The layered compound CaClFeP is an Arsenic-free high $T_c$ iron-pnictide

Xun-Wang Yan$^{1,2}$ and Zhong-Yi Lu$^3$

$^1$Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing 100190, China and $^2$Department of Physics, Renmin University of China, Beijing 100872, China

(Dated: October 5, 2010)

We first analyze why the iron pnictides with high $T_c$ superconductivity so far are As-based, by the Hund’s rule correlation picture, then examine the P-based and Sb-based cases, respectively. Consequently, we propose that CaClFeP with ZrCuSiAs-type structure is an As-free high $T_c$ iron-pnictide. The subsequent density functional theory calculations show that the ground state of CaClFeP is of a collinearly antiferromagnetic order on Fe moments with structural distortion, resulting from the interplay between the strong nearest and next-nearest neighbor antiferromagnetic superexchange interactions bridged by P atoms, similar as the As-based pnictides. The other P-based pnictides are either nonmagnetic or magnetic but with weak exchange interactions. The Sb-based pnictides unlike show high $T_c$ superconductivity because of the existence of robust ferromagnetic order.

PACS numbers: 74.70.Xa, 74.20.Pq, 74.20.Mn

The discovery of high transition temperature $T_c$ superconductivity in LaOFeAs by partial substitution of O with F atoms [1] stimulates the intense studies on the iron pnictides. Upon doping or high pressure, there are three types of iron pnictides reported to show superconductivity, i.e. 1111-type or BaFFeAs and SrFFeAs [2], 122-type or CaClFeP with ZrCuSiAs-type structure is an As-free high $T_c$ iron-pnictide. Is it possible to find a P- or Sb-based pnictide without As to show high $T_c$ superconductivity? Physically to answer this question essentially depends upon how we understand the mechanism underlying the high $T_c$ superconductivity in the pnictides. Likewise, solving this question will greatly help us to understand the underlying mechanism. Moreover, setting of this issue is very meaningful and important in practice because Asenic strong toxicity sets the strict safety conditions to synthesize As-based pnictide samples, which confine the samples making in a few research groups worldwide. In this Letter, we show that CaClFeP with the ZrCuSiAs-type structure is an As-free high $T_c$ pnictide with the similar electronic structure and magnetic property as the As-based pnictides.

It was universally found that all the As-based pnictides are in a collinear antiferromagnetic (AFM) order below a tetragonal-orthorhombic structural transition temperature [7, 8]. Accordingly, the superconducting pairing in the As-based pnictides is now considered as being mediated by the spin fluctuations. Regarding the mechanism behind the structural and AFM transitions and their underlying relationship, there are basically two contradictory views, based on the itinerant electron picture [8] and the local moment picture [11, 12] respectively. From the very beginning, we proposed [12] the fluctuating Fe moment and P-based AFM superexchange interactions as the driving force upon the two transitions, effectively described by the $J_1$-$J_2$ Heisenberg model. Here we would like to emphasize the twofold meanings in our proposal [12]: (1) there are localized magnetic moments around Fe ions and embedded in itinerant electrons in real space; (2) it is these bands far from rather than nearby the Fermi energy that determine the magnetic behavior of the As-based pnictides, namely the hybridization of Fe with the neighbor As atoms plays a substantial role. Here the formation of a local moment on Fe ion is mainly due to the strong Hund’s rule coupling on Fe 3$d$ orbitals. Chemically, the spin-degenerated Fe 3$d$ orbitals do.

The main factor competing with the Hund’s rule coupling is the chemical bonding between the Fe 3$d$ orbitals and As 4$p$ orbitals. Meanwhile the hybridization between the Fe 3$d$ orbitals and As 4$p$ orbitals will bridge the superexchange interactions between the Fe magnetic moments induced by the Hund’s rule coupling. It is thus a dilemma to require strong superexchange interactions with robust Fe magnetic moments. Chemically, the spin-degenerated Fe 3$d$ orbitals form stronger bonds with the As 4$p$ orbitals than the spin-polarized Fe 3$d$ orbitals do. For the As-based pnictides, inspection of the calculations [12] shows that the spin degeneration pushes down the en-
energy levels raised by the Hund’s rule coupling, and then strengthens the bonding between the Fe 3d orbitals and As 4p orbitals, which makes substantial energy gain to the nonmagnetic state. However, this is still not enough to completely overcome the Hund’s rule coupling, in need of an additional energy gain of ~0.2 eV/Fe, as suggested by calculated total energy difference between the nonmagnetic state and collinear AFM state \[12\]. Consequently, there are magnetic moments induced around Fe atoms with the AFM superexchange interactions bridged by the As atoms.

In line of pnictogen atoms of P, As, and Sb, P has a much smaller atomic radius with a larger electronegativity than As while Sb has a much larger atomic radius with a smaller electronegativity than As. Hence, it is very likely that in the most P-based pnictides there will form a very strong bonding between P and Fe so that the Hund’s rule coupling is quenched. This is verified by the calculations reported below that the most P-based pnictides are nonmagnetic. On the other hand, in the most Sb-based pnictides there will form a relatively weak bonding between Sb and Fe so that large moments are induced around Fe atoms with robust ferromagnetic spin fluctuations, which is also verified by the calculations reported below. In contrast, Arsenic is in a proper balance to the dilemma. This explains why the iron pnictides with high $T_c$ superconductivity, discovered so far, are As-based rather than P-based or Sb-based. Now we deduce that if the in-plane lattice parameters $a$ and $b$ of a P-based (Sb-based) pnictide are more large (small), its electronic structure and magnetic property are more similar to the ones of the As-based pnictides since the P-Fe (Sb-Fe) bonding is more weakened (strengthened). Referring to the As-based pnictides, we further deduce that CaClFeP has the magnetic structure and property similar to the ones of the As-based pnictides, in great possibility to realize the high $T_c$ superconductivity.

To verify the deduction, we carried out the density functional theory (DFT) electronic structure calculations. In the calculations the plane wave basis method was used \[15\]. We adopted the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof \[16\] for the exchange-correlation potentials. The ultrasoft pseudopotentials \[17\] were used to model the electron-ion interactions. After the full convergence test, the kinetic energy cut-off and the charge density cut-off of the plane wave basis were chosen to be 600eV and 4800eV, respectively. The Gaussian broadening technique was used and a $k$-mesh of $16 \times 16 \times 8$ or $12 \times 12 \times 8$ was adopted to sample the Brillouin zone of $a \times a \times c$ or $\sqrt{2}a \times \sqrt{2}a \times c$ supercell, respectively. In the calculations, the lattice parameters with the internal atomic coordinates were all determined by the energy minimization. CaClFeP is in a tetragonal layered structure with $P4/mnm$ symmetry. A crystal unit cell consists of eight atoms with alternating FeP and CaCl layers along the $c$ axis (Fig. 1(a)).

As analyzed above, our calculations show that 111-type $BFeP$ ($B = Li$ or Na) and 122-type $AFe_2P_2$ ($A = Ba$, Sr, or Ca) are all nonmagnetic semimetals since the strong Fe-P bonding quenches the Fe magnetic moments. Actually, the lattice parameters $a$ and $b$ of these compounds are mainly determined by FeP layers, around 3.8 Å. The large parameters $a$ and $b$ go to the 1111-type, in which the other layers strongly affect the lattice parameters. Indeed, we find the large lattice parameters ($a=b=4.14$ Å, c=8.70 Å) for CaClFeP in magnetic phases.

In Fig. 2 we plot the electronic band structure and Fermi surface of CaClFeP in the nonmagnetic state. There are three cylinder-like Fermi surface sheets, among which the two are of electron-type around M-A and the other one is of hole-type around Γ-Z. The volumes enclosed by these Fermi sheets give 0.19 electrons/cell and equally 0.19 holes/cell, i.e. $1.31 \times 10^{21}$/cm$^3$. The compound CaClFeP is thus a semimetal with a low carrier density, between normal metals and semiconductors. The density of states (DOS) at the Fermi energy is 3.65 states/(eV× unit cell). The corresponding electronic specific heat coefficient $\gamma = 8.60 \text{ mJ/(K}^2 \times \text{ mol})$ and the Pauli paramagnetic susceptibility $\chi_p = 1.49 \times 10^{-9}$ m$^3$/mol. The 10%-replacement of Ca by
La makes the electron-type and hole-type Fermi sheets more matched in shape, as shown in Fig. 3(d) and (e). In order to explore the magnetic structures and clarify the exchange interactions between the Fe-Fe moments, we calculated three different magnetic states, the ferromagnetic, checkerboard (Neel) AFM, and collinear AFM states, which respective energies are calculated to be (0.040, -0.044, -0.132) eV/Fe if the energy of the non-magnetic state is set to zero. The magnetic moment around each Fe atom is found about 2 \( \mu_B \). All these magnetic states can be self-consistently described by the following frustrated Heisenberg model with the nearest and next-nearest neighbor couplings \( J_1 \) and \( J_2 \),

\[
H = J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{<ij>} \vec{S}_i \cdot \vec{S}_j,
\]

whereas \( \langle ij \rangle \) and \( <ij> \) denote the summation over the nearest and next-nearest neighbors, respectively. From the calculated energy data, we find that \( J_1 \sim 20.96 \text{ meV}/S^2 \) and \( J_2 \sim 32.58 \text{ meV}/S^2 \) (the detailed calculation is referred to Appendix of Ref. [12]). The ground state of CaClFeP is thus in a collinear AFM order.

In the collinear AFM phase, a small structural distortion is found to further make energy gain by 1.2 meV/Fe, which changes the angle between two principal axes in ab-plane \( \gamma \) from 90° to 90.4° (see Fig. 3(b)), equivalently, the lattice unit cell slightly expands along the spin-antiparallel direction and slightly shrinks along the spin-parallel direction. Here we emphasize that our calculations show that the driving force upon this tetragonal-orthorhombic structural distortion is nothing but the magnetic interaction. More specifically it is the superexchange interaction \( J_2 \) that induces the Fe-spin collinear AFM order and drives the structural distortion to break the rotational symmetry, as found in LaOFeAs [12]. Moreover, the anti-parallel alignment for the Fe moments between the neighboring FeP-layers was found almost degenerate with the parallel alignment.

From Fig. 3 we notice that the Fermi surface is more distributed along \( ZR' \) or \( \Gamma'X' \) than along \( ZR \) or \( \Gamma X \) direction in Brillouin zone for CaClFeP in the collinear AFM state, similar as in LaOFeAs and BaFe\(_2\)As\(_2\) [12, 18]. This suggests that the spin-antiparallel direction is more conductive than the spin-parallel direction in real space. This anti-intuitive finding was confirmed by the recent experiment on the detwinned BaFe\(_2\)As\(_2\) [19].

Fig. 4 projects the density of states onto the five 3d orbitals of Fe in the collinear AFM of CaClFeP. We see that the five up-spin orbitals are almost filled while the five down-spin orbitals are nearly uniformly partially filled. This shows that the P atom-imposed crystal field splitting is small. The formation of Fe magnetic moments is thus due to the Hund’s rule coupling, which is a universal feature found in all the As-based pnictides [12, 18].

TABLE I: Calculated exchange couplings \( J_1-J_2 \) (Fig. 1(b)) with measured superconductivity transition temperature \( T_c \) (K).

| Compound         | \( J_1 \) (meV/Fe) | \( J_2 \) (meV/Fe) | \( T_c \) (K) |
|------------------|---------------------|---------------------|---------------|
| LaOFeP           | 0.52                | 7.83                | 7[6]          |
| (Fe\(_2\)P\(_2\))(Sc\(_4\)Sc\(_2\)O\(_6\)) | 3.74                | 12.24               | 17[21]        |
| BaFFeP           | 0.62                | 11.20               | -             |
| CaClFeP          | 20.96               | 32.58               | -             |
much larger moments formed at Fe atoms (AFM, and collinear AFM orders, however, there are magnetic orders like the checkerboard AFM, bi-collinear are similar with each other in electronic structures and compounds. We find that all these Sb-based pnictides are nonmagnetic semimetals. We also show that the Sb-based pnictides unlikely show high $T_c$ superconductivity. This work is supported by National Natural Science Foundation of China and by National Program for Basic Research of MOST, China.

Fig. 5(a) shows that for NaFeAs the ferromagnetic order is a maximum energetically, and the magnetic energy versus the angle $\theta$ between the two sublattice spin orientations, from the ferromagnetic order ($\theta = 0^\circ$) to the Neel AFM order ($\theta = 180^\circ$). (a) NaFeAs and (b) NaFeSb.

Activity transition temperature $T_c$ is proportional to $J_2^{18}$. Theoretically, the two-band $t$-$J_1$-$J_2$ model also indicates that the $T_c$ in pnictides is proportional to the $J_2^{20}$.

As we have just shown, CaClFeP takes the similar electronic structure and magnetic property as the As-based pnictides and the exchange couplings $J_1$ and $J_2$ of it are as large as the ones of BaFe$_2$As$_2$$_{18}$. We thus predict that the high $T_c$ (likely over 40K) superconductivity can be realized in CaClFeP. Meanwhile, for LaOFeP and (Fe$_2$P$_2$)/(Sr$_4$Sc$_2$O$_6$) the smallness of calculated $J_1$ and $J_2$ is consistent with the observed low $T_c$ (Table I).

We have performed the DFT calculations on Sb-based pnictides, including 111-type, 122-type, and 1111-type compounds. We find that all these Sb-based pnictides are similar with each other in electronic structures and magnetic properties. In magnetic states, they show rich magnetic orders like the checkerboard AFM, bi-collinear AFM, and collinear AFM orders, however, there are much larger moments formed at Fe atoms ($\sim 3\mu_B$/Fe) in the Sb-based pnictides than in the As-based pnictides because of the strong Hund’s rule effect and the weak Fe-Sb bonding, as analyzed above. Besides, even though the collinear AFM order is the most stable energetically, there exists a stable ferromagnetic order in the Sb-based pnictides, independent of the AFM fluctuations. This is essentially different from the As-based pnictides, in which a ferromagnetic order is never stable.

Fig. 5(a) shows that for NaFeAs the ferromagnetic order is a maximum energetically, and the magnetic energy versus the angle $\theta$ between the two sublattice spin orientations is well described by the nearest neighbor exchange Heisenberg model. The calculations also show that CaClFeP behaves likewise. In contrast, for NaFeSb the ferromagnetic state is a local minimum in the energy landscape, lower than the nonmagnetic state (Fig. 5(b)). And the variation of the magnetic energy with the angle $\theta$ severely deviates from the exchange Heisenberg model. This shows that the ferromagnetic state has a different exchange interaction origin than the AFM states, which is likely related to the possible orbital ordering. This ferromagnetic state can be stable until applying a high pressure of 25 GPa. Since such ferromagnetic correlations are against the superconducting pairing induced by the AFM fluctuations, we don’t think there is the high $T_c$ superconductivity realized in Sb-based pnictides. To our knowledge, no Sb-based pnictides are reported to show high $T_c$ superconductivity in experiment.

In summary, by the Hund’s rule correlation picture we may well understand the iron pnictides, in which the different magnetic structures and properties result mainly from the competition between the Hund’s rule effect on Fe 3d-orbitals and the Fe-P, Fe-As, or Fe-Sb bonding. In search for an As-free high $T_c$ pnictide, we show that CaClFeP is an AFM semimetal with the strong P-bridged nearest and next-nearest neighbor AFM superexchange interactions, which give rise to the collinear AFM order on Fe moments in the ground state, similar as LaOFeAs and BaFe$_2$As$_2$. Upon doping or high pressure, CaClFeP is predicted to show high $T_c$ superconductivity. The other 1111-type P-based iron-pnictides are also AFM semimetals but with weak exchange interactions, while both 111-type and 122-type P-based iron-pnictides are nonmagnetic semimetals. We also show that the Sb-based pnictides unlikely show high $T_c$ superconductivity.

* Electronic address: zhu@ruc.edu.cn

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