Impurity effects and ferromagnetism in excitonic insulators

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Both nonmagnetic and magnetic impurity effects in spin singlet and triplet excitonic insulators were investigated. The bound state energies caused by single impurity were given. The different compositions of the bound states can be used to detect the symmetry of the excitonic insulators. In finite concentration problems, nonmagnetic impurities showed same pair-breaking effect in singlet and triplet excitonic insulators while magnetic impurities showed weaker pair-breaking effect in triplet excitonic insulators than in singlet ones. The pair-breaking effects suppressed the ferromagnetic range via doping and gave a natural explanation for experimental results.

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I. INTRODUCTION

The excitonic phase has been researched for a long time since 1960.1,2 It was proposed in semimetals, in which there is a band overlap and the normal states are unstable. The true ground state becomes a state with electron-hole pairs due to the Coulomb interaction. This kind of state can also occur in semiconductors once the energy gap becomes smaller than the binding energy of an exciton.3 This so-called ‘excitonic insulator’ has been discussed for many years theoretically but materials in experiment were seldom reported so far. 1T - TiSe2, among the transition-metal dichalcogenides, may be one example of the excitonic insulators which obtained more and more direct evidences from experiments.4,5 Another possible example is CaB6. The latter one has gained more attention since weak ferromagnetism was found in slightly doped CaB6 in 1999.6 Theoretically many authors relate this to the historical excitonic insulators.7–11. By now there are still debates on this proposal, especially about the band gap. The angle-resolved photoemission spectrum showed a gap of 1eV,12 which is too large for excitonic instability and another large gap of 0.8eV is given by the LDA+GW calculations.13 Band overlap and semimetal framework were demonstrated by the de Haas-van Alphen and Shubnikov-de Haas experiments14,15 and local density approximation band structure calculations.16–18 Though there are controversies on the band structure, the excitonic insulator scenario is nevertheless a very promising explanation for the main physics in CaB6.

In Ca1-xLaxB6, slightly La doping would induce not only the carriers but also impurities/disorders inevitably and the impurity effects played an important role in the formation of the weak ferromagnetism. According to the first principle calculations, the defects or vacancies in the boron sublattice can result in impurity bands or localized gap states and this modification may be important to the origin of ferromagnetism in CaB6.19,20 From the language of excitonic insulators, the impurities will induce in-gap bound states and it was confirmed by tunneling measurements on high-quality defect-controlled single crystals.21 Therefore the impurity effect can not be neglected in the excitonic insulator theory for CaB6. To explore how the charged impurity doping can affect the excitonic insulators constitutes one of the motivations of this paper. Another motivation originates from the incompleteness of the research on impurity effects in excitonic insulators. Historically the impurity scattering in excitonic insulators was investigated by J. Zittartz in 196722 and in that work only intra-band nonmagnetic impurity in exciton insulators with no regard for the spin freedom was studied. Inter-band nonmagnetic impurity scattering was investigated by T. Ichinomiya23 and other works concentrated in the bilayer systems24,25 in which the spin freedom was already neglected. In this paper we will discuss and compare the inter-/intra-band magnetic/nonmagnetic impurity effect in singlet and triplet excitonic insulators. We will also modify the exciton insulator scenario on ferromagnetism in Ca1−xLaxB6.

This paper is constructed as follows: In the first section we will introduce our model and Hamiltonian. Then we will give the locations of the bound states induced by single magnetic or nonmagnetic impurity. Finite concentration problems of impurities and pair breaking effects will be discussed in the third section. In the fourth section we will investigate the impurity caused-modification to the ferromagnetism in doped exciton insulators. We will leave the summary and further discussion to the last section.

II. MODEL AND HAMILTONIAN

We introduce the noninteracting Hamiltonian in a two band system:

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

here the kinetic energy in two electron bands are $\varepsilon_k^a = \frac{\hbar^2 k^2}{2m_a}$, $\varepsilon_k^b = -\frac{\hbar^2 k^2}{2m_b} + \frac{1}{2}E_G$, in which $E_G$ is the band gap or overlap and $|E_G|$ should be quite small to keep the ground state remain in the excitonic phase. Without losing generality, we consider two symmetric bands, which
means \( m_a = m_b = m \). Now we introduce the interaction term, which reads:

\[
H_I = \frac{U_1}{\Omega} \sum_{k,k',q} a_{k+q}^\dagger b_{k'-q}^\dagger \sigma a_{k'} \sigma
\]

where \( U_1 \) represents the interaction term which comes from the Coulomb interaction. In most of the bulk samples, the system will choose singlet or triplet excitonic phase as the ground state because there is a finite splitting between singlet and triplet states. The splitting may come from short-range Coulomb terms which favor triplet state, or electron-phonon interaction which favors singlet state. In the presence of nesting effect, if the screened Coulomb interaction term dominates there will be a degeneracy between singlet and triplet excitonic phase. In this case there is an SU(2) \( \times \) SU(2) symmetry in the excitonic insulators.

In bilayer systems this splitting is exponentially small because of the inter-layer distance and the barriers between two layers, and spin freedom can thus be neglected. It is also believed that the splitting in CaB\(_6\) is quite small.

Now we introduce the singlet and triplet order parameters: \( \Delta_s \) and \( \Delta_T \) and rewrite the mean-field Model into Nambu space: By introducing the vector \( \psi = (a_{k\uparrow}, a_{k\downarrow}, b_{k\uparrow}, b_{k\downarrow}) \), the Hamiltonian can be written as:

\[
H_{MF} = \sum_k \psi_k^\dagger M \psi
\]

where \( M \) is a \( 4 \times 4 \) matrix, then the bare Green function for singlet excitonic insulators is

\[
G_0^{-1}(k,\omega) = \omega - H_{MF}^S
\]

\[
= \left( \begin{matrix}
(\omega - \frac{\hbar^2 k^2}{2m} + \frac{E_g}{2}) \cdot I & -\Delta_S \cdot I \\
-\Delta_S \cdot I & (\omega + \frac{\hbar^2 k^2}{2m} - \frac{E_g}{2}) \cdot I
\end{matrix} \right)
\]

and triplet excitonic insulators:

\[
G_0^{-1}(k,\omega) = \omega - H_{MF}^T
\]

\[
= \left( \begin{matrix}
(\omega - \frac{\hbar^2 k^2}{2m} + \frac{E_g}{2}) \cdot I & -\Delta_T \cdot \sigma \\
-\Delta_T \cdot \sigma & (\omega + \frac{\hbar^2 k^2}{2m} - \frac{E_g}{2}) \cdot I
\end{matrix} \right)
\]

The impurity scattering term can be written as:

\[
V = \left( \begin{matrix}
J_{1n} \cdot I + J_{1m} \sigma \cdot S & J_{2n} + J_{2m} \sigma \cdot S \\
J_{2n} + J_{2m} \sigma \cdot S & J_{1n} \cdot I + J_{1m} \sigma \cdot S
\end{matrix} \right)
\]

in which \( \nu = n, m \) represents the nonmagnetic and magnetic impurity scattering. \( S \) denotes the spin operator of the magnetic impurity and \( i = 1, 2 \) represents the intra-band and inter-band channel, respectively.

### III. SINGLE IMPURITY PROBLEMS

To obtain the bound state energy, one has to get the T-matrix which can be written as:

\[
T = \frac{V}{1 - G_0(r = 0, \omega)V}
\]

the pole of the T-matrix gives the bound state energy. In singlet excitonic insulators, for nonmagnetic impurity,

\[
E_{B1} = \frac{\Delta_S[1 - (\alpha_{1n} + \alpha_{2n})^2]}{1 + (\alpha_{1n} + \alpha_{2n})^2}; \quad \Delta_S < 0
\]

\[
E_{B2} = \frac{-\Delta_S[1 - (\alpha_{1n} - \alpha_{2n})^2]}{1 + (\alpha_{1n} - \alpha_{2n})^2}; \quad \Delta_S(\alpha_{2n} - \alpha_{1n}) < 0
\]

where \( \alpha_{1n} = J_{1n}\pi N_F \), \( \alpha_{2n} = J_{2n}\pi N_F \). And for magnetic impurity case,

\[
E_{B1} = \frac{\Delta_S[1 - (\alpha_{1m} + \alpha_{2m})^2]}{1 + (\alpha_{1m} + \alpha_{2m})^2}
\]

\[
E_{B2} = \frac{-\Delta_S[1 - (\alpha_{1m} - \alpha_{2m})^2]}{1 + (\alpha_{1m} - \alpha_{2m})^2}
\]

where \( \alpha_{1m} = J_{1m}\pi N_F S(S+1) \), \( \alpha_{2m} = J_{2m}\pi N_F S(S+1) \). Notice some extreme cases in the singlet excitonic insulators, for the negative order parameter and if there is only one scattering channel exists, the bound state energy will have the same form of the single magnetic impurity in s-wave superconductors, which reads \( E_B = \pm \Delta(1 - \frac{\alpha^2}{\Delta^2}) \), \( \Delta(1 - \frac{\alpha^2}{\Delta^2}) \), \( (i=1n,2n,1m,2m) \). In this case the bound state energy will move to the Fermi energy with the increasing of the gap-edge side with the decreasing of impurity scattering. If there is no impurity scattering \( (J_{iv} = 0) \), the excitation will emerge into the normal excitonic gap \( E_B = \pm \Delta \).

In triplet case, the bound state energy can be obtained in the same way. For single nonmagnetic impurity

\[
E_{B1} = \frac{\Delta_T[1 - (\alpha_{1n} + \alpha_{2n})^2]}{1 + (\alpha_{1n} + \alpha_{2n})^2}; \quad \pm(\alpha_{1n} + \alpha_{2n})\Delta_T < 0
\]

\[
E_{B2} = \frac{\Delta_T[1 - (\alpha_{1n} - \alpha_{2n})^2]}{1 + (\alpha_{1n} - \alpha_{2n})^2}; \quad \pm(\alpha_{1n} - \alpha_{2n})\Delta_T < 0
\]

Since the form of the bound state energy for single magnetic impurity in triplet excitonic insulators is quite complex, we only give the numerical results. The bound state energies for single nonmagnetic and magnetic impurity in singlet and triplet excitonic insulators are shown in Fig1.

From Fig1 we can see that location of the bound state energy which is induced by single impurity is very different between singlet excitonic insulators and triplet ones. Furthermore, in excitonic insulators, the quasiparticle induced by single nonmagnetic or magnetic impurity can consist one or two hole \( (\omega < 0) \) or one or two particle type \( (\omega > 0) \) states in some range of \( J_{1n}, J_{2n}, J_{1m}, J_{2m} \). This is quite different from the single magnetic impurity in s-wave superconductors in which hole and electron type excitations must appear symmetrically at the same time. It is well known that both the hole- and electron-type components of the bound states can be detected by the low-temperature tunneling microscope. Thus the results of the bound state energies are valuable since they can be used to detect the symmetry of the excitonic insulators, especially for the materials with quite small splitting of singlet and triplet states.
glet excitonic insulators: other cases and we shall justify this conclusion below. We could expect that finite concentration of impurities are stretching to the Fermi level. Under this condition to the gap edge. With the increasing of the impurity concentration, we can see the bound states caused by single magnetic impurity in singlet excitonic insulators, non-magnetic/magnetic impurity in triplet excitonic insulators, respectively. Please note that in the figure solid symbols represent $\Delta_{S,T} > 0$ and open symbols represent $\Delta_{S,T} < 0$.

Another interesting finding is that magnetic impurity in triplet excitonic insulator is quite different from other cases. We can see the bound states caused by single magnetic impurity in triplet exciton insulators are very close to the gap edge. With the increasing of the impurity concentration an impurity band is expanding and the states are stretching to the Fermi level. Under this condition we could expect that finite concentration of impurities should behave a weaker pair breaking effect than in the other cases and we shall justify this conclusion below.

**IV. Finite Concentration Problems and Pair-Breaking Effects**

To investigate the finite concentration problems we introduce the renormalized Green Function. For spin singlet excitonic insulators:

$$G^{-1}(k, i\omega) = \left( \hat{\omega} - \frac{\hbar^2 k^2 + E_F}{2m} \cdot I - \frac{\Delta_S}{\sqrt{\Delta_S^2 - \omega^2}} \cdot I \right)$$

with the full Born approximation one can get the self-energy:

$$\sum(\omega) = n_{imp} \int \frac{d^3k}{(2\pi)^3} < VG(k, i\omega)V > I$$

where $<>_I$ means averaging all the impurity positions and $n_{imp}$ represents the density of impurities. Then we can calculate the self-energy which is given by

$$\sum(\omega) = \left( \frac{-\frac{1}{\tau_{s1n}}}{\sqrt{\Delta_n^2 - \omega^2}} \cdot I - \frac{\frac{1}{\tau_{s1n}}}{\sqrt{\Delta_n^2 - \omega^2}} \cdot I \right)$$

and define the scattering times:

$$\frac{1}{\tau_{s1n}} = n_{imp} N_F (J_{1n}^2 + J_{2n}^2)$$

$$\frac{1}{\tau_{s2n}} = 2n_{imp} N_F J_{1n} J_{2n}$$

$$\frac{1}{\tau_{s1m}} = n_{imp} N_F (J_{1m}^2 + J_{2m}^2) S(S + 1)$$

$$\frac{1}{\tau_{s2m}} = 2n_{imp} N_F J_{1m} J_{2m} S(S + 1)$$

As we know the renormalized Green Function can be written as:

$$G^{-1}(k, \omega) = G_0^{-1}(k, \omega) - \sum(\omega)$$

then we have the self-consistent equations:

$$\tilde{\omega} = \omega - \frac{1}{\tau_{s2n}} \Delta_S + \frac{1}{\tau_{s1n}} \tilde{\omega}$$

$$\tilde{\Delta}_S = \Delta_S - \frac{1}{\tau_{s1m}} \Delta_S + \frac{1}{\tau_{s2m}} \tilde{\Delta}_S$$

Note here $\Delta_S$ represents the excitonic order parameter of singlet excitonic insulators in the presence of impurities. We consider the one-channel (inter-band or intra-band) impurity scattering case, then the impurity effect only contributes to the renormalization of frequency and the order parameter. Making $\omega \rightarrow i\omega$, the order parameter in zero temperature and the exciton gap can be got from:

$$\Delta = VN_F \int_{\epsilon_C}^{\infty} d\omega \frac{\tilde{\Delta}}{\sqrt{\Delta^2 + \omega^2}}$$

$$\Omega = \Delta (1 - \zeta^{2/3}/3)^{1/2}$$

where $\epsilon_C$ is the cutoff and $\zeta = [f(\tilde{\omega}) - f(\tilde{\Delta})]/\Delta$. In the expression of $\zeta$, $f(\tilde{\omega})$ and $f(\tilde{\Delta})$ can be well defined as the factor of the renormalized frequency and order parameter if only one impurity scattering channel opens ($J_{1\nu} = 0$ or $J_{2\nu} = 0$). They read

$$f(\tilde{\omega}) = -\frac{1}{\tau_{s1m}} \left. \right|_{J_{1\nu} = 0 \text{ or } J_{2\nu} = 0}$$

$$f(\tilde{\Delta}) = -\frac{1}{\tau_{s1m}} \left. \right|_{J_{1\nu} = 0 \text{ or } J_{2\nu} = 0}$$

The same analysis can be applied to the triplet case, in which the renormalized Green-Function can be written as

$$G^{-1}(k, i\omega) = \left( \hat{\omega} - \frac{\hbar^2 k^2 + E_F}{2m} \cdot I - \frac{\Delta_T}{\sqrt{\Delta_T^2 - \omega^2}} \cdot I \right)$$
The self-consistent equations for one channel impurity scattering are:

\[ \tilde{\omega} = \omega + \left( \frac{1}{\tau_{1n}} \right) \frac{\tilde{\omega}}{\sqrt{\Delta^2_T - \tilde{\omega}^2}} \]

\[ \Delta_T = \Delta_T \mp \left( \frac{1}{\tau_{1m}} \right) \frac{\tilde{\Delta}_T}{\sqrt{\Delta^2_T - \tilde{\omega}^2}} \]

Note here the \((+, m)\) represents the magnetic case and \((-n, n)\) represents the nonmagnetic case and \(\Delta_T\) is the excitonic order parameter of triplet excitonic insulators in the presence of impurities. Then the scattering times read:

\[ \frac{1}{\tau_{1n}} = n_{imp} N F J^2_{in} \]

\[ \frac{1}{\tau_{1m}} = n_{imp} N F J^2_{im} S(S + 1) \]

\[ \frac{1}{\tau_{2m}} = \frac{1}{3} n_{imp} N F J^2_{im} S(S + 1) \]

The numerical results for the order parameters and excitation gaps with the impurity doping in singlet and triplet excitonic insulators are shown in Fig2.

![Figure 2](image_url)

Figure 2. The order parameters and the excitonic gaps via the impurity concentration. The left figure is the nonmagnetic impurities in singlet and triplet excitonic insulators and the right figure is for magnetic impurities case. \(\Delta_{S0}\) and \(\Delta_{T0}\) represent the order parameter of singlet and triplet excitonic insulators in the absence of impurities.

From Fig2 we can see that both of magnetic and nonmagnetic impurities have the pair breaking effects in excitonic insulators and there always exists a gapless region between the gaped excitonic insulator phase and the normal phase. This phase transition from gaped phase to gapless phase is of second order as pointed out by J. Zittartz. However, the nonmagnetic impurities have the same pair breaking effect to singlet and triplet excitonic insulators but magnetic impurities behave differently in these two systems. A significant difference can be seen from the right part in Fig2 in which the triplet excitonic insulators are more robust with magnetic impurity doping. Notice that the pair breaking effect coming from the self-consistent equations is decided by the relative amplitude and sign between the factor of renormalized frequency and order parameter in the self-energy. Therefore, to compare the pair-breaking effect in quantization between different cases, we define the pair breaking factor which can be written as

\[ x = \frac{f(\Delta)}{f(\tilde{\omega})} \]

It is analogous to the notations in R. Balian et al. ’s work in p-wave superconductors. According to Abrikosov-Gor’kov theory, in conventional s-wave superconductors, \(x = -1\) stands for magnetic impurities and \(x = 1\) stands for nonmagnetic impurities. Then we list all the pair breaking effects in singlet and triplet excitonic insulators.

\[ x = \left\{ \begin{array}{l} -1 \lambda_{S,n} \\ -1 \lambda_{S,m} \\ -1 \lambda_{T,n} \\ \frac{1}{3} \lambda_{T,m} \end{array} \right\} \]

where \(\lambda_{S,n}, \lambda_{S,m}, \lambda_{T,n}, \lambda_{T,m}\) represent the nonmagnetic impurity scattering and magnetic impurity scattering in the intra-band/inter band channel in singlet and triplet excitonic insulators, respectively.

It is well known that the nonmagnetic impurities are not pair breakers in s-wave conventional superconductors according to Anderson’s theorem. Note in singlet and triplet excitonic insulators nonmagnetic impurities have the same pair-breaking effect. This is analogous to the magnetic impurities in the s-wave superconductors in which the time reversal symmetry is broken due to the spin-flip impurity scattering. The Kramer’s degeneracy is replaced by the particle-hole symmetry in the singlet and triplet excitonic insulators. According to our calculations triplet excitonic insulators are more stable with magnetic impurity doping than singlet samples. \(n_f/n_S = 3\), where \(n_f\) and \(n_S\) are the critical doping concentration of magnetic impurities in triplet and singlet excitonic insulators, respectively. This result is in accordance with the single impurity analysis. From Fig1 we can see that the bound states energy is close to the gap edge for the magnetic impurity in triplet excitonic insulators. And it needs larger impurity concentration in triplet than in singlet excitonic insulators to fill the gap with states.

V. IMPURITY EFFECTS AND FERROMAGNETISM

In undoped CaB\(_6\) the splitting of singlet and triplet excitonic phases is neglectable, then the \(SU(2) \times SU(2)\) symmetry is preserved and in this case the samples show no magnetic signals since there is no polarization in the systems. All kinds of spin polarization states have the
same energy. Once the doping induce extra carriers the degeneracy between singlet and triplet states can be lifted. The doped electrons are aligned in one direction to make the energy minimized. Then the system have two order parameters $\Delta_s$ and $\Delta_t$, which have the relationship with $\Delta_S$ and $\Delta_T$ in doped situation\(^\text{35}\)

\[
\begin{align*}
\Delta_s & = \sqrt{\Delta_0 (\Delta_0 - 4n)} \\
\Delta_t & = \Delta_0
\end{align*}
\]

where $\Delta_S$ and $\Delta_T$ are the singlet and triplet excitonic order parameters of undoped case in the absence of impurities, respectively. $n$ is the concentration of the doping electrons. At zero doping at $T = 0$ we have $\Delta_S = \Delta_T = 0$ and in doped samples we have\(^\text{35}\)

\[
\begin{align*}
\Delta_s & = \sqrt{\Delta_0 (\Delta_0 - 4n)} & (0 < n < \Delta/4) \\
\Delta_t & = \Delta_0 & (0 < n < \Delta/2)
\end{align*}
\]

Now we can see that ferromagnetism can exist in the doping range of $[0, \Delta_0/2]$. In the doping level $[0, \Delta_0/4]$, the doped electrons are polarized (DP). In the doping level $(\Delta_0/4, \Delta_0/2]$, all of the electrons and holes are paired in one direction and system is in the fully polarized phase (FP). When $n > \Delta_0/2$, the excitonic state is no longer favored and system undergoes a first order transition into the normal metallic state. This phase transition is different with the excitonic insulator-metal phase transition we discussed above. The former one is caused by carrier doping and becomes a normal metal after the transition. The latter one is caused by the impurity doping and undergoes a transition into the impure metal phase. Besides, for the impurity induced excitonic insulator-metal phase transition, generally there is a second order phase transition into a gapless region before the excitonic insulator-metal phase transition.

In bulk materials the La doping would induce impurities or disorders inevitably and in this case both the carrier doing and impurity effect must be considered. For CaB\(_6\), since there is no exact experimental data of $\Delta_0$ and if we consider a general excitonic gap of order $\sim 600 K\text{eV}$, the ferromagnetism range via doping should be $0 - 3\%$ and this doping range is much larger than the experimental results $0 - 1\%$. If the excitonic insulators scenario is responsible for the physics in CaB\(_6\), one possible reason for the narrow range of ferromagnetism is the anisotropy of the band structure\(^\text{28}\). However this is not enough and we must involve the pair breaking effects caused by impurity or disorder. A direct evidence for this comes from the tunnelling experiments\(^\text{24}\), in which it is surprising to find that there exists ferromagnetism in 99.9% pure boron of CaB\(_6\) within a small range of carrier doping while there are no magnetic signals in 99.9999% samples. For high purity samples the exciton gap may be too large compared to the doping concentration and the splitting between $\Delta_s$ and $\Delta_t$ is negligible. Therefore the ferromagnetism can not be found. More disorders or impurities in the samples suppress the excitonic order parameters and make it comparable to the doping level. Then the impurity effect results in two changes: a more significant splitting of $\Delta_s$ and $\Delta_t$ and a narrower doping range of ferromagnetism.

To express our physics in detail we carry out the numerical work by replacing the $\Delta$ in (1) with $\Delta_S + T + \Delta_T - \sigma$. For simplification we choose the triplet exciton along the $z$ direction. Then with the same full Born approximation we have the self-consistent equations with nonmagnetic impurity scattering:

\[
\begin{align*}
\tilde{\omega}_1 & = \omega + \frac{\tilde{\omega}_1}{\tau_{21}} + \frac{\tilde{\omega}_2}{\tau_{21}} \\
\tilde{\omega}_2 & = \omega + \frac{\tilde{\omega}_1}{\tau_{21}} + \frac{\tilde{\omega}_2}{\tau_{21}}
\end{align*}
\]

the self-consistent equations with magnetic impurity scattering:

\[
\begin{align*}
\tilde{\omega}_1 & = \omega + \frac{\tilde{\omega}_1}{\tau_{21}} + \frac{\tilde{\omega}_2}{\tau_{21}} \\
\tilde{\omega}_2 & = \omega + \frac{\tilde{\omega}_1}{\tau_{21}} + \frac{\tilde{\omega}_2}{\tau_{21}}
\end{align*}
\]

Taking both the impurity effects and carrier doping into considerations, we have to solve the Equs.(6), (9) and (10) for nonmagnetic impurities and Equs. (6), (9) and (11) for magnetic impurities. Now the ferromagnetic range and the fully polarized range should be $0 - n_1$ and
n_2 - n_1$, where the critical charged impurity concentration $n_1$ and $n_2$ satisfy
\[
\Delta_\tau(n_{imp}^C = n_1) = 0
\]
\[
\Delta_\tau(n_{imp}^C = n_2) = 0
\]

Note here the impurity concentration $n_{imp}$ and density of doping electrons should be replaced with charged impurity concentration $n_{imp}^C$. Our numerical results are shown in Fig3.

In the nonmagnetic impurity scattering, the pair breaking effect is the same for singlet and triplet excitons. But in the magnetic impurity scattering case, the order parameter of singlet and triplet excitons splits with the increasing of the impurity concentration. Both two kinds of order parameters disappear at the same doping concentration at which the excitonic insulator becomes an impure metal. In the situation here we do not consider the gapless excitonic insulator since this regain is quite small ($< 0.05 \Delta_0$). From top to below in Fig3 we can also see that the ferromagnetic region $0 - n_1$ is growing narrower with the increasing of the impurity scattering. To express that clearer we plot the phase diagram in $J - n$ plane in Fig4. It is very clear that the nonmagnetic and magnetic impurities would suppress the ferromagnetic range via doping. In magnetic impurity case, the fully polarized range is destroyed by the impurity scattering in all doping levels. For pure carriers doping the ferromagnetic range should be $0 - 3\%$ and this region are suppressed to $0 - 1\%$ with the impurity scattering $J_{imp}\pi N_F \simeq 2.8$ for nonmagnetic case and $J_{imp}\pi N_F \simeq 2.0$ for magnetic case, where $i = 1, 2$. And this result is in accordance with the experimental data. It is worthy to point out that here we considered the charged impurity case which means the density of doped electrons and impurities have the same value $n = n_{imp} = n_{imp}^C$. In CaB$_6$, the charged impurities are induced by La doping. If there are additional impurities/disorders which are not accompanied with electrons doping, which means $n_{imp} > n$, they can strengthen the pair-breaking effects and these extra impurity scattering terms can be absorbed into the factor of $J_{imp}$ or $J_{imp}$ directly.

VI. DISCUSSION AND SUMMARY

We investigated the nonmagnetic and magnetic impurity effects in singlet and triplet excitonic insulators in the inter-band and intra-band channels. In single impurity problems, the bound states showed different compositions in singlet and triplet excitonic insulators, which can be used to detect the symmetry of excitonic insulators in experiments. In finite concentration problems, all kinds of impurities showed pair-breaking effects. In the presence of impurities, the excitonic insulator scenario for ferromagnetism in CaB$_6$ was modified. The doped excitonic insulators can be characterized in three classes by different kinds of doping:

(1) Electrons doping but no impurity effects induced: Ferromagnetism emerges with the electrons doping and there are two ferromagnetic phases with doping, the polarized phase for the doped electrons and the full polarized phase for all the excitonic pairs.

(2) Impurity effects induced but no electrons brought
in: i. Nonmagnetic impurities in one channel show same pair breaking effects to singlet and triplet excitonic insulators. ii. Magnetic impurities in one channel show weaker pair breaking effect to triplet excitonic insulators than singlet ones.

(3) Both electrons and impurity effect were induced by doping: Nonmagnetic and magnetic impurity effects suppressed the ferromagnetic region and this provides an natural explanation for the quite narrow region for ferromagnetism in the experiments of CaB$_6$. In the magnetic impurity case, the fully polarized phase for all the electron-hole pairs was destroyed in all doping levels.

The model we discussed here is based on two nested bands which have the same effective masses. Once apart from this situation, the two bands have different effective masses, $m_a \neq m_b$. In this case the impurities are still pair breakers because they can be seen as oppositely charged pairs to an exciton.$^{22}$ This may make the quantitative calculations much more difficult but should show the same conclusions as ours qualitatively. The more anisotropy of band structure will obviously reduce the total magnetism and may lead to the well-known Larkin-Ovchinnikov-Fulde-Ferrérl state.$^{7,8}$ which is not considered in this work.

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