulomb energy charge modulations $\rho_{\mathbf{G}}$ must vanish. For an undoped system, when occupation numbers and coefficients $u_{\mathbf{k}\sigma}$ and $v_{\mathbf{k}\sigma}$ are spin independent, this requirement leads to $\text{Tr} M = 0$, i.e. $V_{\text{dir}}$ favors triplet states over the singlet one. For a doped excitonic insulator, $n_{\mathbf{k}\uparrow}^{\alpha} - n_{\mathbf{k}\uparrow}^{\beta} \neq n_{\mathbf{k}\downarrow}^{\alpha} - n_{\mathbf{k}\downarrow}^{\beta}$ and $\rho_{\mathbf{G}}$ becomes nonzero for $\mathbf{M} = \hat{z}$, whereas it still vanishes for $\mathbf{M} = \hat{x}$ or $\hat{y}$. We conclude, therefore, that the perpendicular orientation of $\mathbf{n}$ and $\mathbf{M}$ has the lowest energy.

For transverse polarization of triplet excitons an induced ferromagnetic moment is

$$M^z = \sum_{\mathbf{k}\sigma} (u_{\mathbf{k}\sigma}^2 - v_{\mathbf{k}\sigma}^2) \sigma (n_{\mathbf{k}\sigma}^\alpha - n_{\mathbf{k}\sigma}^\beta). \quad (7)$$

In this case each of the quasiparticles [1] consists of an electron and a hole with opposite spins and, therefore, carries only a small fraction of the Bohr magneton. In addition $M^z$ has an important contribution from a change of the vacuum for spin-up and spin-down quasiparticles. The contribution vanishes exactly for the constant density of states. We used the above expression for $M^z$ to calculate the variation of the ferromagnetic moment in CaB$_6$ under doping, which is presented in Fig. 2. The magnetization depends on electron-hole asymmetry in the density of states. Smaller overlap leads generally to more asymmetry and, consequently, to an increasing value of $M^z$.

For the above choice of parameters we calculated from Eq. (2) concentration dependence of the excitonic transition temperature for Ca$_{1-x}$La$_x$B$_6$ and the stability boundaries of the ferromagnetic polarization, which are shown in Fig. 3. The Curie temperature grows with doping and the maximal $T_C$ is achieved above the concentration at the peak value for the saturation magnetic moment. The direct transition from the normal semimetallic state into a polarized excitonic phase, which exists for a certain range of doping, will split into two separate transitions when the degeneracy lifting Coulomb terms are included in Eq. (5).

Excitonic ferromagnetism offers a natural explanation of weak ferromagnetism of Ca$_{1-x}$La$_x$B$_6$. Recognizing that the dimensionless parameter $r_S$ (ratio of interparticle spacing $a_B$ to the effective Bohr radius $a_B^*$) has a moderate value [4] leads us to conclusion that our explanation is more plausible than the original interpretation based on a ferromagnetism of a low-density electron gas. Calculations within the simplest model of an excitonic insulator yield values of the critical donor concentration, the weak ferromagnetic moment, and the Curie temperature close to the experiment.

We didn’t attempt detailed theoretical predictions mainly because of the limited experimental data available at present. A major uncertainty is the value of the band overlap $E_G$ in CaB$_6$ (and in isoelectronic SrB$_6$). Our LDA calculations gave a small overlap $E_G = -0.2$ eV, whereas the modified LDA+U method gave a small band gap $E_G = 0.15$ eV. In the original theory of the excitonic insulator $E_G$ was considered to be a band parameter that varied continuously through the value $E_G = 0$. Subsequently, the discovery of the electron-hole liquid showed [4] that a first order transition between states with a substantial band gap ($E_G > 0$) and overlap ($E_G < 0$) should occur and that smaller values of $|E_G| \lesssim E_{\text{ex}}$ lie in the unphysical intermediate region. At present there are insufficient experiments to reach a firm conclusion on this point for the hexaborides. In addition theoretical questions such as the role of the multiple X-points in the Brillouin zone and of optical phonons require further study.

Excitonic ferromagnetism offers a qualitative explanation for the three key features of the ferromagnetism of Ca$_{1-x}$La$_x$B$_6$ enumerated in the beginning. Experimental predictions which will be a decisive test of this model are optical edges at the band gaps $2\Delta_+ = 2\Delta_-$ in the infrared optical conductivity of doped hexaborides and also lowlying magnetic excitations in the stoichiometric compounds CaB$_6$ and SrB$_6$, which are the spin-waves of the triplet exciton condensate.
Acknowledgments. We thank L. Degiorgi and H. R. Ott for useful discussions and comments and also L. P. Gor’kov for bringing Ref. 7 to our attention.

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