Theory of Ferromagnetism in Ca$_{1-x}$La$_x$B$_6$

Shuichi Murakami$^1$, Ryuichi Shindou$^1$, Naoto Nagaosa$^{1,2}$, and Andrei S. Mishchenko$^{2,3}$

$^1$Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
$^2$Correlated Electron Research Center, Tsukuba 305-0046, Japan
$^3$RRC ‘Kurchatov Institute’,123182, Moscow, Russia

(October 22, 2018)

Novel ferromagnetism in Ca$_{1-x}$La$_x$B$_6$ is studied in terms of the Ginzburg-Landau theory for excitonic order parameters, taking into account symmetry of the wavefunctions. We found that the minima of the free energy break both inversion and time-reversal symmetries, while the product of these two remains preserved. This explains various novelities of the ferromagnetism and predicts a number of magnetic properties, including the magnetoelectric effect, which can be tested experimentally.

Novel ferromagnetism in Ca$_{1-x}$La$_x$B$_6$ has been the subject of extensive studies due to its high Curie temperature (≈600K) in spite of a small moment (0.07\(\mu_B$/La) and lack of partially filled \(d$- or \(f$- bands. However, its mechanism still remains controversial. Ceperly suggested that this is a first example of the ferromagnetic phase of a dilute electron gas. An alternative explanation is based on the excitonic state of the parent material CaB$_6$. The parent compound CaB$_6$ has a cubic structure, and some band structure calculations predict a small overlap of the conduction and valence bands at the X-points. Matrix elements of the dipole moments vanish between these states at the X-points; the dielectric constant is not enhanced even when the band gap collapses. This makes the excitonic insulator a plausible candidate for the ground state of CaB$_6$. By La-doping the extra electrons are doped into this excitonic insulator, and it has been found in the mean-field approximation that these electrons are perfectly spin-polarized. Nevertheless, there is so far no conclusive explanation for the magnitude of the moment, much smaller than the electronic moment doped by La. Furthermore, the correlation between the La-doping concentration and the magnetic moments are questioned by recent experiments. Several experiments suggest that the ferromagnetism is not a bulk phenomenon, and occurs only in the thin film sample, or near the surface as evidenced by an electron spin resonance (ESR) experiment.

In this letter we study in depth the symmetry properties of the excitonic state in CaB$_6$ in terms of the Ginzburg-Landau (GL) theory, and propose a possible scenario for the novel ferromagnetism. We classify possible states in terms of the magnetic point groups. The idea is that CaB$_6$ is a triplet excitonic insulator with broken time-reversal \((R$) and inversion \((I$) symmetries, while their product \(RI$ is kept intact. This means that CaB$_6$ is an antiferromagnet (AF), and the ferromagnetism is induced by the magneto-electric (ME) effect, and the La-doping and/or the surface works mainly as a source of the electric field. We emphasize that the present theory of ferromagnetism is different from those in \cite{11-13}, though all these theories are based on exciton condensation.

This scenario of exciton condensation is justified when the band structure has a small overlap/gap at the X points. It is, however, still in controversy whether it is the case. Contrary to the LDA calculation, more recent LDA+GW calculation suggested a large gap of 0.8eV, too large compared with the energy scale for exciton binding energy (≈600K). An angle-resolved photoemission spectrum (ARPES) also shows a large gap of order 1eV, and is in good accordance with the GW result. Nevertheless, there are still enough evidences for believing a small gap or a small overlap. First, another recent GW calculation shows a small overlap at the X points. Second, de Haas-van Alphen measurement finds Fermi surfaces of both electrons and holes. Third, the ARPES experiment is surface-sensitive, and one can argue that the ARPES result of the large gap might be attributed to surface effect. Fourth, measurements of X-ray scattering and Raman scattering in CaB$_6$ shows an anomaly at 600K, below which the compound is determined to be tetragonal. This indicates that the material has some ordering and symmetry-breaking even in the parent compound. This ordering is antiferromagnetic, as indicated in \(\mu SR$ measurements. Therefore, a large gap is unlikely, which prohibits any instability and sensitivity to the small amount of doping. Thus, although there is still no consensus on a size of the gap, the excitonic insulator still remains one of the most promising candidates for the novel ferromagnetism.

Let \(Q_x$, \(Q_y$, \(Q_z$ denote the three X points \((\pi$, 0, 0), (0, \(\pi$), (0, 0, \(\pi$) in the cubic Brillouin zone. When excitons are formed, excitonic order parameters \(\langle b_{k\sigma}^* a_{k'\sigma} \rangle$ will have nonzero values, where \(b_{k\sigma}$ and \(a_{k'\sigma}$ are annihilation operators of electrons with spin \(\sigma$ at the conduction and the valence bands respectively. Because the excitonic instability occurs only in the vicinity of the three X points, we make the following assumptions;

(i) The order parameters are \(k$-independent near the X points.
(ii) The order parameters connecting different X points are neglected. 

As a result we keep only the order parameters \( \eta(Q_i)_{\alpha\beta} = \langle h_{Q_i}^\alpha a_{Q_i}^\beta \rangle \). The cubic \((O_h)\) symmetry of \( \text{CaB}_4\) restricts a form of the GL free energy \( \Phi \), as is similar to the GL theory for unconventional superconductors \[13\].

At the X points, the \( k \)-group has a tetragonal \((D_{4h})\) symmetry, and the conduction and the valence band states belong to \( X_3 \) and \( X'_3 \) representations, respectively \[3\]. Without the spin-orbit coupling, the order parameter \( \eta(Q_4)_{\alpha\beta} \) belongs to \( X_3 \times X'_3 = X'_4 \). From now on we shall take the spin-orbit coupling into account. Then, the point-group transformation is accompanied by the spin rotation, and the representation of \( \eta \) will be altered.

Let us consider the triplet channel for the excitons, because the exchange interaction usually favors the triplet compared with the singlet \[3\]. Then the spin-1 representation of the rotation group will be multiplied, and we get \( X'_4 + X_3 \) in the \( D_{4h} \) group. Explicitly, for the triplet excitons at the \( Q_z \), the \( S_z = 0 \) component \( \eta_{\uparrow\downarrow} - \eta_{\uparrow\uparrow} \) obeys the \( X'_4 \) representation, while the \( S_z = \pm 1 \) components \( \eta_{\uparrow\downarrow} \), \( \eta_{\downarrow\uparrow} \) obey the \( X_3 \). Here the spin-quantization axis is taken to be \( \pm \hat{z} \)-direction. Since we are taking into account the spin-orbit coupling, these up- and down-spins should be interpreted as pseudospins \[13\].

When we consider the three X points, the cubic symmetry is restored since the order parameters have a wavevector \( \mathbf{q} = 0 \). The order parameters have nine components in total, which can be classified into irreducible representations of \( O_h \). They split into three 3-dimensional representations: \( \Gamma_{15} + \Gamma_{15} + \Gamma_{25} \). Let us call basis functions as \( \eta_i(\Gamma_{15}, 1) \), \( \eta_i(\Gamma_{15}, 2) \) and \( \eta_j(\Gamma_{25}) \), where \( i = x, y, z \) and \( j = x(y^2-z^2), y(z^2-x^2), z(x^2-y^2) \). These basis functions transform like a vector \((x, y, z)\) for \( \Gamma_{15} \) and like \((x(y^2-z^2), y(z^2-x^2), z(x^2-y^2))\) for \( \Gamma_{25} \). By judicious choice of phase for basis functions, they can be made to transform under the time-reversal \( R \) as complex conjugation, and they are odd under the inversion \( I \); i.e. \( I\eta = -\eta \) and \( R\eta = \eta^* \). The basis functions are given as

\[
\eta_i(\Gamma_{15}, 1) = \frac{1}{\sqrt{2}}(\eta_{\uparrow\downarrow}(Q_z) - \eta_{\uparrow\uparrow}(Q_z)),
\]

\[
\eta_i(\Gamma_{15}, 2) = -\frac{1}{2}\{i(\eta_{\uparrow\downarrow}(Q_y) + \eta_{\downarrow\uparrow}(Q_y)) + (\eta_{\uparrow\downarrow}(Q_x) - \eta_{\downarrow\uparrow}(Q_x))\},
\]

\[
\eta_i(x^2-y^2,\Gamma_{25}) = \frac{1}{2}\{i(\eta_{\uparrow\downarrow}(Q_y) + \eta_{\downarrow\uparrow}(Q_y)) - (\eta_{\uparrow\downarrow}(Q_x) - \eta_{\downarrow\uparrow}(Q_x))\}.
\]

Here, the spin-quantization axis in \( \eta_{\alpha\beta}(Q_i) \) is taken as \( +\hat{i} \)-axis \((i = x, y, z)\). Other components are obtained by cyclic permutation of \( x, y, z \).

Let us now write down the GL free energy in terms of these order parameters. The GL free energy \( \Phi \) should be invariant under the elements of \( O_h \) and under the time-reversal \( R \). We make two remarks helpful in writing down \( \Phi \). First, only even-order terms in \( \eta \) are allowed by the inversion symmetry. Second, owing to the time-reversal symmetry, the order of \( \text{Im} \eta \) in each term should be even. Thus, \( \Phi \) is given up to quadratic order as

\[
\Phi^{(2)} = A_1 \sum_i (\text{Re} \eta_i(\Gamma_{15}, 1))^2 + A_2 \sum_i (\text{Re} \eta_i(\Gamma_{15}, 2))^2 + A_3 \sum \text{Re} \eta_i(\Gamma_{15}, 1)\eta_i(\Gamma_{15}, 2) + A_4 \sum (\text{Re} \eta_j(\Gamma_{25}))^2
\]

\[
+ B_1 \sum_i (\text{Im} \eta_i(\Gamma_{15}, 1))^2 + B_2 \sum_i (\text{Im} \eta_i(\Gamma_{15}, 2))^2 + B_3 \sum \text{Im} \eta_i(\Gamma_{15}, 1)\eta_i(\Gamma_{15}, 2) + B_4 \sum (\text{Im} \eta_j(\Gamma_{25}))^2
\]

Therefore, as the temperature is lowered, one of the following states will be realized;

(A) \( \text{Re} \eta(\Gamma_{15}, 1) = c \text{Re} \eta(\Gamma_{15}, 2) \neq 0 \),

(B) \( \text{Re} \eta(\Gamma_{25}) \neq 0 \),

(C) \( \text{Im} \eta(\Gamma_{15}, 1) = c \text{Im} \eta(\Gamma_{15}, 2) \neq 0 \),

(D) \( \text{Im} \eta(\Gamma_{25}) \neq 0 \),

where \( c \) is a nonzero constant. Therefore, a condensation of excitons in \( \Gamma_{15} \) and in \( \Gamma_{25} \) do not occur simultaneously. In each case among (A)-(D), all directions of the vector \( \eta \) are degenerate, and this degeneracy will be lifted in the quartic order, as we shall see later. All these states are accompanied by a lattice distortion. This distortion, however, is expected to be rather small because it couples to the order parameter in the quadratic order, not linear order. Indeed the tetragonal distortion detected by X-ray scattering is as small as 0.03% \[13\].

The states (A),(B) preserve time-reversal symmetry and thus nonmagnetic. From symmetry consideration, this implies that neither the ME nor the piezomagnetic (PM) effect will be observed \[19\]. Roughly speaking these states are far from showing ferromagnetism.

To study which state is realized, we should know the coefficients \( A_i, B_i \) in eq.\[3\], which are related to the following matrix elements for the exchange interaction by the Hartree-Fock approximation \[3\].

\[
\int \text{d}x\int \text{d}x'\phi^a_{Q_i}(x)\phi^a_{Q_j}(x)\phi^b_{Q_i}(x')\phi^b_{Q_j}(x'),
\]

where \( \phi^a_{Q_i}(x) \) is Bloch wave function of the c-band \((c = a,b)\) at \( k = Q_i \), \( \varepsilon \) is a dielectric constant. In the calculation of these matrix elements, we neglect the spin-orbit coupling. To calculate \( \phi^a_{Q_i}(x) \) we proceed as follows. We define \( \phi^b_{Q_i, X_3} \) and \( \phi^b_{Q_i, X'_3} \) as linear combinations of \( p \)-orbitals of \( B \) with \( X_3 \) and \( X'_3 \), respectively, and \( \phi^a_{Q_i, X'_3} \) as a linear combination of \( d \)-orbitals of \( Ca \) with \( X'_3 \). Then, \( \phi^a_{Q_i}(x) \) is defined as a bonding orbital of \( \phi^b_{Q_i, X_3} \) and \( \phi^a_{Q_i, X'_3} \), and \( \phi^a_{Q_i}(x) \) is equal to \( \phi^b_{Q_i, X_3} \), with
proper normalization. We evaluated the coefficients in (1), and found that even if coupling terms between the three X-points are included, the coefficients for the imaginary parts of the order parameters are smaller than those for the real parts. Therefore, the states (C) and (D) would be favorable than (A) or (B). Thus, from now on we shall concentrate on (C) and (D).

The states (C) and (D) break both the inversion and the time-reversal symmetries; they are magnetic states. A crucial observation is that they preserve the time-reversal symmetries; they are magnetic states. Therefore, the states (C) and (D) are antiferromagnetic. This agrees with the result of the μSR measurement [10] with a moment of 0.0039μB/mol. Note that the magnetic unit cell is identical with the original unit cell. Thus, no extra Bragg spots appear below the AF transition. (II) The RI symmetry also prohibits the PM effect. This follows because a stress cannot break the RI symmetry which impedes ferromagnetism. Nevertheless, a gradient of stress can break this symmetry and will induce ferromagnetism. We note in passing that if intervalley excitons condense, i.e. the assumption (ii) is violated, the PM effect can occur. (III) The RI-invariance results in the linear ME effect, as observed in Cr2O3 [23]. This effect will occur only below the Néel temperature. Generally, RI-invariant materials with broken R- and I-symmetry will exhibit the NR effect [23].

Let us consider quartic order terms Φ(4) in the GL free energy, which lifts the degeneracy in the direction of 1/2. We do not write down its lengthy formula here [24]. By minimizing Φ(2) + Φ(4), we find four possibilities:

- C-1 Im η(Γ15, 1) = c1 Im η(Γ15, 2) = (0, 0, c2),
- C-2 Im η(Γ15, 1) = c1 Im η(Γ15, 2) = (c2, c2, c2),
- D-1 Im η(Γ25) = (0, 0, 0),
- D-2 Im η(Γ25) = (c, c, c),

where c's are constants. The direction of the lattice distortion is tetragonal in (C-1) and (D-1) and is trigonal in (C-2) and (D-2). Magnetic point groups G for these states are (C-1) 4/mmm, (C-2) 3m, (D-1) 4'/mmm, (D-2) 3m'. In each case among (C-1)-(D-2), there are two types of degenerate AF domains, when we fix the axis of tetragonal or trigonal distortion. Since there are three and four choices of axes for tetragonal and trigonal cases, respectively, total degeneracy is six in (C-1)(D-1) and eight in (C-2)(D-2), which is equal to an order of the quotient group (Oh × (E, R))/G. We can draw some analogies with anisotropic superconductivity (SC).

The order parameters η of triplet excitons correspond to the d-vector in triplet SC. It is nevertheless misleading to look for SC counterparts of our phases (C-1)-(D-2), because our order parameters are confined in the neighborhood of the three X points. They are triplet and even functions in k, which never occurs in the SC.

Information for an ME effect can be obtained from ref. [19]. When we write a bilinear term of H and E in the free energy as αijHjEj, the property tensor αij is

\[
\begin{align*}
\text{(C-1)} & \begin{pmatrix} 0 & \alpha_1 & 0 \\ -\alpha_1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
\text{(C-2)} & \begin{pmatrix} 0 & \alpha_1 & -\alpha_1 \\ -\alpha_1 & 0 & \alpha_1 \\ \alpha_1 & -\alpha_1 & 0 \end{pmatrix}, \\
\text{(D-1)} & \begin{pmatrix} 0 & \alpha_1 & 0 \\ \alpha_1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
\text{(D-2)} & \begin{pmatrix} 0 & \alpha_2 & \alpha_2 \\ \alpha_2 & 0 & \alpha_2 \\ \alpha_2 & \alpha_2 & 0 \end{pmatrix}.
\end{align*}
\]

These explicit forms of α contain information on a direction of magnetization M under an electric field E and that of polarization P under a magnetic field B. In particular, in (C-1) and (C-2), M ⊥ E and P ⊥ B always hold. Thus, measurement of the ME effect with a single crystal of CaB6 will manifest which of these four is realized. Experimentally, domain structure of the AF develops, and the sign of α is reversed when the staggered magnetization is reversed. In measurement of the ME effect, the domain structure can be aligned by a magnetoelectric annealing, in which the sample is cooled under both electric and magnetic fields. Domain boundaries between the two AF domains can exhibit interesting properties. As in boundaries between two SC domains with broken time-reversal symmetry [13], localized current and magnetic moment are induced near the boundary. In the present case it is interpreted as the ME effect.

We remark on the recent results of X-ray scattering and Raman scattering [15], which strongly support our theory. They show a tetragonal distortion below 600K, which indicates that (C-1) or (D-1) is the case. Furthermore, inversion-symmetry breaking does not appear in the Raman spectrum [24], which is consistent with (C) or (D), but not with (A) or (B). Thus, (C-1) and (D-1) are the only possibilities totally consistent with [15].

The ferromagnetism in the thin-film CaB6 is interpreted as caused by an electric field between vacuum and the substrate. For the powder experiment and the La-doping experiment, the explanation is more delicate. We
believe that the carriers by La-doping are trapped by impurities/defects and create local electric fields. Therefore, an internal electric field and/or a gradient of a strain has a random direction, and hence the magnetic moment is induced locally due to this mechanism. At first sight they appear to cancel with each other, giving zero or quite small uniform magnetization, which contradicts with the experiments. However the random direction of the frozen electric field and the external magnetic field determine the domain structure of the AF; the free energy to be minimized is composed of (i) the energy gain due to the magnetization in the external magnetic field and (ii) the elastic energy loss of the spatial change of the order parameter. Therefore, the pinning of the domain-wall motion leads to the hysteresis behavior, which is regarded as the experimental signature of the “ferromagnetism”. The detailed study of the magnetization curve including its dependence on the sweeping time, however, can distinguish it from the real ferromagnetism.

Other peculiarities of Ca$_{1-x}$La$_x$B$_6$ can also be explained as well. The high Curie temperature (∼600K) is nothing but a Néel temperature of the parent compound CaB$_6$, and is not contradictory with a tiny magnetic moment. A rather narrow range ($x \lesssim 0.01$) of La-doping allowing ferromagnetism is attributed to fragility of excitonic state by a small amount of impurities [26,27]. Moreover, our scenario is also consistent with the experimental results that deficiency in Ca sites [28] or doping of divalent elements like Ba [1] or Sr [29] induces ferromagnetism. It is also confirmed numerically by a supercell approach that imperfections and surfaces can induce a local moment [30]. It is hard to explain them within the spin-doping scenario [1]. Furthermore, strangely enough, it is hard to find a correlation between magnetism and electrical resistivity, as seen in magnetization [28] and in nuclear magnetic resonance [31]. This novelty is a natural consequence of our scenario: electrical resistivity is mainly due to doped carriers, while the magnetization is due to local lattice distortion and/or electric field.

The ESR experiments by Kunii [10] also support the above scenario. The ESR data show that in a disk-shaped Ca$_{0.995}$La$_{0.005}$B$_6$, the magnetic moment only exists within the surface layer of ∼1.5μm thick. Furthermore, the moment $\mathbf{M}$ does not orient in the direction of $\mathbf{H}$, i.e. it feels strong magnetic anisotropy to keep the moment within the disk plane. This might be due to the long-range dipolar energy, and not due to the above scenario. Nevertheless, it is unlikely that the long-range dipolar energy causes such a strong anisotropy. This point requires further investigation.

Let us, for the moment, assume that this strong anisotropy is mainly caused by the exciton condensation and the ME mechanism. Since this electric field should be perpendicular to the plane, the strong easy-plane anisotropy parallel to the surface implies that $\mathbf{M} \cdot \mathbf{E}$. Therefore, among the four cases, (C-1) or (C-2) are compatible. Together with the result of Raman scattering, (C-1) is the most promising candidate for CaB$_6$.

We mention here a role of the spin-orbit coupling. In the limit of zero spin-orbit coupling, the states (C) and (D) become degenerate, and the quartic-order terms in the GL free energy do not lift this degeneracy. Sixth-order terms will lift it, and a resulting state will belong to either 4/m/m/m or 4/m/m/m. Both of them still lead to the ME effect in the absence of the spin-orbit coupling; this ME effect must be generated from an orbital motion. Thus, the AF state in CaB$_6$ has an orbital nature as well as a spin nature. With spin-orbit interaction, these two are inseparably mixed together.

In conclusion, we have studied the symmetry properties of the excitonic state in CaB$_6$, and found that the triplet excitonic state with broken time-reversal and inversion symmetries offers a natural explanation, in terms of the ME effect, for the novel ferromagnetism emerging in La-doping or thin-film fabrication. This scenario can be tested experimentally by measurements of the ME effect and the optical non-reciprocal effect in single crystal of the parent compound CaB$_6$.

The authors thank helpful discussion with Y. Tokura, H. Takagi, Y. Tanabe and K. Ohgushi. We acknowledge support by Grant-in-Aids from the Ministry of Education, Culture, Sports, Science and Technology.

* E-mail address: murakami@appi.t.u-tokyo.ac.jp
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The pure imaginary order parameters in this letter correspond to Class II and III in \cite{5}, which break time-reversal symmetry. Likewise the real parts correspond to Class I and IV in \cite{5}, with time-reversal symmetry being preserved. Thus our observation that the order parameters become pure imaginary coincides with the result in \cite{5} that the mixture of Classes II and III is the most favorable state in the presence of spin-orbit coupling, provided the electron-phonon coupling is not so strong.