Magnetism and electronic structures of novel layered CaFeAs$_2$ and Ca$_{0.75}$(Pr/La)$_{0.25}$FeAs$_2$

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I. INTRODUCTION

Similar to high-$T_c$ cuprates, an antiferromagnetic (AFM) spin-density-wave (SDW) state is the precursor of the superconducting iron pnictides, which leads to a strong suggestion that the spin fluctuations contribute the pairing force of the Cooper pairs and possible s-wave odd pairing symmetry. Empirically, it was found that the superconducting transition temperature considerably rises when the spatial distance of conducting layers is enlarged in cuprate superconductors. Therefore, fabricating a compound with large separation between the FeAs layers is an important way to search for materials with higher $T_c$. On the other hand, since iron-based superconductors are composed of stacking of Fe$_2$Pn$_2$ or Fe$_2$Ch$_2$ ($Pn=\text{P,As and Ch=S,Se,Te}$) layers and blocking layers such as LaO or K, to design and search compound with new blocking layers is promising for discovering new high-$T_c$ superconductors through enhancing spin fluctuations.

Recently, two novel iron pnictides compounds (Ca,Pr)FeAs$_2$ and Ca$_{1-x}$La$_x$FeAs$_2$ have been synthesized, and the superconducting transition temperatures are 20 K and 45 K, respectively. Though pure CaFeAs$_2$ was not synthesized yet, the compounds Ca$_{1-x}$La$_x$FeAs$_2$ ($R=\text{La, Pr, etc.}$) share a common blocking layers of As atoms. These As atoms in arsenic layers form zigzag chains, and they are quite different from the anions square network in LaOFeAs. The unique electronic structure of newly synthesized compound Ca$_{0.75}$(Pr/La)$_{0.25}$FeAs$_2$ may play important roles in considerably lifting the $T_c$. So in this paper, we perform density functional theory (DFT) calculation to investigate the electronic and magnetic structures of parent phase and its doped compounds. We find that the Fermi surface of CaFeAs$_2$ in nonmagnetic phase (NM) has two pairs of double cones located at around $G$ point in Brillouin zone, and each pair of double cones is connected by their tips, which is different from other research, and the Fermi surface nesting drives its ground state as a bad metal with striped AFM (SAFM) phase. The As in arsenic layers is negative monovalent and acts as blocking layers enhancing two-dimensional character by increasing the spatial distance between the FeAs layers. This favors strong antiferromagnetic fluctuations mediated pairing, implying higher $T_c$ in Ca$_{0.75}$(Pr/La)$_{0.25}$FeAs$_2$ than Ca$_{0.75}$(Pr/La)$_{0.25}$Fe$_2$As$_2$. © 2015 AIP Publishing LLC.
The additional hole pocket consists of 3$d_{xz}/3$d_{yz}$ orbital. This hole pocket mainly originates from the hybridization between Fe 3$d_{xz}/3$d_{yz}$ orbital and As1 4$p$ orbital in the FeAs1 layer. Meanwhile, the characteristic bands show that the four electron cones are mainly derived from the As2 $p_z$ orbitals. Our Fermi surfaces are very similar to those reported by Katayama et al., except that our Fermi surfaces have two Dirac-type cones around the G point. We attribute this difference to the insufficient number of k-points for Fermi surfaces calculation in Katayama et al. results.

To study the magnetic instability of CaFe$\text{As}_2$, we further analyze the Fermi surface topology in the NM phase. The top view of Fermi surface sheets is shown in Fig. 2(a). Narrow Fermi surface sheets around the corner of Brillouin zone (G point) clearly reflect the two-dimensional character of Fermi surface, which is almost dispersionless along $k_z$ direction, and consistent with layered crystal structure of CaFe$\text{As}_2$. Meanwhile, the outer sheets of the G point almost coincide with the outer sheets of hole pockets around the G point after the translation along the diagonal direction, implying a Fermi surface nesting phenomenon and an AFM SDW instability. The nesting vector is $Q_{\text{SDW}} = (\pi/a, \pi/a, 0)$, as illustrated in Fig. 2(a). We anticipate that such an SDW instability would lead to anomalies in temperature-dependent magnetic susceptibility, electrical resistivity, and specific heat, which expect further experiments.

Furthermore, in order to clarify the Fermi surface nesting and the SDW instability quantitatively, we have also calculated the spin susceptibility of the electrons

$$\chi^s(q) = -\frac{1}{N} \sum_{k,m,n} f(\varepsilon_m(k + q)) - f(\varepsilon_n(k))$$

(1)

The $q$-dependence of the real part of $\chi^s$ in the momentum space is shown in Fig. 2(b). The maximum of $\chi^s$ appears at $(\pi, \pi, 0)$. It is in agreement with the above nesting vector, suggesting stable SAFM configuration as shown below.

The calculated DOS near the Fermi level in NM phase show a strong Fe-3$d$ character with a small contribution of As-4$p$ orbital states. We find that the $d_{xy}$, $d_{xz}$, and $d_{yz}$ components of Fe-3$d$ orbitals contribute to the most of Fermi surface, particularly from the $d_{xy}$ orbital.

In the low-temperature ground state, both the comparison of total energies of six possible magnetic configurations in Table I and the spin susceptibility analysis in Fig. 2(b) have shown that the magnetic ground state of CaFe$\text{As}_2$ is SAFM. Fig. 3 shows the electronic band structures and Fermi surfaces of CaFe$\text{As}_2$ in the SAFM phase. The band structures near the Fermi energy $E_F$ mainly consist of Fe 3$d$ and As2 4$p$ states, as seen in Fig. 3(a). The Fe 3$d$ states account for the bands between $-3.5$ and 1.0 eV, with the Fe 3$d$ and As1 4$p$ hybridization below $-2.5$ eV. Though the distributions of As2 4$p$ states extend from $-3.5$ to 2.5 eV, the distance between As2 and FeAs1 is nearly 5 Å, the hybridization between Fe and As2 is little due to large separation between As2 layer and FeAs1 layer and blocking Ca layer. We expect that the AFM fluctuations in CaFe$\text{As}_2$ may provide stronger superconducting pairing force than that in LaFeAsO and CaFe$\text{As}_2$.3$
We also obtain the Fermi surfaces of SAFM CaFeAs₂, as shown in Fig. 3(b). Unlike the NM phase, the Fermi surface sheets consist of two parts, one hole pocket in the zone center and electron pockets in the zone edges. The dispersion character of the zone-center hole pocket is mainly attributed to the As₂\(p_z\) orbital, while Fe \(d_{x^2-y^2}\) orbital contributes the Fermi surface along the \(z\)-direction. Similar to the NM phase, two electron cones near the zone-edges are mainly derived from the \(p_x\) and \(p_y\) orbitals of the As₂ layer. So the Fermi surface due to As₂ layers is almost not affected by Fe magnetic configuration in the FeAs layer. This implies the As₂ layer only weakly interplays with superconducting FeAs layer, which enhances the low dimensionality and magnetic fluctuations and favors high \(T_c\).

The DOS near the Fermi level show a strong Fe 3\(d\) character with a small contributions of As 4\(p\) orbital and Ca 4\(s\) orbital states. The magnetic moments of Fe1 and Fe2 are antiparallel. The hybridization between Fe 3\(d\) and As 4\(p\) orbitals in the FeAs1 layer ranges from \(-1\) to \(-3\) eV below \(E_F\), which is reminiscent of the cuprate situations where Cu 3\(d\) and O 2\(p\) are significantly mixed. Considerable DOS at the Fermi level suggests that the ground state of CaFeAs₂ is a metal. It is found that spin-down DOS mainly distribute from \(-0.5\) to \(-3\) eV, while spin-up DOS mainly locates from \(-2\) eV to \(E_F\), their splitting contributes to the magnetic moment.

We find the electron occupations are nearly uniformly distributed among these five 3\(d\) orbitals. The orbital resolved magnetic moments are 0.41, 0.53, 0.34, 0.42, and 0.39 \(\mu_B\) for the \(3z^2-r^2\), \(x^2-y^2\), \(xy\), \(xz\), and \(yz\) orbitals, respectively, giving rise to the total magnetic moment about 2.1 \(\mu_B\) around each Fe atom. The orbital resolved properties in SAFM CaFeAs₂ are summarized in Table II. This indicates that the crystal field splitting imposed by As atoms is relatively small and the Fe 3\(d\)-orbitals hybridize strongly with each other.

Obviously, the electron doping in CaFeAs₂ is an efficient way to suppress the Fermi surface nesting in Fig. 2, hence destroy the SDW order, since the shifting of Fermi level mismatches the electron and hole Fermi surfaces. We thus further present the electronic properties of doped CaFeAs₂.

It was observed experimentally that La or Pr doping may induce superconductivity in CaFeAs₂. To get insight the variation of electronic structures with doping, we have also obtained the band structure of CaFeAs₂ with 25% La- and 25% Pr-doping by supercell calculation. Considering the strong correlation of the 4\(f\) electrons in Pr, we apply the GGA+U (U = 9 eV) code for Pr-doped compound. We plot the DOS and Fermi surface of Pr/La doped CaFeAs₂ in Fig. 4, displaying the total and atomic orbital-resolved partial DOS for Ca₀.₇₅(Pr/La)₀.₂₅FeAs₂ in the NM phase. The contribution of Fe-3\(d\) electrons to the Fermi surface is also dominant. By comparing Fig. 4(a) with Fig. 4(c), one can see that the DOS peaks concentrated in the energy range from 2 to 3 eV above \(E_F\) arise from the empty 4\(f\) orbital of La. On the other hand, by comparing Fig. 4(b) with Fig. 4(d), one finds

| TABLE II. The orbital resolved properties in striped antiferromagnetic CaFeAs₂. |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe atom          | \(d_z\)         | \(d_{x^2-y^2}\) | \(d_{xy}\)      | \(d_{xz}\)      | \(d_{yz}\)      |
| Magnetic moment  | 0.41            | 0.53            | 0.35            | 0.42            | 0.39            |
| Occupation       | 1.29684         | 1.20068         | 1.24786         | 1.25321         | 1.26146         |
that the 4f DOS peaks in Pr-doped compound are situated from $-4.5$ to $-5.3\,\text{eV}$ below $E_F$, in agreement with the LDA+DMFT (dynamical mean-field theory) results for PrFeAsO.\textsuperscript{17} It is clearly seen that the Fermi surface nesting is effectively suppressed with the doping of Pr and La. This indicates that SDW transition can be suppressed through La or Pr doping. Comparing with the Fermi surfaces in CaFeAs$_2$ in Fig. 2(a), we find that the Fermi surface sheets in Ca$_{0.75}$Pr$_{0.25}$FeAs$_2$ becomes rather complicated, due to the involvement of 4$f$ electrons of Pr in the formation of Fermi surfaces. The SDW order no longer exists in Ca$_{0.75}$(Pr/La)$_{0.25}$FeAs$_2$, favoring the superconducting ground state.

### III. CONCLUSION

In summary, the electronic and magnetic properties of mother material CaFeAs$_2$ have shown that the ground state of orthorhombic CaFeAs$_2$ is the striped antiferromagnetic phase driven by the Fermi surface nesting. The arsenic layers consist of negative monovalent As$_2$ which contributes electrons to the FeAs1 layer to increase its carrier density. What is more, the arsenic layers also act as blocking layers enhancing two-dimensional character of the material by increasing the spacing between the FeAs1 layers. Electronic and magnetic structures in electron-doped phase Ca$_{0.75}$(Pr/La)$_{0.25}$FeAs$_2$ show that SDW order is suppressed by La/Pr-substitution, favoring the establishment of superconducting state.

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