Impurity-induced ferromagnetism in a doped triplet excitonic insulator

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The theory of impurities in excitonic insulator is investigated in the light of the recent experiments on hexaborides. First, we study the bound state around the impurity and find that the bound-state emerges when $\text{Re}\,\Delta$ is positive. Second, we study the continuum state using Abrikosov-Gor'kov's approach. We find that the energy gap is reduced strongly when $\text{Im}\,\Delta = 0$. Finally, we solve Bogoliubov–de Gennes equations for excitonic insulator numerically. We get the results consistent with the analytic ones. We also find that incomplete ferromagnetism appears in doped triplet excitonic insulator with impurity. We make a short qualitative discussion on the ferromagnetism of doped hexaborides using our result.

I. INTRODUCTION

The discovery of weak ferromagnetism in La-doped CaB_6 is one of the greatest surprises in the recent study of ferromagnetism.[1] This material shows ferromagnetism with high Curie temperature about $T_c \sim 600$ K and with small magnetic moment. Zhitomirsky *et al.*[2] claimed that the theory of the excitonic ferromagnetism, which was originally proposed by Volkov *et al.*,[3] can account for this curious ferromagnetism. Their proposal has brought renewed interests in excitonic insulator, which was vigorously studied theoretically in 1960's.

After the proposal by Zhitomirsky *et al.*, some authors tried to improve their theory. Balents and Varma[4] and Barzykin and Gor'kov[5] independently discussed that, to explain this ferromagnetism, the approximation of excitonic insulator should be improved by considering the formation of superstructure or long-range Coulomb interaction.

The effect of impurities will also be important for the excitonic insulator. In this paper, we study the effect of impurities in excitonic insulators.

The destruction of excitonic insulator by the impurity was discussed by Zittartz.[6] He showed that the intraband scattering by impurity reduces the energy gap just as the magnetic impurity in superconductor. In this paper we study the interband scattering by impurity. We show that the interband scattering cause the formation of the bound states and the reduction of the energy gap. We also show that this interband scattering breaks the $U(1)$ symmetry of Hamiltonian. This is due to the fact that the phase of the order parameter is determined by the difference of phase between conduction and valence bands. The reduction of the energy gap and the energy of the the bound state is controlled by the phase of order parameter. The phase dependence of the energy gap and the bound state brings the ferromagnetic ordering of doped electrons in a triplet excitonic insulator, because the phase of order parameter differs by π between $\Delta_\uparrow$ and $\Delta_\downarrow$.

This paper is constructed as follows. In the next section, we introduce the Hamiltonian and show the breaking of $U(1)$ symmetry by the interband scattering. In Secs. III and IV we investigate the effect of impurities on the bound and continuum states. It is shown that the bound states emerge only when $\text{Re}\,\Delta$ is positive and that the binding energy de-

pends on the phase of the order parameter. We also show that in the continuum states the energy gap is strongly suppressed when $\text{Re}\,\Delta = 0$. In Sec. V we solve the Bogoliubov–de Gennes equation for excitonic insulator numerically. The results support the analytic discussion above. We also find that, when ϕ is close to $\pi/2$, the magnetic moment of doped electrons is reduced. In the last section, for summary and discussion, we discuss about the application of our results to the ferromagnetism in hexaborides.

II. BREAKING OF $U(1)$ SYMMETRY BY INTERBAND SCATTERING

First we study the following Hamiltonian:

$$H_0 = \sum_{k,\sigma} (\epsilon_k^a a_{k,\sigma}^\dagger a_{k,\sigma} + \epsilon_k^b b_{k,\sigma}^\dagger b_{k,\sigma})$$

$$+ \frac{V}{\Omega} \sum_{k,k',q,\sigma,\sigma'} a_{k,\sigma}^\dagger b_{q-k,\sigma'}^\dagger b_{q-k',\sigma'} a_{k',\sigma}$$

$$+ \frac{U}{\Omega} \sum_{k,k',q,\sigma,\sigma'} a_{k,\sigma}^\dagger b_{q-k,\sigma'}^\dagger a_{q-k',\sigma'} b_{k',\sigma}. \quad (1)$$

Here $a_{k,\sigma}$ and $b_{k,\sigma}$ are annihilation operators of electrons in the lower and upper band, ϵ_k^a and ϵ_k^b are kinetic energy of electrons, and V and U are exchange and direct interaction between two bands. The nesting of Fermi surfaces between two of the electron bands brings the formation of excitonic order parameter.[7]

We introduce the interband scattering by impurity H_{imp} as

$$H_{\text{imp}} = \sum V_{\text{imp}} a_{i\sigma}^\dagger b_{i\sigma} + \text{c.c.} \quad (2)$$

This interband scattering is important because this term breaks the $U(1)$ symmetry of the system. The Hamiltonian (1) for the clean system is invariant under the $U(1) \times U(1)$ transformation, $a_i \to a_i e^{i\phi_1}$ and $b_i \to b_i e^{i\phi_2}$. However, the interband scattering term reduces this symmetry to the diagonal $U(1)$ symmetry because the $U(1) \times U(1)$ transformation changes the impurity term as $V_{\text{imp}} a_{i\sigma}^\dagger b_{i\sigma} \to V_{\text{imp}} a_{i\sigma}^\dagger b_{i\sigma} e^{i(\phi_2 - \phi_1)}$, unless $\phi_1 \neq \phi_2$. This means that to

discuss the impurity effect, we must take the phase of excitonic order parameter, which corresponds to $\langle a^\dagger b\rangle$, into account.

Here we note that in real materials this $U(1)$ symmetry is generally broken even without impurities due to other interactions that are not included in the Hamiltonian (1). The interband pair scattering term $V'a_{k\sigma}^\dagger a_{k'-\sigma}^\dagger b_{k'-\sigma}b_{k\sigma}$ is one of such interactions. Therefore we suppose the phase ϕ is determined by such a term. It is interesting to study the stable phase ϕ and discuss the phase dynamics, however, this is beyond the scope of this paper.

Volkov *et al.*, noticed that localized states with uncompensated spin appears in the doped triplet excitonic insulator.[8] They concluded that the bound states appears only when Δ is positive. Their result means that the phase of the order parameter determines the existence of bound state. However, they assume Δ to be real, which needs to be justified by further study. In this paper, we treat the order parameter as the complex variable. Here we introduce the excitonic mean-field order parameter $\Delta_{\sigma\sigma'}$ and write down the mean-field Hamiltonian in pure excitonic system

$$H_{\mathrm{MF}}=\sum_{\sigma,k}\epsilon_k^a a_{k\sigma}^\dagger a_{k\sigma}+\epsilon_k^b b_{k\sigma}^\dagger b_{k\sigma}-\sum_{\sigma,\sigma',k}(\Delta_{\sigma\sigma'}b_{k\sigma'}^\dagger a_{k\sigma}$$
$$+\Delta_{\sigma\sigma'}^\dagger a_{k\sigma}^\dagger b_{k\sigma})-\mu\sum_{\sigma,k}(a_{k\sigma}^\dagger a_{k\sigma}+b_{k\sigma}^\dagger b_{k\sigma}). \quad (3)$$

When we use the Hamiltonian (1), the order parameter $\Delta_{\sigma\sigma'}$ is defined as

$$\Delta_{\sigma\sigma'}=V\sum_k\langle a_{k\sigma}^\dagger b_{k\sigma'}\rangle-U\sum_{k,\sigma''}\delta_{\sigma\sigma'}\langle a_{k\sigma''}^\dagger b_{k\sigma''}\rangle. \quad (4)$$

This Hamiltonian is invariant under the transformation $a_i\rightarrow a_i e^{i\phi_1}$, $b_i\rightarrow b_i e^{i\phi_2}$, and $\Delta_{\sigma\sigma'}\rightarrow e^{i(\phi_2-\phi_1)}$. It is convenient to assume the order parameter $\Delta_{\sigma\sigma'}$ to be real by choosing the appropriate gauge. In this case, the impurity scattering term (2) shows phase dependence,

$$H_{\mathrm{imp}}'=\sum V_{\mathrm{imp}}e^{i\phi}a_{i\sigma}^\dagger b_{i\sigma}+\mathrm{c.c.} \quad (5)$$

In the following two sections, we use Hamiltonians (3) and (5).

III. BOUND-STATE FORMATION AT AN IMPURITY

First, we study the bound state around the impurity in excitonic insulator. We here consider the one-impurity problem. For simplicity, we assume the order parameter $\Delta_{\sigma\sigma'}$ to be diagonal, $\Delta_{\sigma\sigma'}=\Delta_\sigma\delta_{\sigma\sigma'}$. In the singlet excitonic insulator this assumption is correct. We note that in the triplet excitonic insulator we can justify this assumption if the three components of the triplet order parameter $\Delta_i=\sum_{\alpha,\beta}(\sigma_i)_{\alpha\beta}\Delta_{\alpha\beta}$ ($i=x,y,z$) are degenerate. In this case, we can treat up spin and down spin separately. Then from Eq. (3) the Green's function in the mean-field theory is given by

$$G_{\sigma\sigma'}^0(k,\omega)=\begin{pmatrix}\omega-\epsilon_k^a+\mu & -\Delta_\sigma \\ -\Delta_\sigma^* & \omega-\epsilon_k^b+\mu\end{pmatrix}^{-1}\delta_{\sigma\sigma'}. \quad (6)$$

Assuming the impurity potential as pointlike, we can calculate the Green's function $G_{\sigma\sigma'}(k,\omega,k'.\omega)$ using the T-matrix approximation,

$$G_{\sigma\sigma'}(k,\omega,k',\omega)$$
$$=G_{\sigma\sigma'}^0\delta_{kk'}+\sum_{\sigma''}G_{\sigma\sigma''}^0(k,\omega)\Gamma_{\sigma''\sigma''}G_{\sigma''\sigma'}^0(k',\omega),$$
$$(7)$$

$$\Gamma_{\sigma\sigma'}=V_{\sigma\sigma'}^{\mathrm{imp}}+V_{\sigma\sigma''}^{\mathrm{imp}}\sum_{k'}G_{\sigma''\sigma'''}^0(k',\omega)\Gamma_{\sigma'''\sigma'}, \quad (8)$$

and

$$V_{\sigma\sigma'}^{\mathrm{imp}}=\begin{pmatrix}0 & V_{\mathrm{imp}}e^{i\phi} \\ V_{\mathrm{imp}}e^{-i\phi} & 0\end{pmatrix}\delta_{\sigma\sigma'}. \quad (9)$$

After some calculation with the assumption $\epsilon^a(k)=-\epsilon^b(k)$ and constant density of states, we get

$$\Gamma_{\sigma\sigma'}=V_{\sigma\sigma'}^{\mathrm{imp}}\left[1-\sum_k G^0(k)V^{\mathrm{imp}}\right]^{-1}, \quad (10)$$

and

$$\sum_k G^0(k)V^{\mathrm{imp}}=\delta_{\sigma\sigma'}\frac{\pi N_F V_{\mathrm{imp}}}{\sqrt{\Delta_\sigma^2-(\omega+\mu)^2}}$$
$$\times\begin{pmatrix}\Delta_\sigma e^{-i\phi} & (-\omega-\mu)e^{i\phi} \\ (-\omega-\mu)e^{-i\phi} & \Delta_\sigma e^{i\phi}\end{pmatrix},$$
$$(11)$$

where N_F is the density-of-states at Fermi energy.

The determinant of matrix $D=1-\Sigma_k G_{\sigma\sigma}^0(k)V^{\mathrm{imp}}$ is given as

$$\det D=\left(1-\frac{\tilde{V}\Delta_\sigma e^{-i\phi}}{\sqrt{\Delta_\sigma^2-(\omega+\mu)^2}}\right)\left(1-\frac{\tilde{V}\Delta_\sigma e^{i\phi}}{\sqrt{\Delta_\sigma^2-(\omega+\mu)^2}}\right)$$
$$-\frac{\tilde{V}^2(\omega+\mu)^2}{\Delta_\sigma^2-(\omega+\mu)^2}$$
$$=1+\tilde{V}^2-2\frac{\tilde{V}\Delta_\sigma\cos\phi}{\sqrt{\Delta_\sigma^2-(\omega+\mu)^2}}, \quad (12)$$

where $\tilde{V}=\pi N_F V_{\mathrm{imp}}$. From this expression, we find that when $\mathrm{Re}(\tilde{V}\Delta\cos\phi)$ is positive, D^{-1} has poles at $\omega=-\mu\pm\sqrt{(1-(4\tilde{V}^2\cos^2\phi)/(1+\tilde{V}^2)^2)}\Delta_\sigma$ and two bound states appear. On the other hand, when $\mathrm{Re}(\tilde{V}\Delta\cos\phi)$ is negative, there exists no bound state. We conclude that the phase of the order parameter controls the energy and existence of bound states. If we set Δ real and positive, there exist bound states at $\omega=-\mu\pm(1-\tilde{V}^2)/(1+\tilde{V}^2)\Delta_\sigma$ when $\phi=0$. Here

we note that this bound state exists even if V_{imp} is very weak. As ϕ changes from 0 to $\pi/2$, the energies of bound states approach to $\omega = -\mu \pm \Delta$ and at $\phi = \pi/2$ the bound states touch the edges of the continuum.

It should be noticed there exists a great difference in the effect of impurities between the singlet excitonic insulator and the triplet one. In the singlet excitonic insulator, $\Delta_\uparrow = \Delta_\downarrow$ and both up-spin and down-spin bound states have the same energy. On the other hand, in the triplet excitonic insulator, $\Delta_\uparrow = -\Delta_\downarrow$ and the bound states of up-spin and down-spin electrons cannot exist at the same time. Therefore spins of the electrons doped into the triplet excitonic insulator align ferromagnetically. For $\phi = \pi/2$, marginal bound states exist for both spin states and the excitonic insulator remains paramagnetic.

IV. REDUCTION OF ENERGY GAP BY IMPURITIES

In the previous section, we studied the formation of a bound state around an impurity. We found that a bound state appears only when $\mathrm{Re}(\tilde{V}\Delta \cos \phi)$ is positive. However, the impurity will also influence the continuum state. For example, it is well known that magnetic impurities in a superconductor reduce the energy gap. Zittartz discussed the effect of intraband scattering by impurities in excitonic insulator and found that it reduces the energy gap in exactly the same way as magnetic impurities do in a superconductor.[6] In this section, we consider the reduction of energy gap by an interband scattering term.

To study the suppression of the energy gap, we use the same technique as Abrikosov and Gor'kov[9] used for a superconductor. For simplicity we again assume that the order parameter is diagonal in spin space. We introduce the renormalized Green's function $\tilde{G}$

$$\tilde{G}_{\sigma\sigma'}(k,\omega) = \begin{pmatrix} \tilde{\omega} - \epsilon_k^a + \mu & -\tilde{\Delta}_\sigma \\ -\tilde{\Delta}_\sigma^* & \tilde{\omega} - \epsilon_k^b + \mu \end{pmatrix}^{-1} \delta_{\sigma\sigma'}. \quad (13)$$

Here $\tilde{\omega}$ and $\tilde{\Delta}$ are the renormalized frequency and order parameter, respectively, and we recovered the translational invariance of Green's function of continuum states by averaging over the impurity positions.

Using the Born approximation, we get

$$\tilde{G}_{\sigma\sigma'}(k,\omega)^{-1} = G_{\sigma\sigma'}^0(k,\omega)^{-1} - \Sigma_{\sigma\sigma'}(k,\omega) \quad (14)$$

and

$$\Sigma_{\sigma\sigma'}(k,\omega) = n_{\mathrm{imp}} \int \frac{d^3k'}{(2\pi)^3} V_{\sigma\sigma''}^{\mathrm{imp}} \tilde{G}_{\sigma''\sigma'''}(k',\omega) V_{\sigma'''\sigma'}^{\mathrm{imp}}. \quad (15)$$
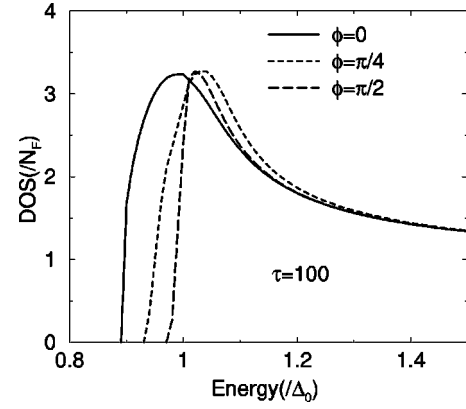
Integrating over k' we obtain

FIG. 1. Phase dependence of density-of-states when $\tau = 100$.

$$\Sigma_{\sigma\sigma'}(k,\omega) = \frac{V_{\mathrm{imp}}^2 n_{\mathrm{imp}} \pi N_F}{\sqrt{|\tilde{\Delta}_\sigma|^2 - (\tilde{\omega}+\mu)^2}}$$
$$\times \begin{pmatrix} \tilde{\omega}+\mu & -\tilde{\Delta}_\sigma^* e^{2i\phi} \\ \tilde{\Delta}_\sigma e^{-2i\phi} & -\tilde{\omega}+\mu \end{pmatrix} \delta_{\sigma\sigma'}, \quad (16)$$

where we assumed $\epsilon_k^a = -\epsilon_k^b$ and constant density-of-states as before. After some calculations we get the following equations for $\tilde{\omega}$ and $\tilde{\Delta}_\sigma$:

$$\tilde{\omega} = \omega + \frac{1}{\tau} \frac{\tilde{\omega}+\mu}{\sqrt{|\tilde{\Delta}_\sigma|^2 - (\tilde{\omega}+\mu)^2}}, \quad (17)$$

$$\tilde{\Delta}_\sigma = \Delta_\sigma - \frac{1}{\tau} \frac{\tilde{\Delta}_\sigma^* e^{-2i\phi}}{\sqrt{|\tilde{\Delta}_\sigma|^2 - (\tilde{\omega}+\mu)^2}}. \quad (18)$$

Here $\tau = 1/n_{\mathrm{imp}} N_F V_{\mathrm{imp}}^2$. If $\phi = 0$, these equations are the same as those for magnetic impurities in a superconductor. Therefore if $\phi = 0$, the energy gap is strongly suppressed by impurities. As ϕ develops from 0, the energy gap increases and at $\phi = \pi/2$, the energy gap becomes almost the same as that of pure excitonic insulator, because at $\phi = \pi/2$ Eqs. (17) and (18) have the same form as those for nonmagnetic impurities in a superconductor.

The density-of-states of electrons $N(\omega)$ is given by

$$N(\omega) = -\frac{1}{2\pi} \mathrm{Im} \int \mathrm{Tr}\, G(k,\omega) \frac{d^3k}{(2\pi^3)}$$

$$= -N_F \mathrm{Im} \sum_\sigma \left(\frac{\tilde{\omega}+\mu}{|\tilde{\Delta}_\sigma|^2 - (\tilde{\omega}+\mu)^2} \right). \quad (19)$$

For some typical values of ϕ, we plot the density-of-states in Fig. 1. From this figure, we find that the reduction of the energy gap is a maximum at $\phi = 0$. This is consistent with the above discussion.

V. NUMERICAL SOLUTION OF
BOGOLIUBOV−de GENNES EQUATION

From the analysis in the previous sections, we found that the phase of the order parameter determines the existence of the bound state as well as the reduction of the energy gap. These two effects are not independent. For example, for the finite concentration of impurities, the bound states will form an impurity band. On the other hand, if the energy gap of the continuum is strongly reduced, the energy of the bound state present for a single impurity model may be absorbed into the continuum for a finite impurity concentration. To study such possibilities, in this section we solve the Bogoliubov–de Gennes (BdG) equations for excitonic insulator numerically. We confine ourselves to the triplet case, because in the triplet excitonic insulators impurity may invoke magnetic moment as discussed in Sec. III. We also show that incomplete ferromagnetism can appear.

We start from the following Hamiltonian:

$$H_{\text{BdG}} = \sum_{\langle i,j \rangle, \sigma} (-t^a a_{i\sigma}^{\dagger} a_{j\sigma} - t^b b_{i\sigma}^{\dagger} b_{j\sigma})$$

$$- \sum_{i,\sigma,\sigma'} (\Delta_{i,\sigma\sigma'} b_{i\sigma'}^{\dagger} a_{i\sigma} + \text{c.c.}) + V_{\text{imp}} \sum_i (b_{i\sigma}^{\dagger} a_{i\sigma}$$

$$+ \text{c.c.}) - E_a \sum_{i,\sigma} a_{i\sigma}^{\dagger} a_{i\sigma} - E_b \sum_{i,\sigma} b_{i\sigma}^{\dagger} b_{i\sigma}. \qquad (20)$$

The first term is the kinetic term of electrons. Here we assume two-dimensional square lattice and the summation is carried out with nearest neighbor $\langle i,j \rangle$. In the theory of the excitonic insulator, it is often assumed that $\epsilon_k^a = -\epsilon_k^b$, so we take $t^a = -t^b = 1$. In this case, $\epsilon_k^a = -2(\cos k_x + \cos k_y) - E_a$ and $\epsilon_k^b = 2(\cos k_x + \cos k_y) - E_b$. The second term is the interaction term. The order parameter $\Delta_{i,\sigma\sigma'}$ is determined from the Hamiltonian (1) as

$$\Delta_{i\sigma\sigma'} = V\langle a_{i\sigma}^{\dagger} b_{i\sigma'} \rangle - U \delta_{\sigma\sigma'} \sum_{\sigma''} \langle a_{i\sigma''}^{\dagger} b_{i\sigma''} \rangle. \qquad (21)$$

While for $U=0$ the triplet state and singlet state are degenerate, and positive U suppresses the singlet state. In the following numerical calculation we take U large enough to suppress the singlet state completely. The third term describes the impurity scattering and the sum is carried out on the impurity site. The last two terms are the energy-gap term, which determines the overlap of two bands. In the following, we set $E_a = -E_b$. Under this assumption, the Fermi surfaces of two electron bands coincide when we do not dope an electron. The size of the Fermi surfaces depends on E_a. For $E_a < -4t$, $\epsilon_k^a < \epsilon_k^b$ for any k, and the system is a band insulator. On increasing E^a, the Fermi surface emerges near $k = (\pi, \pi)$ and the system becomes a semimetal. When $E_a > 4t$ it becomes a band insulator again, because $\epsilon_k^b < \epsilon_k^a$.

We solve Eqs. (20) and (21) numerically keeping the number of electrons constant. First, we diagonalize the Eq. (20) and calculate the eigenenergy and eigenstates. Next we take the eigenstates with small eigenvalues, up to the number of electrons. The order parameter is calculated by Eq. (21).
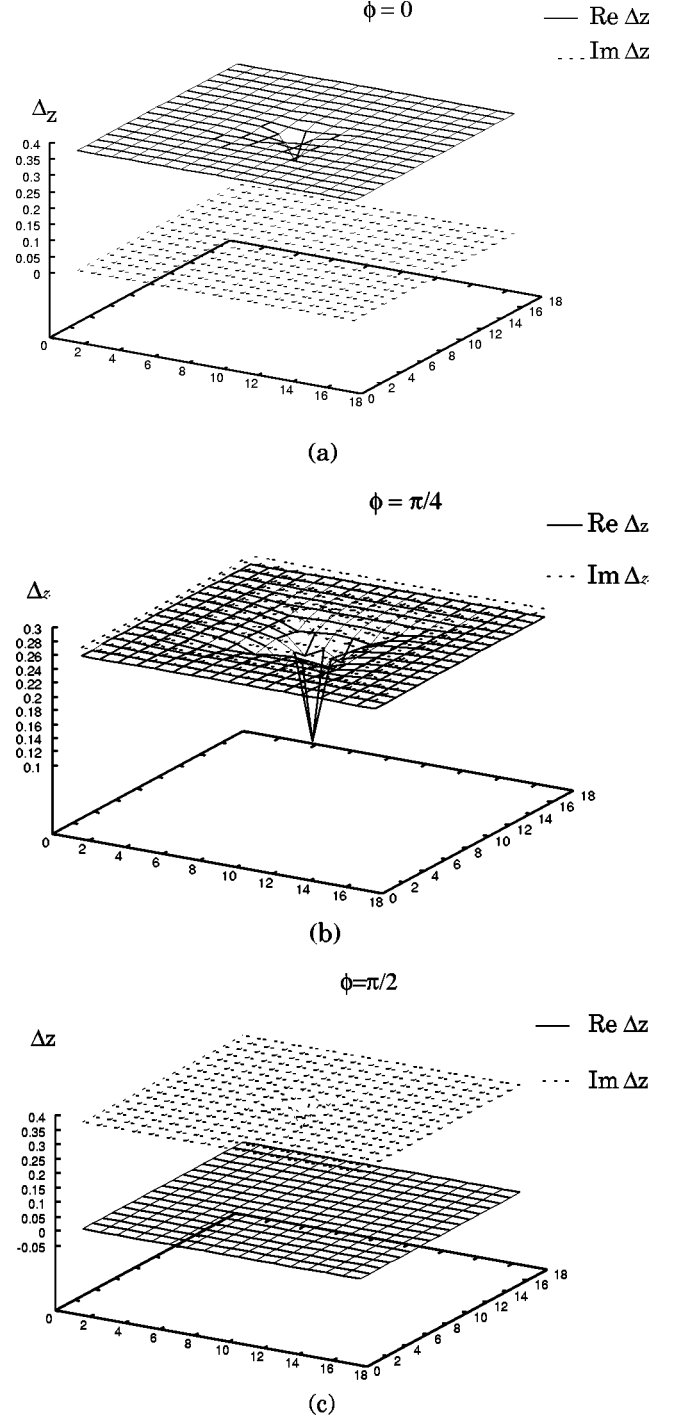

(a)

(b)

(c)

FIG. 2. Real and imaginary part of triplet order parameter when (a) $\phi=0$, (b) $\phi=\pi/4$, and (c) $\phi=\pi/2$.

We repeat these procedures iteratively until the solution converges. We change the phase ϕ by choosing the initial values of Δ, and check the phase after convergence.

We set parameters $U=1.0$, $V=2.0$, $V_{\text{imp}}=1.0$, and $E_a = -E_b = 0$. The calculation is carried out on 17×17 lattices.

First we consider the case when the impurities are introduced into the nondoped excitonic insulator. In Fig. 2 we present the triplet order parameter Δ_z axis when one impurity is introduced, setting the initial condition $\phi=0$, $\pi/4$, and
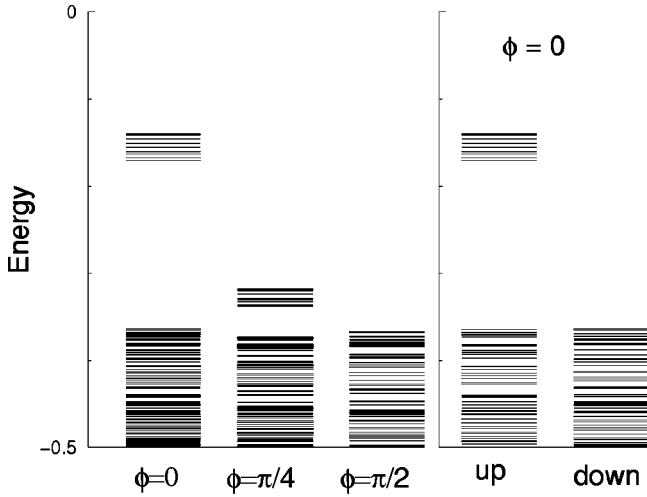
FIG. 3. Phase dependence of energy spectra near $\epsilon = 0$. Phase ϕ is set to 0, $\pi/4$, and $\pi/2$. The right figure shows the spectrum of up-spin and down-spin electrons separately, when $\phi = 0$.

$\pi/2$. The order parameter is reduced at the impurity site. We note that in Fig. 2(b) ϕ differs from $\pi/4$. This is due to the fact that after iteration ϕ deviates from the initial values. However, from Fig. 2 we find that the difference is small.

To see the reduction of energy gap, we need finite concentration of impurities. In Fig. 3 we plot the single-particle spectrum near $\epsilon = 0$ when 10 impurities are introduced periodically. We find that the bound states appear around $E = 0.2$ when $\phi = 0$. It should be noted that the all electrons in the bound state has up spin, as shown in the right of the figure. The number of localized eigenstates with negative energy is the same as that of impurities. The energy of the bound states become large as ϕ changes from 0 to $\pi/2$, and vanish at $\pi/2$, consistent with our discussion. We also note that at $\phi = \pi/4$ the energy gap is larger than the case when $\phi = 0$. This is consistent with the result of Sec. IV. We note that at $\phi = \pi/2$ the gap seems to be smaller than the case when $\phi = \pi/4$. At $\phi = \pi/2$, the bound states touch the edge of the continuum and hybridize with the continuum. The energy of eigenstates is lowered by this hybridization.

Now we turn to the case when electrons are doped. When doped into a triplet excitonic insulator, electrons will align ferromagnetically if $\phi \neq \pi/2$. In the case of $La_xCa_{1-x}B_6$, La acts as both the impurity and electron donor. Therefore we consider the case when the number of impurities and doped electrons are the same. In Fig. 4 we plot $n_{i,\uparrow} - n_{i,\downarrow}$ when 10 electrons and impurities are doped for $\phi = 0$, $7\pi/16$, and $\pi/2$. When $\phi = 0$, we can see that localized magnetic moment appears around the impurity. Total magnetic moment amounts to 10, which means that all doped electrons have spin up. On the other hand, when $\phi = \pi/2$, no magnetic moment appears. Therefore we can conclude when $\phi = \pi/2$ the doped triplet excitonic insulator is paramagnetic. These results are also consistent with our discussion. In the middle of these two limits, there may exist incomplete ferromagnetism. In Fig. 4(b), we show the same plot for $\phi = 7\pi/16$. We can see that magnetic moment become small, being 6 in total. This incomplete ferromagnetism is considered as follows. If
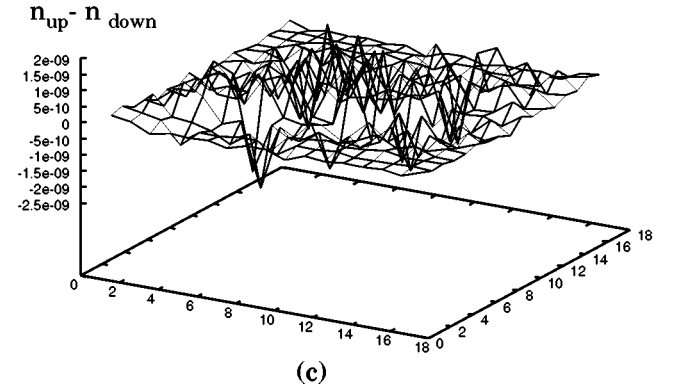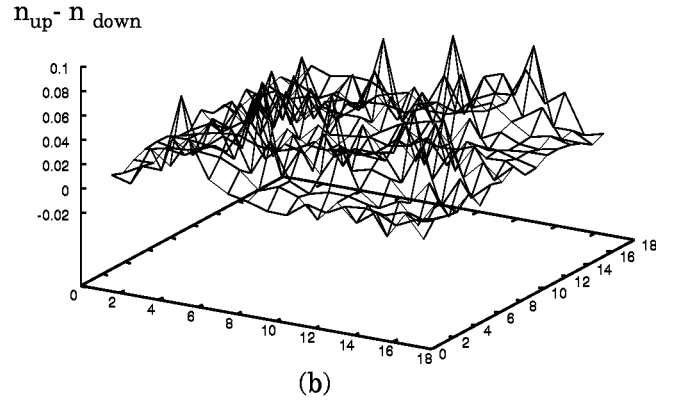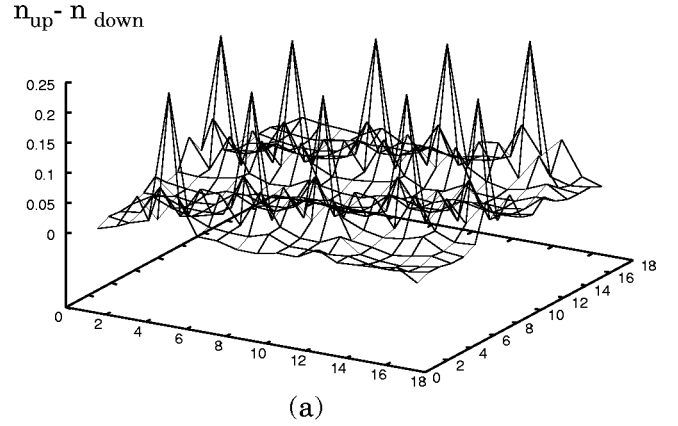

(a)

(b)

(c)

FIG. 4. Spatial pattern of magnetization when (a) $\phi = 0$, (b) $\phi = 7\pi/16$, and (c) $\phi = \pi/2$, when the number of electrons and the number of impurities are both 10.

the concentration of impurities is finite, associated impurity bound states form an impurity band. Since the bound-state energy approaches Δ as $\phi \rightarrow \pi/2$, this impurity band has a finite overlap with the continuum state for ϕ sufficiently close to $\pi/2$. In this case the ferromagnetic moment due to doped electrons will be reduced.

VI. CONCLUSION AND DISCUSSION

On the basis of the results of the preceding sections, we first discuss the weak ferromagnetism in doped hexaborides. As discussed in this paper, doped triplet excitonic insulator with impurities shows ferromagnetism if phase ϕ is between $-\pi/2$ and $\pi/2$. The incomplete ferromagnetism can also oc-

cur when the energy gap becomes smaller than the bound-state energy. Here we discuss the possibility that the ferromagnetism of La-doped CaB_6 is caused by impurities. We assume that CaB_6 is the triplet excitonic insulator. When we dope La, it acts as impurity and causes interband scattering. As discussed in this paper, in the presence of interband scattering up spin and down spin does not compensate because of the emergence of localized moment if $\phi \neq \pi/2$. Therefore ferromagnetism emerges, which becomes incomplete when the reduced energy gap is smaller than the highest energy of the impurity band. Here we discuss the possibility of the impurity-induced ferromagnetism by this mechanism.

First, we notice the ferromagnetism emerges only when excitonic order is spin triplet. It is well known that a direct interaction term suppresses the singlet order, while exchange interaction stabilizes both singlet and triplet order by an equal amount. Therefore only a triplet order parameter will be realized when direct interaction is large enough. It seems natural to assume that the exchange interaction is the same order as the direct interaction. As shown in Sec. V, triplet excitonic insulator is realized when U and V are the same order.

Second, the phase of order parameter must not be $\pi/2$, in other words, the minimum of the total energy is achieved when $\phi \neq \pi/2$. In our discussion, we do not discuss the value of ϕ that minimizes the total energy. In our numerical calculation the change of energy by phase is very small. As noted in Sec. II in real materials there exist some other interactions, which is not discussed here, such as interband pair scattering. These interactions also depend on the phase. Because these interactions exist even without impurities, we think that the stable phase ϕ will be determined by such a term. Further study will be needed to determine the stable ϕ, however, there exists no reason to restrict $\phi = \pi/2$.

Third, the minimum of the energy gap must be smaller than the energy of the impurity band. In our calculation it means that ϕ is close to $\pi/2$. However, it should be noticed that there exists other origins of the reduction of the energy gap. For example, intraband scattering by impurities also decreases the energy gap, as discussed by Zittartz.[6] In this paper we assume La acts as the interband scattering potential. However, there exist other impurities or disorder in $La_xCa_{1-x}B_6$. These impurities and disorder will also acts as impurity potential. If this scattering is large enough, the energy gap will be reduced such that the energy of the bound states is larger than the gap. We conclude that the minimum of the gap can be smaller than the energy of the bound states.

One may think that our model is too simplified to describe the La-doped hexaborides. In the following we briefly comment on the physics neglected in our model.

First, we only consider one pair of Fermi surfaces, which shows complete nesting without doping. However, the band calculation of CaB_6 shows that there exist three pairs of incompletely nested Fermi surfaces. Balents and Varma[4] discussed that in CaB_6 we must consider the possibility of the co-existence of gapped and ungapped Fermi surfaces. In this case, the bound state discussed in Sec. III will become a virtual bound state. Therefore ferromagnetism will occur. On the other hand, the formation of Larkin-Ovchinnikov-Fulde-

Ferrel (LOFF) state discussed by Barzykin and Gorkov[5] modifies our result. If a LOFF state appears, order parameter Δ shows spatial modulation, such as $\Delta(r) = \Delta \exp(iqr)$. In this case, total magnetic moment will diappear, because the direction of local magnetic moment depends on the phase at impurity site.

Another important point we have neglected is the symmetry of the energy band. Band calculation shows that the conduction band and the valence band have different symmetries, X_3' and X_3. When we substitute Ca by La at a single site, the symmetry will be reduced. However, if we set the impurity site as the origin of the coordinate axes, the rotational and parity symmetries are not changed. This leads to the conclusion that interband scattering by La is forbidden by the symmetry. Therefore for our theory we must assume the symmetry is lowered at the impurity site. For example, if the impurity locates at a less symmetric position, these symmetries break down and intraband scattering is permitted. The disorder of the lattice that breaks these symmetries will also act as the interband scattering potential.

The readers will also notice that intraband scattering is neglected in our model. However we can show that the bound state can survive even if intraband scattering exists. When one impurity causes both interband and intraband scattering, the energy of a localized state is determined by

$$(1 + \widetilde{V}_{imp}^2 - \widetilde{V}_{imp}'^2)[\Delta^2 - (\omega + \mu)^2]$$
$$+ 2\widetilde{V}_{imp}'(\omega + \mu) - 2\widetilde{V}_{imp}\Delta \cos\phi = 0, \quad (22)$$

where $\widetilde{V}_{imp}' = \pi N_F V_{imp}'$ and V_{imp}' is the strength of intraband scattering. If $|\widetilde{V}_{imp}'| < \widetilde{V}_{imp} \cos\phi$, Eq. (22) has two bound states when $\widetilde{V}_{imp}\Delta \cos\phi > 0$. In this case the discussion above is not qualitatively modified. On the other hand, $|\widetilde{V}_{imp}'| > \widetilde{V}_{imp} \cos\phi$, Eq. (22) has one bound state, independent of the sign of $\widetilde{V}\Delta \cos\phi$. However here we note the energy of bound state differs between positive and negative Δ. Therefore we conclude the ferromagnetism will also survive, though some modification will be needed.

So far there is no direct evidence of this impurity-induced incomplete ferromagnetism in the hexaborides. However we note that we can account for the experimental inconsistencies on the value of the saturation moment of $La_xCa_{1-x}B_6$ by this scenario. For example, in the first paper of Fisk *et al.*, the saturation moment is about $0.07\mu_B$ per electron when $x \sim 0.005$, while Terashima *et al.*, reports that the saturation moment is about $0.25 \mu_B$ with same doping, more than three times larger than that of Fisk.[10] We can explain this discrepancy by the difference of the density of impurities. More careful experiments on the magnetism will be needed to test the present theory. The measurement of the local magnetic moment will give much information about this.

In summary, we have investigated the effect of the impurity in the excitonic insulator. The effect depends on the phase of the order parameter. The bound state appears when Re Δ is positive, and the energy of the bound state depends

on the phase of the order parameter. On the other hand, the reduction of the energy gap of continuum state becomes maximum when $\text{Im}\,\Delta = 0$. Numerical solution of the BdG equation supports these discussions. Based on these results, we proposed a new mechanism of incomplete ferromagnetism and applied it to the hexaborides. Our theory qualitatively explains experiments, though further study will be needed.

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