Theory of Ferromagnetism in $Ca_{1-x}La_xB_6$

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*

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Novel ferromagnetism in $Ca_{1-x}La_xB_6$ is studied in terms of the Ginzburg-Landau theory for excitonic-order parameters, taking into account symmetry of the wave functions. 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 novelties of the ferromagnetism and predicts a number of magnetic properties, including the magnetoelectric effect, which can be tested experimentally.

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Novel ferromagnetism in $Ca_{1-x}La_xB_6$ [1] has been the subject of extensive studies due to its high Curie temperature (~600 K) 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 [2]. An alternative explanation [3,4] is based on the excitonic state [5] of the parent material CaB_6. The parent compound CaB_6 has a cubic structure, and some band structure calculations [6,7] 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 [3]. By La doping the extra electrons are doped into this excitonic insulator, and it has been found in the mean-field approximation that their spins are perfectly polarized [3]. 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 ferromagnetic moments are questioned [8]. Several experiments suggest that the ferromagnetism is not a bulk phenomenon, and occurs only in the thin film sample [9], or near the surface as evidenced by an electron spin resonance (ESR) experiment [10].

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 [3] with broken time-reversal (R) and inversion (I) symmetries, while their product RI is kept intact [3]. This means that CaB_6 is an antiferromagnet (AF), and the ferromagnetism is induced by the magnetoelectric (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 [3,4], though all these theories are based on exciton condensation.

This scenario of exciton condensation is justified when the band structure has a small overlap or gap at the X points. It is, however, still in controversy whether it is the case. Contrary to the calculation using the local density approximation (LDA) [6,7], more recent LDA + GW calculation [11] suggested a large gap of 0.8 eV, too large compared with the energy scale for exciton binding energy (~600 K). An angle-resolved photoemission spectrum (ARPES) [12] also shows a large gap of order 1 eV, and is in good accordance with the GW result. Nevertheless, there is still enough evidence for believing a small gap or a small overlap. First, another recent GW calculation [13] shows a small overlap at the X points. Second, de Haas–van Alphen measurement [14] finds Fermi surfaces of both electrons and holes. Third, the ARPES experiment is surface sensitive, and one can argue that the ARPES result [12] of the large gap might be attributed to surface effect. Fourth, measurements of x-ray scattering and Raman scattering in CaB_6 [15] shows an anomaly at 600 K, 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 AF, as indicated in muon spin resonance (μSR) measurements [16]. 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 $\mathbf{Q}_x$, $\mathbf{Q}_y$, $\mathbf{Q}_z$ denote the three X points $(\pi, 0, 0)$, $(0, \pi, 0)$, $(0, 0, \pi)$ in the cubic Brillouin zone. When excitons are formed, excitonic order parameters $\langle b^\dagger_{\mathbf{k}\alpha} a_{\mathbf{k}'\beta}\rangle$ will have nonzero values, where $b_{\mathbf{k}\sigma}$ and $a_{\mathbf{k}\sigma}$ are annihilation operators of electrons with spin σ at the conduction and the valence bands, respectively [5]. Because the excitonic instability occurs only in the vicinity of the three X points, we assume the following: (i) The order parameters are $\mathbf{k}$ independent near the X points. (ii) The order parameters connecting different X points are neglected [4]. As a result we keep only the order parameters $\eta(\mathbf{Q}_i)_{\alpha\beta} = \langle b^\dagger_{\mathbf{Q}_i\alpha} a_{\mathbf{Q}_i\beta}\rangle$. The cubic ($O_h$) symmetry of CaB_6 restricts

a form of the GL free energy Φ, as is similar for unconventional superconductors [17,18]. At the X points, the $\mathbf{k}$ group has a tetragonal (D_{4h}) symmetry, and the conduction and the valence band states belong to X_3' and X_3 representations, respectively [6,7]. Without the spin-orbit coupling, the order parameter $\eta(\mathbf{Q}_i)_{\alpha\beta}$ belongs to $X_3 \times X_3' = X_1'$. 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 η 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 will be multiplied, and we get $X_4' + X_5'$ in the D_{4h} group. Explicitly, for the triplet excitons at the $\mathbf{Q}_z$, the $S_z = 0$ component $\eta_{\downarrow\downarrow} - \eta_{\uparrow\uparrow}$ obeys the X_4', while the $S_z = \pm 1$ components $\eta_{\uparrow\downarrow}, \eta_{\downarrow\uparrow}$ obey the X_5'. Here the spin-quantization axis is taken to be $+z$ direction. Since we are taking into account the spin-orbit coupling, these up and down spins should be interpreted as pseudospins [18].

When we consider the three X points, the cubic symmetry is restored since the order parameters have a wave vector $\mathbf{q} = 0$. 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 Γ_{15} and like $(x(y^2 - z^2), y(z^2 - x^2), z(x^2 - y^2))$ for Γ_{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

$$\eta_z(\Gamma_{15}, 1) = \frac{i}{\sqrt{2}}[\eta_{\downarrow\downarrow}(\mathbf{Q}_z) - \eta_{\uparrow\uparrow}(\mathbf{Q}_z)], \tag{1}$$

$$\eta_z(\Gamma_{15}, 2) = -\tfrac{1}{2}\{i[\eta_{\uparrow\downarrow}(\mathbf{Q}_y) + \eta_{\downarrow\uparrow}(\mathbf{Q}_y)] + [\eta_{\uparrow\downarrow}(\mathbf{Q}_x) - \eta_{\downarrow\uparrow}(\mathbf{Q}_x)]\}, \tag{2}$$

$$\eta_{z(x^2-y^2)}(\Gamma_{25}) = \tfrac{1}{2}\{i[\eta_{\uparrow\downarrow}(\mathbf{Q}_y) + \eta_{\downarrow\uparrow}(\mathbf{Q}_y)] - [\eta_{\uparrow\downarrow}(\mathbf{Q}_x) - \eta_{\downarrow\uparrow}(\mathbf{Q}_x)]\}. \tag{3}$$

Here the spin-quantization axis in $\eta_{\alpha\beta}(\mathbf{Q}_i)$ is taken as $+i$ 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 Φ should be invariant under the elements of O_h and under the time-reversal R. We make two remarks helpful in writing down Φ. First, only even-order terms in $\boldsymbol{\eta}$ are allowed by the inversion symmetry. Second, owing to the time-reversal symmetry, the order of $\mathrm{Im}\boldsymbol{\eta}$ in each term should be even. Thus, Φ is given up to quadratic order as

$$\Phi^{(2)} = A_1 \sum_i (\mathrm{Re}\eta_i(\Gamma_{15}, 1))^2 + A_2 \sum_i (\mathrm{Re}\eta_i(\Gamma_{15}, 2))^2 + A_3 \sum_i \mathrm{Re}\eta_i(\Gamma_{15}, 1)\,\mathrm{Re}\eta_i(\Gamma_{15}, 2) + A_4 \sum_j (\mathrm{Re}\eta_j(\Gamma_{25}))^2 + B_1 \sum_i (\mathrm{Im}\eta_i(\Gamma_{15}, 1))^2 + B_2 \sum_i (\mathrm{Im}\eta_i(\Gamma_{15}, 2))^2 + B_3 \sum_i \mathrm{Im}\eta_i(\Gamma_{15}, 1)\,\mathrm{Im}\eta_i(\Gamma_{15}, 2) + B_4 \sum_j (\mathrm{Im}\eta_j(\Gamma_{25}))^2. \tag{4}$$

Therefore, as the temperature is lowered, one of the following states will be realized: (A) $\mathrm{Re}\boldsymbol{\eta}(\Gamma_{15}, 1) = c\,\mathrm{Re}\boldsymbol{\eta}(\Gamma_{15}, 2) \neq 0$, (B) $\mathrm{Re}\boldsymbol{\eta}(\Gamma_{25}) \neq 0$, (C) $\mathrm{Im}\boldsymbol{\eta}(\Gamma_{15}, 1) = c\,\mathrm{Im}\boldsymbol{\eta}(\Gamma_{15}, 2) \neq 0$, and (D) $\mathrm{Im}\boldsymbol{\eta}(\Gamma_{25}) \neq 0$, where c is a nonzero constant. A condensation of excitons in Γ_{15} and in Γ_{25} do not occur simultaneously. In each case among (A)–(D), all directions of the vector $\boldsymbol{\eta}$ are degenerate, and this degeneracy is lifted in the quartic order, as we shall see later. All these states are accompanied by a lattice distortion. This distortion is expected to be 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% [15].

The states (A),(B) preserve time-reversal symmetry and thus are 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. (4), which are related to the following matrix elements for the exchange interaction by the Hartree-Fock approximation [5]:

$$\int d\mathbf{x} \int d\mathbf{x}'\, \phi^c_{\mathbf{Q}_i}(\mathbf{x})\phi^{c'}_{\mathbf{Q}_j}(\mathbf{x})\, \frac{e^2}{\varepsilon|\mathbf{x} - \mathbf{x}'|}\, \phi^{c''}_{\mathbf{Q}_j}(\mathbf{x}')\phi^{c'''}_{\mathbf{Q}_i}(\mathbf{x}'),$$

where $\phi^c_{\mathbf{Q}_i}(\mathbf{x})$ is the Bloch wave function of the c band ($c = a, b$) at $\mathbf{k} = \mathbf{Q}_i$, ε is a dielectric constant. In the calculation of these matrix elements, we neglect the spin-orbit coupling. To calculate $\phi^c_{\mathbf{Q}_i}(\mathbf{x})$ we proceed as follows. We define $\phi^{B:p}_{\mathbf{Q}_i,X_3}$ and $\phi^{B:p}_{\mathbf{Q}_i,X_3'}$ as linear combinations of p orbitals of B with X_3 and X_3', respectively, and $\phi^{\mathrm{Ca}:d}_{\mathbf{Q}_i,X_3'}$ as a linear combination of d orbitals of Ca with X_3'. Then, $\phi^b_{\mathbf{Q}_i}(\mathbf{x})$ is defined as a bonding orbital of $\phi^{B:p}_{\mathbf{Q}_i,X_3'}$ and $\phi^{\mathrm{Ca}:d}_{\mathbf{Q}_i,X_3'}$, and $\phi^a_{\mathbf{Q}_i}(\mathbf{x})$ is equal to $\phi^{B:p}_{\mathbf{Q}_i,X_3}$, with proper normalization [6]. We evaluated the coefficients in (4), 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 more favorable than (A) or (B). Thus, from now on we shall concentrate on (C) and (D) [20].

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 *RI* symmetry [3], leading to interesting consequences listed below. (I) The *RI* symmetry prohibits a uniform magnetic moment. Dzyaloshinskii used this symmetry to explain why weak ferromagnetism is present in α-Fe_2O_3 while not in Cr_2O_3 [21]. Thus the states (C) and (D) are antiferromagnetic. This agrees with the result of the μSR measurement [16] with a moment of $0.0039\mu_B$/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 prohibits the PM effect, 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 Cr_2O_3 [22]. This occurs because an external electric field $\mathbf{E}$ breaks this *RI* symmetry and enables ferromagnetism [22]. An electric field $\mathbf{E}$ belongs to the Γ_{15}, and couples linearly with the order parameters in Γ_{15} as

$$\delta\Phi = -C_1\mathbf{E}\cdot\mathrm{Re}\boldsymbol{\eta}(\Gamma_{15},1) - C_2\mathbf{E}\cdot\mathrm{Re}\boldsymbol{\eta}(\Gamma_{15},2).$$

Here the imaginary parts of the order parameters are absent due to invariance of $\delta\Phi$ under time reversal. Thus, in the presence of $\mathbf{E}$, both the real and imaginary parts of the order parameters acquire nonvanishing values, resulting in a uniform moment. As for the Γ_{25}, a similar effect can be found. (IV) The optical nonreciprocal (NR) effect in reflection is predicted to occur, as is similar to Cr_2O_3 [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 $\Phi^{(4)}$ in the GL free energy, which lifts the degeneracy in the direction of $\boldsymbol{\eta}$. We do not write down its lengthy formula here [24]. By minimizing $\Phi^{(2)} + \Phi^{(4)}$, we find four possibilities: (C1) $\mathrm{Im}\boldsymbol{\eta}(\Gamma_{15},1) = c_1\,\mathrm{Im}\boldsymbol{\eta}(\Gamma_{15},2) = (0,0,c_2)$, (C2) $\mathrm{Im}\boldsymbol{\eta}(\Gamma_{15},1) = c_1\,\mathrm{Im}\boldsymbol{\eta}(\Gamma_{15},2) = (c_2,c_2,c_2)$, (D1) $\mathrm{Im}\boldsymbol{\eta}(\Gamma_{25}) = (0,0,c)$, and (D2) $\mathrm{Im}\boldsymbol{\eta}(\Gamma_{25}) = (c,c,c)$, where c's are constants. The direction of the lattice distortion is tetragonal in (C1) and (D1) and is trigonal in (C2) and (D2). Magnetic point groups G for these states are (C1) $4/m'mm$, (C2) $\bar{3}'m$, (D1) $4'/m'm'm$, (D2) $\bar{3}'m'$. In each case among (C1)-(D2), 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 (C1) (D1) and eight in (C2) (D2), which is equal to an order of the quotient group $(O_h \times \{E,R\})/G$. We can draw some analogies with superconductivity (SC). The order parameters $\boldsymbol{\eta}$ of triplet excitons correspond to the d vector in triplet SC. It is nevertheless misleading to look for SC counterparts of our phases (C1)-(D2), because our order parameters are confined near the three X points. They are triplet and even functions in $\mathbf{k}$, which never occurs in the SC.

Information for an ME effect can be obtained from Ref. [19]. When we write a bilinear term of $\mathbf{H}$ and $\mathbf{E}$ in the free energy as $\alpha_{ij}H_iE_j$, the property tensor α_{ij} is

$$\text{(C1)}\begin{pmatrix} 0 & \alpha_1 & 0 \\ -\alpha_1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \text{(C2)}\begin{pmatrix} 0 & \alpha_1 & -\alpha_1 \\ -\alpha_1 & 0 & \alpha_1 \\ \alpha_1 & -\alpha_1 & 0 \end{pmatrix},$$

$$\text{(D1)}\begin{pmatrix} 0 & \alpha_1 & 0 \\ \alpha_1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \text{(D2)}\begin{pmatrix} \alpha_1 & \alpha_2 & \alpha_2 \\ \alpha_2 & \alpha_1 & \alpha_2 \\ \alpha_2 & \alpha_2 & \alpha_1 \end{pmatrix}.$$

These explicit forms of $\boldsymbol{\alpha}$ contain information on a direction of magnetization $\mathbf{M}$ under an electric field $\mathbf{E}$ and that of polarization $\mathbf{P}$ under a magnetic field $\mathbf{B}$. In particular, in (C1) and (C2), $\mathbf{M} \perp \mathbf{E}$ and $\mathbf{P} \perp \mathbf{B}$ always hold. Thus, measurement of the ME effect with a single crystal of CaB_6 will manifest which of these four is realized. Experimentally, domain structure of the AF develops, and the sign of $\boldsymbol{\alpha}$ 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 [18], localized current and magnetic moment are induced near the boundary. In the present case it is interpreted as the ME effect.

We comment on the recent results of x-ray scattering and Raman scattering [15], which strongly support our theory. They show a tetragonal distortion below 600 K, which indicates that (C1) or (D1) is the case. Furthermore, inversion-symmetry breaking does not appear in the Raman spectrum [25], which is consistent with (C) or (D), but not with (A) or (B). Thus, (C1) and (D1) are the only possibilities totally consistent with [15].

The ferromagnetism in the thin-film CaB_6 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 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 determines 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 hysteresis, which is regarded as the experimental signature of the "ferromagnetism."

Other peculiarities of $Ca_{1-x}La_xB_6$ can also be explained as well. The high Curie temperature ($\sim$600 K) is nothing

but a Néel temperature of the parent compound CaB_6. A rather narrow range ($x \lesssim 0.01$) of La doping allowing ferromagnetism is attributed to fragility of excitonic order 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 [3]. 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 exists only within the surface layer of ~ 1.5 μm thick. Furthermore, the moment $\mathbf{M}$ 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 ME mechanism. Since this electric field is perpendicular to the plane, the strong easy-plane anisotropy parallel to the surface implies that $\mathbf{M} \perp \mathbf{E}$. Therefore, among the four cases, (C1) or (C2) are compatible. Together with the result of Raman scattering, (C1) 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 $4/m'mm$ 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 nonreciprocal effect in a single crystal of the parent compound CaB_6.

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*Email address: murakami@appi.t.u-tokyo.ac.jp

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