Magnetism and superconductivity in the layered hexagonal transition metal pnictides

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We investigate the electronic and magnetic structures of the 122 (AM2B2) hexagonal transition-metal pnictides with A=(Sr, Ca), M=(Cr, Mn, Fe, Co, Ni) and B=(As, P, Sb). It is found that the family of materials share critical similarities with those of tetragonal structures that include the famous iron-based high temperature superconductors. In both families, the next nearest neighbor (NNN) effective antiferromagnetic (AFM) exchange couplings reach the maximum value in the iron-based materials. While the NNN couplings in the latter are known to be responsible for the C-type AFM state and to result in the extended s-wave superconducting state upon doping, they cause the former to be extremely frustrated magnetic systems and can lead to an time reversal symmetry broken d + id superconducting state upon doping. The iron-based compounds with the hexagonal structure, thus if synthesized, can help us to determine the origin of high temperature superconductivity.

I. INTRODUCTION

The accidental discovery of iron-based superconductors in 2008[1] was a great surprise to the entire high temperature (high Tc) superconductivity research community. Since then, the iron-based superconductors have been one of the most active research fields in condensed matter physics. It was wildly cheered that the study of the materials might eventually lead us to understand the superconducting mechanism of unconventional high temperature superconductors. Nevertheless, even if many rich physics in these materials have been discovered and well understood, the superconductivity mechanism remains a controversial subject.

Theoretically, to understand high Tc superconductivity, different electronic properties or phenomena have been selected and emphasized in different approaches and models. The essential difficulty in solving high Tc mechanism lies on how to identify indispensable features that are directly tied to high Tc superconductivity among complex electronic structures and physical phenomena. In principle, a successful identification should also lead us to predict new families of high Tc superconductors.

If we assume that there should be one unified superconducting mechanism for unconventional high temperature superconductors including cuprate[2], it is possible to make the identification by comparing different classes of materials. Considering the 122 family of iron-based superconductors, the iron atoms can be fully replaced by other transition metal atoms, such as Cr, Mn, Co, Ni and Cu. These compounds have the same lattice structures as the 122 iron-based superconductors. Accumulative experimental evidences[3-5] suggest that they do not exhibit high Tc superconductivity. These facts lead us to ask a profound question: why is iron so special for high Tc superconductivity?

If we compare all these similar materials, only the iron-based materials exhibit the C-type AFM order[6] and the superconductivity emerges when the magnetic order is suppressed. The C-type AFM state indicates the presence of strong effective AFM exchange couplings between two NNN iron atoms. The NNN AFM couplings are known to stem from the superexchange mechanism through the couplings between the t2g iron d-orbitals and the anion p-orbitals. In many previous theoretical studies[5,6,7], these AFM interactions are shown to generate strong superconducting pairings with extended s-wave symmetry. Recently we have also pointed out that the d6 configuration at Fe2+ is an unique configuration to isolate the t2g orbitals near Fermi energy[10]. Thus, the special electronic structure in which the t2g orbitals are isolated near Fermi energy to generate the maximum superexchange AFM interactions in the vicinity of the d6 configuration at Fe2+ is suggested to be the key the high Tc mechanism. This speciality is also satisfied in cuprate[3] in which the single d_{x^2-y^2} orbital of Cu2+ which is responsible for the superexchange interactions is isolated near Fermi energy.

In this paper, we argue that the hexagonal 122 transition-metal pnictides, AM2B2 with A=(Sr, Ca), M=(Cr, Mn, Fe, Co, Ni) and B=(As, P, Sb), which have the trigonal CaAl2Si2-type structure, can be a new family of materials to test the above identification of the superconducting mechanism. We compare the magnetic properties between the tetragonal and hexagonal 122 families of pnictides obtained from density functional theory (DFT) calculations and find that the overall trend of magnetism in the hexagonal structure as the change of transition metal atoms is very similar to the one in the tetragonal structure. Their similarities include: (1) the NNN AFM exchange interactions reach maximum in Fe-based materials; (2) the nearest neighbor (NN) AFM interactions, which are mainly attributed to direct magnetic exchange mechanism, are very strong in Cr/Mn.
based materials; (3) in Co/Ni/Cu based materials, magnetic interactions are very weak or negligible. Because of the strong NNN AFM interactions, the iron-based hexagonal materials are extremely frustrated magnetic systems. Their electronic structure near Fermi energy is mainly attributed to $t_{2g}$ orbitals that form two quasi two-dimensional electron pockets. Upon doping, the superconductivity with $d+id$ spin singlet pairing symmetry can be developed.

The paper is organized as following. In Section II we present the calculation results from density functional theory (DFT) and study the crystal structure of hexagonal 122 transition-metal pnictides $A_{3}B_{2}(A=Sr, Ca; M=Cr, Mn, Fe, Co, Ni; B=As, P, Sb)$. In Section III we review and summarize the magnetic properties of the tetragonal family. In Sec. IV we investigate the effective magnetic exchange interactions in the hexagonal family. In Sec. V we investigate the pressure effect on the magnetic order. In Section III, we discuss the electronic structures of the hexagonal $CaFe_{2}As_{2}$ and analyze the possible superconducting state. Finally, Sec. VIII we give a summary and provide the main conclusions of our paper.

### II. CRYSTAL STRUCTURES AND CALCULATION METHODS

The 122 tetragonal and hexagonal crystal structures are shown in Fig. 1. The 122 iron-based superconductors, such as $BaFe_{2}As_{2}$, has a body-centered-tetragonal structure as shown in Fig. 1(c) with space group $I4/mmm$. Besides iron-based materials, materials with this crystal structure have been synthesized for Cr, Mn, Co, Ni and Cu as well. The hexagonal 122 structure is shown in Fig 1(a). This structure is referred as the trigonal $CaAl_{2}Si_{2}$-type structure with space group $P3m1$. ($Sr, Ca)Mn_{2}As_{2}$ with this structure have been synthesized. Here we use the DFT calculations to systematically investigate these families of materials. The 122 tetragonal family has been intensively investigated. The magnetic states have been correctly obtained by the DFT calculations. Although the hexagonal 122 structure has also been investigated, there is no systematic DFT results.

Our DFT calculations employ the projector augmented wave (PAW) method encoded in Vienna ab initio simulation package (VASP) and generalized-gradient approximation (GGA) for the exchange correlation functional is used. We relax the lattice constants and internal atomic positions for hexagonal family, where the plane wave cutoff energy is 600 eV and these $k$ points are $13 \times 13 \times 7$. Forces are minimized to less than 0.01 eV/Å in the structural relaxation. Throughout this work, the cutoff energy of 500 eV for tetragonal family and 450 eV for hexagonal family are taken for expanding the wave functions into plane-wave basis. The number of these $k$ points are $7 \times 7 \times 3$ for tetragonal family and $7 \times 11 \times 7$ for hexagonal family in the calculation of the electronic structures. The GGA plus on-site repulsion $U$ method (GGA+$U$) in the formulation of Dudarev et al. is employed to describe the electron correlation effect associated.

In the 122 tetragonal family, the A site has very limited effect on electronic physics. So in our calculations and analysis, we set A site to Ba atom. We adopt the experimental lattice constants in our calculations as all those materials have been synthesized are shown in Table I. For the hexagonal family, $CaMn_{2}As_{2}$, $CaMn_{2}P_{2}$, $CaMn_{2}Sb_{2}$, $SrMn_{2}P_{2}$ and $SrMn_{2}As_{2}$ have been synthesized. Similar to the tetragonal family structure, the A site atoms have little affect on the electronic and magnetic structure near the fermi level. In the following calculations and analysis, we set A site to Ca atom. The trigonal $CaAl_{2}Si_{2}$-type structure is shown in Fig. 1(a). The M site sublattice forms the corrugated honeycomb lattice, which is shown in Fig. 1(b). The purple and gray M atoms belong to the up and low trigonal layers respectively. The lattice constants are listed in Table I. $CaMn_{2}As_{2}$ has been reported with antiferromagnetic (AF) order. However, the other materials in $CaM_{2}B_{2}(M=Cr, Fe, Co, Ni)$ have not been synthesized. In order to study their magnetic structures, we relax the lattice constants and internal atomic positions with the GGA+$U$ method in the AFM ordered states. By relaxing the lattice constants and internal atomic positions for $CaMn_{2}As_{2}$ and $CaMn_{2}P_{2}$ with $U_{eff}=(0, 0.5, 1, 1.5, 2, 2.5) eV$, we find that when $U_{eff}=1.5 eV$, the optimized lattice constants are the most close to the experimental data for both $CaMn_{2}As_{2}$ and $CaMn_{2}P_{2}$, which are given in Table I. Therefore, we adopt the value $U_{eff}=1.5 eV$ to relax the other materials $CaMn_{2}As_{2}(CaMn_{2}P_{2})(M=Cr, Fe, Co, Ni)$ with the experimental lattice constants of $CaMn_{2}As_{2}(CaMn_{2}P_{2})$ as the input parameters. The results of the optimized structural parameters are listed in Table III. In the calculations of the magnetic states of the trigonal $CaAl_{2}Si_{2}$-type structure $CaM_{2}B_{2}$, we double the primitive cell as unit cell, which is indicated by the red frame in Fig. 1.
is given by the effective magnetic properties of the tetragonal \( \text{BaM}_2 \text{B}_2 \) \((\text{M}=\text{Cr}, \text{Mn}, \text{Fe}, \text{Co, Ni}; \text{B}=\text{As, P, Sb})\), the trigonal \( \text{CaAl}_2 \text{Si}_2 \) type structure(space group \( \text{P}3\text{m}1\), No. 164); (b) the corrugated honeycomb lattice formed only by the M atoms in the \( ab \) plane. Exchange interactions between NN \( J_1 \), NNN \( J_2 \), and third NN \( J_3 \) are indicated; (c) the crystal structure of AM \( \text{B}_2 \) \((\text{A}=\text{Sr, Ca}; \text{M}=\text{Cr, Mn, Fe, Co, Ni}; \text{B}=\text{As, P})\) with the body-centered-tetragonal structure(space group \( \text{I}4/\text{mmmm}, \text{No. 139}\)). The in-plane NN magnetic exchange interaction \( J_1 \), the in-plane NNN exchange interaction \( J_2 \) and the out-of-plane NN along \( c \) axis exchange interaction \( J_3 \) are indicated.

**FIG. 1:** (color online). (a) The crystal structure of the hexagonal AM\( _2 \text{B}_2 \)\((\text{A}=\text{Sr, Ca}; \text{M}=\text{Cr, Mn, Fe, Co, Ni}; \text{B}=\text{As, P, Sb})\), the trigonal CaAl\( _2 \)Si\( _2 \) type structure(space group \( \text{P}3\text{m}1\), No. 164); (b) the corrugated honeycomb lattice formed only by the M atoms in the \( ab \) plane. Exchange interactions between NN \( J_1 \), NNN \( J_2 \), and third NN \( J_3 \) are indicated; (c) the crystal structure of AM\( _2 \text{B}_2 \)\((\text{A}=\text{Sr, Ca}; \text{M}=\text{Cr, Mn, Fe, Co, Ni}; \text{B}=\text{As, P})\) with the body-centered-tetragonal structure(space group \( \text{I}4/\text{mmmm}, \text{No. 139}\)). The in-plane NN magnetic exchange interaction \( J_1 \), the in-plane NNN exchange interaction \( J_2 \) and the out-of-plane NN along \( c \) axis exchange interaction \( J_3 \) are indicated.

**TABLE II:** Experimental and optimized structural parameters of CaMn\( _2 \)B\( _2 \)(\( \text{B}=\text{As, P} \)) by using GGA+\( U(\text{U}_{\text{eff}}=1.5 \text{ eV}) \) in the AFM ordered state.

| Material       | Parameter 1 | Parameter 2 | \( z_X \) | \( z_Y \) |
|----------------|-------------|-------------|---------|---------|
| CaMn\( _2 \)As\( _2 \)(relax) | 4.258 | 7.002 | 0.6203 | 0.2574 |
| CaMn\( _2 \)P\( _2 \)(relax) | 4.096 | 6.848 | 0.6246 | 0.2612 |
| CaMn\( _2 \)P\( _2 \)(relax) | 4.109 | 6.775 | 0.6213 | 0.2644 |

**III. THE MAGNETISM IN THE TETRAGONAL 122 TRANSITION-METAL PNICTIDES**

In this section, we review and investigate the magnetic properties of the 122 tetragonal BaM\( _2 \)B\( _2 \)(\( \text{M}=\text{Cr, Mn, Fe, Co, Ni}; \text{B}=\text{As, P} \)). We consider four competing collinear magnetic states, the ferromagnetic(FM) state, the G-type AFM state and two stripe states. We distinguish two stripe states as the stripe FM state with ferromagnetic alignment of adjacent spins along the \( c \) axis and the C-type AFM state with antiferromagnetic alignment. The above four magnetic states are shown in Fig. 2. It has been known that the magnetism can be described by the effective \( J_1 - J_2 - J_3 \) Heisenberg model, which is given by

\[
H = J_1 \sum_{\langle ij \rangle} S_i \cdot S_j + J_2 \sum_{\langle ijj \rangle} S_i \cdot S_j + J_3 \sum_{\langle ij \rangle} S_i \cdot S_j
\]

whereas \( \langle ij \rangle \) and \( \langle ijj \rangle \) denote the summation over the in-plane NN, in-plane NNN and out-of-plane NN along \( c \) axis, respectively. The exchange interaction parameters \( J_1, J_2 \) and \( J_3 \) are indicated in Fig. 1(c). \( S_i \) is the spin operator for the \( i \)th site. Throughout this paper, a positive \( J \) corresponds to an antiferromagnetic interaction and a negative \( J \) to a ferromagnetic interaction. The classical energies of the above magnetic states are

\[
E_{FM} = NS^2(2J_1 + 2J_2 + J_3) + E_0
\]

\[
E_{G-type} = NS^2(-2J_1 + 2J_2 - J_3) + E_0
\]

\[
E_{\text{stripeFM}} = NS^2(-2J_2 + J_3) + E_0
\]

\[
E_{C-type} = NS^2(-2J_2 - J_3) + E_0
\]

where \( E_0 \) is the energy of nonmagnetic state.

We calculate the magnetic moments and the total energies of the above magnetic states with GGA+\( U \). If the calculated local magnetic moments at M sites are very close to each other, we can extract the magnetic exchange coupling constants by Eq. (2). The results show that, in BaCr\( _2 \)As\( _2 \) the average moments of the four magnetic states vary \( 2.3 - 3.4 \mu_B \). The values increase when \( U_{\text{eff}} \) increases. The order moments do not vary significantly in the above four magnetic states. The average

**TABLE III:** The optimized crystal structure parameters for CaM\( _2 \)B\( _2 \)(\( \text{M}=\text{Cr, Mn, Fe, Co, Ni}; \text{B}=\text{As, P} \)) with the trigonal CaAl\( _2 \)Si\( _2 \)-type structure(space group \( \text{P}3\text{m}1\)) by using GGA+\( U(\text{U}_{\text{eff}}=1.5 \text{ eV}) \) in the AFM ordered state.

| Material       | \( a(\text{Å}) \) | \( c(\text{Å}) \) | \( z_X \)  | \( z_Y \)  |
|----------------|-------------|-------------|---------|---------|
| CaCr\( _2 \)As\( _2 \) | 4.122 | 7.269 | 0.6180 | 0.2553 |
| CaMn\( _2 \)As\( _2 \) | 4.258 | 7.002 | 0.6203 | 0.2574 |
| CaFe\( _2 \)As\( _2 \) | 4.086 | 6.834 | 0.6237 | 0.2740 |
| CaCo\( _2 \)As\( _2 \) | 3.891 | 6.761 | 0.6269 | 0.2894 |
| CaNi\( _2 \)As\( _2 \) | 3.965 | 6.714 | 0.6299 | 0.2869 |
| CaCr\( _2 \)P\( _2 \) | 3.972 | 7.023 | 0.6203 | 0.2630 |
| CaMn\( _2 \)P\( _2 \) | 4.109 | 6.775 | 0.6213 | 0.2644 |
| CaFe\( _2 \)P\( _2 \) | 3.858 | 6.639 | 0.6236 | 0.2859 |
| CaCo\( _2 \)P\( _2 \) | 3.715 | 6.602 | 0.6263 | 0.2973 |
| CaNi\( _2 \)P\( _2 \) | 3.788 | 6.558 | 0.6271 | 0.2919 |

**FIG. 2:** (color online) The sketch of the four collinear magnetic states, including the FM states, the G-type AFM state, the stripeFM state and the C-type AFM state.
moments vary 3.5 – 4.1µB in BaMn2As2 and 2.0 – 2.9µB in BaFe2As2. For BaCo2As2, the moments are very small. Finally, in the BaNi2As2, the moments are zero within the range of error 0.001µB and there are no energy gain for magnetic states. These results are consistent with previous calculations\textsuperscript{10–50}. For BaNi2As2, our results consistent with the angle-resolved photoemission spectroscopy experiment\textsuperscript{51}, which show that collinear spin-density-wave magnetic ordering does not exist in BaNi2As2.

We can extract the magnetic exchange parameters by Eqs. (2). The results are summarized below. For Co-based materials, as the magnetic moment is too small, it is not reliable to extract these exchange parameters. For Ni-based materials, the calculated magnetic exchange parameters are zero. For other three materials, the results are consistent with previous calculations as well as experimental measurements. As the energy gain in the magnetic state is proportional to \( J < S > ^2 \) and the ordered magnetic moments are large in all three materials, we can assume the atoms are close to the high spin states for simplicity. In the above effective model, we take the spin values to be the high spin of the atoms. For example, the Cr\textsuperscript{2+} ion has four electron so that the spin \( S=2 \). Similarly, we take \( S=\frac{3}{2} \) in Mn\textsuperscript{2+} ion, \( S=2 \) in Fe\textsuperscript{2+} ion.

In the case of \( U_{eff} = 0 \), our calculated \( J_2/J_1 \) value of BaCr2As2 is –0.74. It is very close to –0.85, which is give in the previous work\textsuperscript{51}. And our results show that \( J_1 > 0 \) and \( J_2 < 0 \) in all \( U_{eff} \) values, which suggests that the BaCr2As2 has G-type AFM order. This is consistent with the theoretical calculations\textsuperscript{52} and powder neutron diffraction experiment\textsuperscript{53}. In BaMn2As2, our calculated exchange parameters are \( J_1 = 15.30 \text{ meV} \), \( J_2 = 2.33 \text{ meV} \) and \( J_z = 1.08 \text{ meV} \) with high spin values for \( U_{eff} = 0 \), which is very close to the values given in the previous calculation\textsuperscript{50}. We also obtain that \( J_1/J_2 < \frac{1}{2} \), which suggests that the BaMn2As2 has G-type AFM order. And in our calculation, the G-type AFM order has the lowest energy among the four magnetic order given above. Our results are consistent with the theoretical calculation\textsuperscript{50} and neutron diffraction measurement\textsuperscript{54}. The neutron diffraction experiment also shows that the ordered moment is 3.88(4)µB\textsuperscript{53}. Our results give that the ordered moment is 3.856µB in the G-type state with \( U_{eff} = 1.5\text{eV} \). In the case of \( U_{eff} = 0 \), our calculated exchange parameters are \( J_1S^2 = 31.39 \text{ meV} \) and \( J_2S^2 = 33.51 \text{ meV} \) for BaFe2As2, which is similar to the values \( J_1S^2 = 25.5 \text{ meV} \) and \( J_2S^2 = 33.8 \text{ meV} \) given in the previous calculations\textsuperscript{55}. \( J_1/J_2 > \frac{1}{2} \) in all \( U_{eff} \) values, which suggests that BaFe2As2 has a C-type AFM order state. These results are consistent with the neutron diffraction experiment measurements\textsuperscript{55}.

The existence of large NNN AFM exchange couplings in iron-based materials, namely, \( J_2 \), is the key difference to separate them from Cr/Mn-based counterpart\textsuperscript{10}. Different from the NN exchange couplings, \( J_1 \), which stems from the direct exchange mechanism, the \( J_2 \) exchange couplings are mainly contributed from the superexchange mechanism through the d-p coupling. In the Fig. 3 we plot \( J_2 \) exchange coupling constants as a function of transition metal elements. Fig. 3(a) is for BaMn2As2 (M=Cr, Mn, Fe, Co, Ni) and Fig. 3(b) is for BaFe2B2 (B=P, As). From this result, it is clear that significant AFM \( J_2 \) only exists in iron-based materials. This result is a strong support to the high temperature superconductivity in the iron-based superconductors is directly tied with the AFM \( J_2 \)\textsuperscript{57}.

IV. THE MAGNETISM IN HEXAGONAL 122 TRANSITION-METAL PNICTIDES

In this section, we use the same method in above section to study the magnetic properties of CaMn2B2(M=Cr, Mn, Fe, Co, Ni; B=As, P) with hexagonal structure. We consider four possible collinear magnetic states, the FM state, the AFM state, the zigzag state and the stripe state, which are shown in Fig. 3. It is also reasonable to assume that the magnetic properties can be approximately described by the \( J_1 - J_2 - J_3 \) Heisenberg model\textsuperscript{58–60}, which is well study on the honeycomb lattice\textsuperscript{61}. And the above four collinear magnetic states
are contained in the classical phase diagram of the model on the honeycomb lattice. The couplings between the layers, namely \( J_z \), is ignored here as it is of a different order of magnitude.

\[
H = J_1 \sum_{\langle ij \rangle} S_i \cdot S_j + J_2 \sum_{\langle\langle ij \rangle\rangle} S_i \cdot S_j + J_3 \sum_{\langle\langle\langle ij \rangle\rangle\rangle} S_i \cdot S_j
\]  
(3)

where \( \langle ij \rangle \), \( \langle\langle ij \rangle\rangle \) and \( \langle\langle\langle ij \rangle\rangle\rangle \) denote the summation over the NN, NNN and third NN, respectively. \( S_i \) is the spin operator for the \( i \)th site, \( J_3 \) is the third NN exchange coupling constant. The classical energies of the above magnetic states are

\[
E_{FM} = NS^2(6J_1 + 12J_2 + 6J_3)/4 + E_0
\]
\[
E_{AFM} = NS^2(-6J_1 + 12J_2 - 6J_3)/4 + E_0
\]
\[
E_{zigzag} = NS^2(2J_1 - 4J_2 - 6J_3)/4 + E_0
\]
\[
E_{stripe} = NS^2(-2J_1 - 4J_2 + 6J_3)/4 + E_0
\]  
(4)

where \( E_0 \) is the energy of nonmagnetic state.

We calculated the magnetic moments and the total energies of the above magnetic states with GGA+\( U \). If the calculated local magnetic moments on M site are very close to each other, we can extract the magnetic exchange coupling constants by Eqs. (4). For the \( S \) values, we also adopt the high spin values the same in Section III.

Our calculations suggest that the magnetism in the hexagonal materials has very similar trend as those of the tetragonal counterparts in the previous section. In CaCr\(_2\)As\(_2\) the average moments of the four magnetic states range from 3.2 to 3.7 \( \mu_B \) and the values increases when the \( U \) increases. The moments vary weakly in the above four magnetic states in each \( U \). The case in CaCr\(_2\)P\(_2\) is very similar to the case in CaCr\(_2\)As\(_2\), but the moments values are a little smaller than the values in CaCr\(_2\)As\(_2\), in which the average moments of the four magnetic states are in the range 3.0 – 3.6\( \mu_B \), except that the average moment is 2.47\( \mu_B \) at \( U_{eff} = 0 \). The average moments at different \( U_{eff} \) are in the range 3.7 – 4.2\( \mu_B \) (3.4 – 4.1\( \mu_B \)) in CaMn\(_2\)As\(_2\) (CaMn\(_2\)P\(_2\)) and 2.3 – 3.1\( \mu_B \) (1.6 – 2.7\( \mu_B \)) in Fe\(_2\)As\(_2\) (Fe\(_2\)P\(_2\)). In Co\(_2\)As\(_2\) the moments are very small and the moments vary more strongly than the Co\(_2\)As\(_2\) (Co\(_2\)P\(_2\)), Mn\(_2\)As\(_2\) (Mn\(_2\)P\(_2\)) and Fe\(_2\)As\(_2\) (Fe\(_2\)P\(_2\)). Finally, in the Ni\(_2\)As\(_2\) (Ni\(_2\)P\(_2\)) the moments are zero within the range of error 0.005\( \mu_B \) and the energies are nearly degeneracy. Note that, our DFT result show that the AFM state has the lowest energy in CaMn\(_2\)As\(_2\), which is consistent with the experiment result[38]. Following the same procedure in the previous section, we can extract the magnetic exchange coupling parameters by Eqs. (4) quite accurately for CaCr\(_2\)As\(_2\) (CaCr\(_2\)P\(_2\)), CaMn\(_2\)As\(_2\) (CaCr\(_2\)P\(_2\)) and CaFe\(_2\)As\(_2\) (CaCr\(_2\)P\(_2\)). However, the calculated exchange parameters are also not accurate in Co\(_2\)As\(_2\) (Co\(_2\)P\(_2\)) due to small magnetic...
moments and the calculated magnetic exchange parameters in CaNi$_2$As$_2$(CaNi$_2$P$_2$) are also zero. The results are summarized in Fig. 5.

From these results, we can also find that $J_2$ is AFM and reaches the maximum in CaFe$_2$As$_2$ and it is small and even ferromagnetic in Cr/Mn-based counterparts. In CaFe$_2$P$_2$, $J_2$ exchange is AFM and significant when $U_{\text{eff}} \geq 1.5$eV. $J_2$ is also larger in CaFe$_2$As$_2$ than in CaFe$_2$P$_2$ for the same value of $U$ as shown in Fig. 5.

In summary, we find that the trend of the magnetism in the hexagonal materials from Cr to Ni-based is very similar to those of the tetragonal counterparts. The strong AFM exchange coupling between two NNN transition metal atoms only exists in Fe-based materials. As we will show later in this paper, the presence of strong NNN AFM in iron-based materials is consistent with the existence of two near half filling bands that are attributed to the $t_{2g}$ d-orbitals which have large d-p coupling to mediate superexchange AFM couplings.

V. PRESSURE EFFECT ON MAGNETISM

Both magnetism and superconductivity in the tetragonal iron-based superconductors are known to be sensitive to external pressure. Here we investigate that the pressure effect on the magnetism of the hexagonal structure CaFe$_2$As$_2$.

We relax the lattice constants and internal atomic positions with the GGA+$U$ method($U_{\text{eff}} = 1.5$eV) in the AFM ordered state under pressure. Then we use the optimized structural parameters to calculate the energies of the above four magnetic states with $U_{\text{eff}} = 2$ eV. Using the same method in Section IV, we can get the magnetic moments of the above four magnetic states and the exchange coupling parameters. Figure 6(a) shows the pressure dependence of the magnetic moments for FM, AFM, zigzag and stripe states of CaFe$_2$As$_2$. The magnetic moments in the magnetic states decrease almost linearly with pressure. The magnetic moments are larger than $2\mu_B$ when the pressures are in the range 0-10 Gpa. Figure 6(b) shows the change of the exchange coupling constants $J_1$ and $J_2$ as a function of the pressure. We can find that both $J_1$ and $J_2$ are very robust against pressure. $J_1$ increases slightly while $J_2$ only slightly decreases under increasing pressure.

These results are similar to to those in the tetragonal AFe$_2$As$_2$ (A=Ca, Sr, Ba). The only difference is that the value of $J_1$ decreases in the latter under increasing pressure.

VI. ELECTRONIC STRUCTURES ON THE HEXAGONAL CaFe$_2$As$_2$

The electronic structures of CaFe$_2$As$_2$ in the paramagnetic state, including the band structure, density of states (DOS) and fermi surface of CaFe$_2$As$_2$ with the optimized structural parameters, are shown in Fig. 7.

As shown in Fig. 7(a, b), there are three Fermi surface sheets, contributed from the three bands crossing the Fermi energy. Among them, the two big quasi-two dimensional cylinder-like Fermi surface sheets centered around $\Gamma$ point are electron pockets. The remain one centered around $M$ point forms a small three dimensional Fermi surfaces. These pockets are attributed to the 3d orbitals of Fe, which are located from -1.5 eV to 2.5 eV as shown in Fig. 7(a). If we ignore the couplings between FeAs layers along z-direction, the electronic structure simply includes the first two electron pockets.

We can also notice some intriguing features in the distribution of the five Fe 3d orbitals in the electronic band structure. In the hexagonal lattice structure, the three $t_{2g}$ d orbitals in the tetrahedron FeAs$_4$, which have higher energy than the $e_g$ orbitals, include $d_{xz}$ and two other orbitals which are formed by linear combinations of the other four d-orbitals in which $d_{x^2-y^2}$ carry larger weight than $d_{xz/yz}$. In Fig. 7(a), we notice that the DOS of $d_{xz}$ orbital near the fermi energy is almost zero. This feature can be understood as follows. The distance between two NN Fe atoms is very short, which is about 2.902 Å. And the distance between two NNN Fe atoms is about 4.086 Å. Due to the short NN Fe-Fe distance, the $d_{xz}$ orbital in the two Fe strongly couples to each other.

FIG. 6: (color online) (a) The magnetic moments as functions of pressure; (b) the superexchange antiferromagnetic interaction constants $J_1$ and $J_2$ as a function of the pressure for CaFe$_2$As$_2$. 
and form two molecular orbitals which can be called as bonding and antibonding orbitals. The bonding orbital is push down below the fermi energy while the antibonding orbital is push up above the fermi energy. This is similar to the \( d_{xy/yz} \) orbital in tetrahedral iron-based superconductors. Near Fermi level, the \( d_{xy/yz} \) orbitals have the largest weight. This is consistent with the presence of the large AFM \( J_2 \) obtained for the iron materials but not others in the previous section because the \( d_{xy/yz} \) orbitals have larger in-plane coupling to \( p \)-orbitals of As than the other orbitals.

We can construct a microscopic electronic model to capture the band structure of CaFe\(_2\)As\(_2\) by using maximally-localized Wannier orbital calculations. These maximally localized Wannier functions, centered at the two Fe sites in the unit cell, have five orbital/\( (1:d_{3z^2-r^2}, 2:d_{xz}, 3:d_{yz}, 4:d_{x^2-y^2}, 5:d_{xy}) \) for each Fe site. Thus, ten orbitals are needed to describe the tight binding model. As shown in the Fig. 7(a), the band dispersion is very similar between \( k_z = 0 \) plane and and \( k_z = \pi \) plane, except the \( d_{z^2} \) orbital above the fermi level. This suggests that the electronic physics is quasi-two dimensional, similar to both cuprates and iron-based superconductors in which the intrinsic interesting physics is known to be two dimensional. Therefore, for simplicity, we construct a two dimensional model with the in-plane tight binding couplings,

\[
H = \sum_{i} \sum_{m/n} \sum_{\mu \nu} t_{i\Delta,\mu\nu}^m e_i^\dagger \epsilon_{i,m\mu\sigma} e_{i+\Delta,m\nu\sigma} + \sum_{m\mu} (\epsilon_{m\mu} - \mu) n_{m\mu}(5)
\]

where \( t_{i\Delta,\mu\nu}^m \) are in-plane hopping integrals, \( \Delta \) is the hopping vector, \( m/n = A, B \) are sublattice indices and \( \mu/\nu = 1, ... , 5 \) denote orbitals. \( \rho_1 \) is the NN bond, \( R_1 \) is the NNN bond, \( r_1 \) is the third NN bond, \( \delta_1 \) is the fourth NN bond and \( \gamma_1 \) is the fifth NN bond. Other hopping integrals can be obtained by applying the symmetry operations as described in the main text.

| NN | 3rd NN | 4th NN | 5th NN |
|----|--------|--------|--------|
| \( \Delta = \rho_1 \) | \( \Delta = R_1 \) | \( \Delta = r_1 \) | \( \Delta = \delta_1 \) |
| \( \Delta = \gamma_1 \) | \( \Delta = A \) | \( \Delta = B \) | \( \Delta = A \) |
|\( (1,1) \) | -0.33 | 0.10 | -0.02 | 0.00 | -0.00 |
|\( (1,2) \) | 0.14 | 0.05 | 0.00 | -0.01 | 0.00 |
|\( (1,3) \) | 0 | 0.07 | 0 | 0.01 | 0 |
|\( (1,4) \) | 0.15 | 0.03 | 0.01 | 0.02 | -0.01 |
|\( (1,5) \) | 0 | -0.07 | 0 | 0.01 | 0 |
|\( (2,2) \) | -0.69 | -0.05 | 0.00 | -0.03 | -0.01 |
|\( (2,3) \) | 0 | -0.03 | 0 | 0.00 | 0 |
|\( (2,4) \) | 0.04 | -0.02 | 0.00 | 0.00 | -0.01 |
|\( (2,5) \) | 0 | -0.10 | 0 | 0.03 | 0 |
|\( (3,3) \) | 0.16 | 0.05 | 0.07 | 0.00 | 0.00 |
|\( (3,4) \) | 0 | 0.10 | 0 | -0.01 | 0 |
|\( (3,5) \) | -0.04 | 0.16 | -0.01 | 0.00 | 0.00 |
|\( (4,4) \) | -0.05 | 0.14 | 0.01 | 0.01 | 0.02 |
|\( (4,5) \) | 0 | -0.11 | 0 | 0.01 | 0 |
|\( (5,5) \) | 0.18 | 0.19 | 0.00 | 0.01 | 0.02 |

TABLE IV: (Unit in eV) A subset of hopping integrals \( t_{i\Delta,\mu\nu}^m \) up to the fifth NN. \( \Delta \) is the hopping vector, \( m/n = A, B \) are sublattice indices and \( \mu/\nu = 1, ... , 5 \) denote orbitals. \( \rho_1 \) is the NN bond, \( R_1 \) is the NNN bond, \( r_1 \) is the third NN bond, \( \delta_1 \) is the fourth NN bond and \( \gamma_1 \) is the fifth NN bond.
In this section, we discuss possible superconducting states in the hexagonal iron-based materials under the assumption that it is the superexchange couplings to cause superconductivity.

Since the crystal structure of CaFe$_2$As$_2$ belongs to the point group of D$_{4h}$, the pairing symmetry of CaFe$_2$As$_2$ can be classified according to the irreducible representations of the D$_{4h}$ point group. Moreover, only even parity spin-singlet pairing is allowed if the superconductivity is driven by the AFM exchange couplings. In this case, there are two possible superconducting states with $A_{1g}$ (extended s-wave) and $E_g$ (d-wave). For the $E_g$ d-wave states, there are two degenerate states. The superconducting condensation energy can be further lowered by forming the time-reversal symmetry breaking d+id-wave states. Thus we just need to focus on comparing the energies between the extended s-wave and the d+id-wave states.

A selection rule to determine the superconducting state, which we refer as Hu-Ding principle, has been proposed to unify the d-wave pairing in cuprates and s-wave pairing in iron-based superconductors. The principle states that in order to generating high $T_c$ superconductivity, the momentum space form factor of the superconducting pairing gap function which is determined by the AFM superexchange couplings must have large overlap with Fermi surfaces. The most favored pairing symmetry is the one which has the largest overlap strength. The overlap strength can be defined as

$$ W = \int dk_x \int dk_y |\Delta_k|^2 \delta(\epsilon_k - \mu), $$

where $\Delta_k$ is the momentum space SC gap function. In our case, the gap function stems from the NNN AFM superexchange couplings. For the extended s-wave, $\Delta(k) = \sqrt{2\cos \frac{\sqrt{3}}{2} k_x \cos \frac{1}{2} k_y} + \cos k_y$, and the d+id-wave order parameter $\Delta(k) = \sqrt{2\cos \frac{\sqrt{3}}{2} k_x \cos \frac{1}{2} k_y + i\sqrt{3}\sin \frac{\sqrt{3}}{2} k_x \sin \frac{1}{2} k_y}$, where $\Delta$ is a constant. In Fig. 8, we plot the overlap strength for both the s-wave Fig. 8(a) and d+id-wave Fig. 8(b) cases for 0.2 electron doping. The overlap strength for the d+id-wave is 2.85 times larger than the s-wave case (with an energy cutoff 0.05eV from the Fermi energy), so the most favored pairing symmetry for the hexagonal CaFe$_2$As$_2$ is the d+id-wave. Therefore, the d+id superconducting state is favored.

VIII. DISCUSSION AND CONCLUSION

In summary, we have shown that the hexagonal transition metal pnictrides have very similar trend in magnetic exchange interactions as those tetragonal counterparts. In both cases, the iron-based materials maximize the NNN antiferromagnetic interactions and those d-orbitals which are responsible for the largest superexchange interactions dominate near Fermi surfaces. The superexchange interactions make the hexagonal iron materials as extremely magnetic frustrated systems and can also lead to d-id superconducting ground states upon doping. As the energy scales of the NNN AFM superexchange couplings in both hexagonal and tetragonal iron materials are close to each other, we expect that the hexagonal materials can host high $T_c$ superconductivity, just like the tetragonal counterparts.

Although the hexagonal Mn-based pnictides have been successfully synthesized, the iron-based counterparts have not been obtained. However, it is worth to mention that the iron-based materials are stable in our theoretical investigation. Their phonon spectra do not show any imaginary modes. Our study can be extended to include transition metal chalcogenides. The similar results can be expected for those chalcogenides with the similar hexagonal structures.

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55 J. Hu, B. Xu, W. Liu, N.-N. Hao, and Y. Wang, Phys. Rev. B 85, 144403 (2012).
56 D. E. McNally, J. W. Simonson, J. J. Kistner-Morris, G. J. Smith, J. E. Hassinger, L. DeBeer-Schmitt, A. I. Kolesnikov, I. A. Zaliznyak, and M. C. Aronson, Phys. Rev. B 91, 180407 (2015).
57 E. Rastelli, A. Tassi, and L. Reatto, Physica B+C 97, 1 (1979).
58 J. B. Fouet, P. Sindzingre, and C. Lhuillier, The European Physical Journal B - Condensed Matter and Complex Systems 20, 241 (2001).
59 J. Oitmaa and R. R. P. Singh, Phys. Rev. B 84, 094424 (2011).
60 M. S. Torikachvili, S. L. Bud’ko, N. Ni, and P. C. Canfield, Phys. Rev. Lett. 101, 057006 (2008).
61 T. Park, E. Park, H. Lee, T. Klimczuk, E. D. Bauer, F. Ronning, and J. D. Thompson, Journal of Physics: Condensed Matter 20, 322204 (2008).
62 P. L. Alireza, Y. T. C. Ko, J. Gillett, C. M. Petrone, J. M. Cole, G. G. Lonzarich, and S. E. Sebastian, Journal of Physics: Condensed Matter 21, 012208 (2009).
63 N. Marzari and D. Vanderbilt, Physical Review B 56, 12847 (1997), pRB.
64 I. Souza, N. Marzari, and D. Vanderbilt, Physical Review B 65, 035109 (2001), pRB.
65 K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki, Phys. Rev. Lett. 101, 087004 (2008).
66 W. E. Pickett, Rev. Mod. Phys. 61, 433 (1989).
67 J. Hu and H. Ding, Sci Rep 2, 381 (2012).
68 J. C. S. Davis and D.-H. Lee, Proceedings of the National Academy of Sciences 110, 17623 (2013).