Ferromagnetism and Superstructure in $Ca_{1-x}La_xB_6$

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We critically investigate the model of a doped excitonic insulator, which has recently been invoked to explain some experimental properties of the ferromagnetic state in $Ca_{1-x}La_xB_6$. We demonstrate that the ground state of this model is intrinsically unstable towards the appearance of a superstructure. In addition, the model would lead to a phase separation of doped carriers into electron-enriched and neutral domains, which may be prevented by Coulomb forces only. Recent experiments indicate that a superstructure may indeed show up in this material.

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A fundamentally new low temperature state was recently discovered in $Ca_{1-x}La_xB_6$ in the pioneering paper by Young *et al.* [1]. Namely, at low La doping a ferromagnetic state with a small magnetic moment ($\lesssim 0.07\mu_B$) sets in at a large Curie temperature ($T_c \sim 900$ K), which is comparable to the Fermi energy for doped carriers. Conventional theories (such as the Stoner theory of ferromagnetism) provide no explanation of what is observed. Wigner crystal interpretation discussed in Ref. [1] is also deficient because both types of carriers usually are present in these materials. Hexaborides in general possess a number of unusual properties. Having been intensively studied since the 1950's, they represent new and challenging systems, where the Mott metal-insulator transition may be governed by minor doping. More often than not the Mott transition is accompanied by strong antiferromagnetic correlations or results in an insulating antiferromagnetic state. The onset of the ferromagnetic ground state accompanied by characteristic changes in resistivity reveals unusual metal-insulator transition phenomena, which revive theoretical interest in the so-called excitonic transition vigorously discussed in the 1960's and 1970's [2–6] (see [7] for a review).

The properties of hexaborides are intermediate between semimetals and semiconductors, as found experimentally from studies of such materials as CaB_6 or SrB_6. Band structure calculations [8] indicate that hexaborides, DB_6, may, in fact, be semimetals owing to an accidental small band overlap at the three X points of the Brillouin zone, two bands at each X point having symmetry X_3, X_3'. Based on this Zhitomirsky *et al.* [9] have proposed the explanation that uses the energy mechanism for ferromagnetism first suggested in Refs. [10,11]. This model treats the metal-insulator transition due to formation of bound electron-hole pairs as a simplified scheme. Namely, the two branches of electron spectrum cross each other in a way that the two Fermi surfaces coincide (nesting) with each other. This feature makes the model mathematically similar to the BCS model, and this simplifies the theoretical analysis significantly.

Assuming that the basic physics of hexaborides is properly accounted for by this oversimplified weak coupling scheme, in what follows we study in some more detail the zero temperature phase diagram as a function of the doping level and its stability to anisotropy features. The main result is that the system almost inevitably develops a superstructure on the background of the initially cubic lattice. Our explanation of the small magnetic moment per doped lanthanum ion differs from the one suggested in Ref. [9]. Contrary to their results, we note that the magnetic moment per carrier can be large in this model (see Ref. [10]). We show that it can be significantly reduced due to effects of Fermi surface anisotropy.

Ferromagnetism is known to appear in this model and was investigated in detail by Volkov *et al.* [10,11]. We first briefly recall the mechanism of magnetic moment formation in this model. It is well known [4] that if the screened Coulomb interaction between an electron and a hole in two bands,

$$H_{\rm int} = \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} \sum_{\alpha\beta} V(\mathbf{q}) a_{1\alpha}^{\dagger}(\mathbf{k}+\mathbf{q}) a_{2\beta}^{\dagger}(\mathbf{k}'-\mathbf{q}) \times a_{2\beta}(\mathbf{k}') a_{1\alpha}(\mathbf{k}), \quad (1)$$

is dominant, and the electron and hole Fermi surfaces do coincide ("nesting"), the excitonic transition has a degeneracy for the onset of the charge density wave (CDW) ("singlet") and the spin density wave (SDW) ("triplet") excitonic order parameter. This degeneracy is lifted only by additional weak short-range Coulomb terms, which favor the triplet excitonic order parameter [7,9], or electron-phonon interactions, which favor the singlet (CDW) state. This splitting, however, being usually considered to be weak at $\delta g \sim g^2$, where $g = V(0)N_0 \ll 1$ is the screened Coulomb coupling constant, $N_0 = mk_F/(2\pi^2)$, is the density of states per spin for a single band; the temperatures of the triplet or the singlet excitonic transitions are close (on the exponential scale, $T_c \sim \exp[-g^{-1}]$), $T_{s0} \sim T_{t0}$. Then, as it was first shown in Refs. [10,11] and applied to the physics of hexaborides in Ref. [9], ferromagnetism can appear as a result of doping due to the development

of a triplet excitonic instability in the presence of a singlet order, or vice versa. Ferromagnetism is the direct result of the fact that in the presence of these two condensates both crystalline and time-reversal symmetries get broken. Summation of the leading logarithmically divergent terms in the presence of one condensate explicitly confirms the divergent Curie-Weiss behavior of the spin susceptibility with some Curie temperature found in Ref. [11].

We start with the analysis of ferromagnetism in the doped state at low temperatures where we neglect the small differences in the energy spectrum of the SDW or the CDW ground state. The energetic analysis is straightforward in cases where the triplet and the singlet coupling constants are equal [9], since then equations for different spin polarizations are decoupled. Indeed, for a simple model with two isotropic bands, $m_e = m_h = m$, and $\epsilon_e(\mathbf{k}) = \frac{\mathbf{k}^2}{2m} - \mu + \frac{E_g}{2}$, $\epsilon_h(\mathbf{k}) = \frac{\mathbf{k}^2}{2m} + \mu + \frac{E_g}{2}$, the zero temperature excitonic gap in the unpolarized state is given by

$$\Delta_\alpha^2 = \Delta_0(\Delta_0 - 2n), \tag{2}$$

where $\Delta_0 = 2\epsilon_c \exp(-g^{-1})$ is the excitonic gap at zero doping, ϵ_c is a cutoff energy around the Fermi surface, and $n = N/4N_0$ is the concentration of doped carriers in energy units (the level of the chemical potential in the bare metallic phase is $\mu = n$). The same analysis as in Ref. [9] shows that the energy of a spin-polarized excitonic state has a minimum for the complete polarization of added carriers. Therefore, below T_c, there are two order parameters, Δ_s and $\mathbf{\Delta}_t$, and, correspondingly, two different gaps in the spectrum for different spin polarizations:

$$\begin{aligned} \Delta_\downarrow &= \sqrt{\Delta_0(\Delta_0 - 4n)} \qquad 0 < n < \Delta_0/4\,, \\ \Delta_\uparrow &= \Delta_0 \qquad\quad 0 < n < \Delta_0/2\,. \end{aligned} \tag{3}$$

Hence at $T = 0$ electrons and holes are paired for only one spin direction when $\Delta_0/4 < n < \Delta_0/2$. (The system undergoes a first order phase transition into the unpolarized normal metal at $n_{\rm cr} = \Delta_0/2$.) Thus, this mechanism gives a large effective moment equal to $1\mu_B$ per doped La atom, and some efforts have been applied in Ref. [9] to argue that this moment may be forced to become small if the interaction between the orientation of the magnetic moment and the direction $\mathbf{d}$ of the triplet order parameter (SDW), $\mathbf{\Delta}_t(p) = (\mathbf{d}(p)\boldsymbol{\sigma})$, was taken into account. The mechanisms of Ref. [9] seem to us too artificial, first of all, because the energy difference between the CDW and the SDW states was ignored. Meanwhile, it is easy to see that an anisotropy of electron and hole pockets would reduce the net magnetization. Indeed, the two opposite spin polarizations preferred by the system are governed by the position of the chemical potential. First, an anisotropic solution for the order parameter, $\Delta(\mathbf{p})$, would result in variation of the gap itself along the Fermi surface. Secondly, even a small anisotropy ("antinesting") of the electron and hole spectra hinders the excitonic gap, even leading to the gapless pockets along the initial Fermi surface [12,13]. Therefore, while starting from the spin-up and spin-down spectra for the isotropic gap shown in Fig. 1a ($1\mu_B$ per La), one would end up with doped electrons to spill over between the two energy branches thus obviously reducing the total magnetization, as it is shown in Fig. 1b.

We will not pursue the detailed calculations for these mechanisms, since the weak coupling model [3] of an excitonic transition suffers from several obvious deficiencies, each of which results in an instability towards a formation of an inhomogeneous structure. First of all, for the homogeneous excitonic state to exist, the electron and hole Fermi surfaces should be sufficiently close to nesting. Indeed, a quick calculation shows that in a model with mass anisotropy

$$\begin{aligned} \epsilon_h(\mathbf{p}) &= \frac{p_x^2}{2m + \delta m} + \frac{p_y^2}{2m - \delta m} + \frac{p_z^2}{2m} + (1/2)E_g\,, \\ \epsilon_e(\mathbf{p}) &= \frac{p_x^2}{2m - \delta m} + \frac{p_y^2}{2m + \delta m} + \frac{p_z^2}{2m} + (1/2)E_g\,, \end{aligned} \tag{4}$$

a homogeneous excitonic phase disappears at

$$\frac{\delta m}{m} > \frac{2e\Delta_0}{|E_g|}\,, \tag{5}$$

where Δ_0 is the excitonic gap for the isotropic situation ($\delta m = 0$); $e = 2.718\,28$. Since Δ_0 is exponentially small in terms of $\epsilon_c \sim E_g$, $\Delta_0 = 2\epsilon_c \exp(-1/g)$, the weak coupling model allows only a modest mass anisotropy.

The range of anisotropy for exciton formation may be extended beyond Eq. (5), however, since at larger anisotropies it leads to an inhomogeneous state with long-wavelength oscillations of spin and/or electron densities [14]. A similar drawback of the Keldysh-Kopaev model becomes obvious when one considers doping even

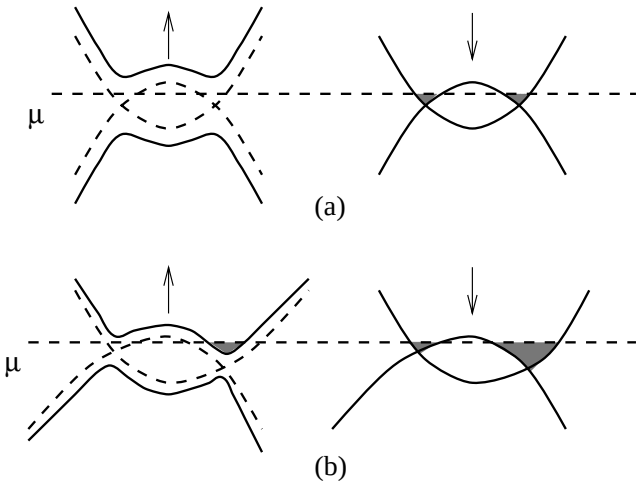

FIG. 1. (a) Energy bands and spin directions in the isotropic excitonic insulator; (b) the value of the total magnetic moment depends on the shape of the energy spectrum in momentum space along the Fermi surface when the gap anisotropy and/or antinesting are taken into account.

in a model with the perfect nesting. Mathematically the problem in the last case becomes equivalent to the problem of the coexistence of the superconductivity and ferromagnetism [15]. The exchange field, I, in that model is equivalent to the chemical potential μ in the excitonic state. Thus, the gap equation has two solutions: (1) $\Delta = \Delta_0$ and (2) $\Delta^2 = 2I\Delta_0 - \Delta_0^2$, where Δ_0 is the gap at $I = 0$. The energies of the ground state are easily found: (1) $\Omega - \Omega_0 = -N_0\Delta_0^2$; (2) $\Omega - \Omega_0 = -N_0(4\Delta_0 I - \Delta_0^2 - 2I^2)$. The branch (2) is not stable for the homogeneous superconductor [16]. The physical difference between the problems of the doped excitonic insulator and the ferromagnetic superconductor is that in the case of an excitonic insulator the number of added dopants is fixed, not the chemical potential. Then the "stable" solution (1) corresponds to zero doping, the case when the chemical potential μ lies below the gap edge Δ_0. The dependence of a homogeneous solution for the gap on doping then is given by (2), with I replaced by μ and μ expressed in terms of added dopants, $\mu = \sqrt{n^2 - \Delta^2}$ (where n is in energy units). Thus the "unstable" solution (2) reproduces Eq. (2) and the effects considered by Volkov *et al.* [10,11] and Zhitomirsky *et al.* [9].

The instability of the homogeneous solution at larger n is seen from the form of $T_c(n)$, explicitly calculated (see Fig. 2) in Ref. [14]:

$$T_c = \frac{\gamma\Delta_0}{\pi}\exp\Big[\Psi\Big(\frac{1}{2}\Big) - \frac{1}{2}\Psi\Big(\frac{1}{2} + i\,\frac{n}{2\pi T_c}\Big) - \frac{1}{2}\Psi\Big(\frac{1}{2} - i\,\frac{n}{2\pi T_c}\Big)\Big]. \quad (6)$$

At high enough densities, $n > \Delta_0/2$, $T_c(n)$ displays a reentrant behavior from the excitonic insulator into the metallic state at low temperatures. The behavior indicates some sort of an instability or a first order phase transition. However, similar to the case of nonperfect nesting above, one can again check for an instability towards a transition into an excitonic state with an incommensurate wave vector $\mathbf{q}$, searching for a maximum $T_c(|\mathbf{q}|)$.

The result of our numerical calculation is shown in Fig. 2. At low dopings T_c corresponds to the homogeneous state with $\mathbf{q} = 0$. The dashed line in Fig. 2 shows the temperature for the onset of an inhomogeneous phase, $T_c(|\mathbf{q}|)$, where the value of $|\mathbf{q}|$ itself depends on n. (At low T_c $|\mathbf{q}| = 2.4n/v_F$.) The excitonic regime at $T = 0$ for such an inhomogeneous state appears by a first order transition at $n^* = 0.71\Delta_0$ (see below) and extends to $n_{c1} \simeq 0.755\Delta_0$. (The inhomogeneous state was first discussed by Rice in connection with itinerant antiferromagnetism in chromium [17].)

Assuming again that the CDW and the SDW states have equal energies ($\delta g = 0$), it is easy to show that T_c in the presence of magnetic field B initially increases with B, as follows from $T_c(n, B)$ obtainable by a mere substitution:

$$T_c(n, B) \equiv T_c(n - \mu_B B), \quad (7)$$

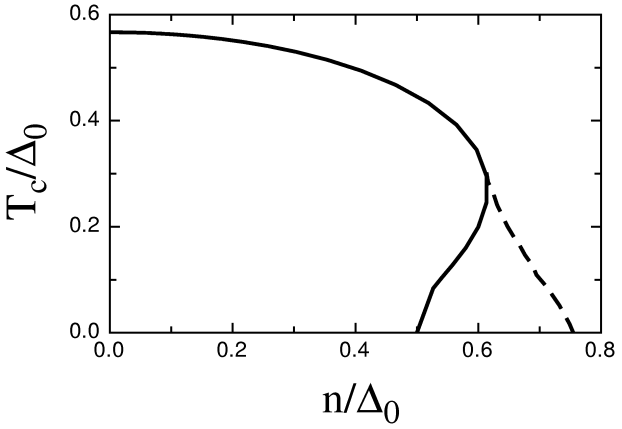

FIG. 2. Transition temperature into the excitonic state as a function of the concentration of dopants, $n = N/(4N_0)$. The dashed line shows the phase transition into inhomogeneous excitonic insulator with the wave vector $\mathbf{q}$.

from Eq. (6). The $|\mathbf{q}|$ value in the presence of the magnetic field B also follows from the same substitution. This result may also be considered as another manifestation of the system's tendency towards a ferromagnetic state. According to Eq. (7), at a higher doping the magnetic field may cause reentrance into the excitonic insulator phase.

The vicinity of the upper concentration, n_{c1}, where the nonhomogeneous solution first appears if the concentration is *decreased* from the side of the normal metal, may be studied in the same manner as for the corresponding superconductivity problem, producing the well-known Larkin-Ovchinnikov-Fulde-Ferrell state [18,19]. The solution in our case [we need to find $\mu(n)$] again secures the stripe phase as the most energetically favorable one. The density of carriers then oscillates according to

$$n(x) = n - n[\Delta_b^2/n_{c1}^2][1 + 1.3\cos(2qx)], \quad (8)$$

where $qv = 2.4(n_{c1} + \delta n/15.7)$, $\Delta(x) = 2\Delta_b\cos(qx)$, and

$$|\Delta_b|^2 = 0.936 n_{c1}(n_{c1} - n). \quad (9)$$

Here v is the Fermi velocity.

An inhomogeneous distribution Eq. (8) of a weak enough charge on the scale of a coherence length $\xi_0 > \xi_{\mathrm{TF}}$, where ξ_{TF} is the Thomas-Fermi screening radius, should not present major trouble since the lattice can adjust itself to produce a periodic modulation. Yet it remains unclear how at low T the system evolves when one proceeds from the metallic end by further decrease of the concentration of dopants.

In any event, if the Coulomb forces are completely neglected, with further concentration decrease the homogeneous phase is restored through the phase separation regime. This starts to take place at the point $n^* = \Delta_0/\sqrt{2}$ [16]. To find the two phases and how they coexist in our case turns out to be completely equivalent to minimizing

the energy of the intermediate state of the I^{st}-type superconductor in a fixed magnetic field. The same energy considerations show that the system separates into the mixture of two phases: the one with $n_e = n_h$ and the other with $n_e - n_h = n^* = \Delta_0/\sqrt{2}$. The relative volume fraction of each phase is given by

$$V_1/V = 1 - n/n^*, \qquad V_2/V = n/n^*. \tag{10}$$

The domain sizes would be determined by the surface energy. Without the bulk Coulomb forces such phase separation is energetically even more favorable than ferromagnetism. On the other hand, the Coulomb energy would work against the spatial charge separation, which, hence, may stabilize a homogeneous regime in a range of small enough n. In view of these uncertainties we made no attempt to address the other issue, namely, that for a complete description of the true ground state of $D\mathrm{B}_6$ in the frameworks of the model [3,8] one has to account for the three X points in the cubic system related to each other by the symmetry transformations. This has been done recently in Ref. [20] for the problem of *multiband superconductors*, and the results of Ref. [20] are immediately mapped onto the problem of the excitonic insulator with the spectrum of Ref. [8].

In conclusion, we have shown that the excitonic model [3], even though it captures a qualitatively correct physics, necessarily leads to the appearance of a superstructure as far as the doping dependence is concerned. We are aware of the only experimental observation yet of such a superstructure [21] which, at least, does not contradict our expectations above. We emphasize again that, unlike in Ref. [9], in our model small magnetic moments may appear as the result of anisotropy. The magnetic moment can be as big as $\sim 1\mu_B$ per doped La in the model [10]. Effects of anisotropy and changes in the energy spectrum through doping would change this significantly, as mentioned above. Recent experiments [22] on BaB_6 doped with La have produced moments about $0.4\mu_B$ at $x = 0.05$.

After this work was performed, the authors have discovered the preprint Ref. [23] by Balents and Varma. We shall not discuss their results regarding the three different X points. We note that our results on the doping dependence agree for the most part. We do not agree, however, with the claim that the results of [9–11] contain significant errors, since the macroscopic phase separation is to be made difficult by the Coulomb terms.

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