Enhanced Orbital Degeneracy in Momentum Space for LaOFeAs

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The Fermi surfaces (FS) of LaOFeAs (in \( k_z=0 \) plane) consist of two hole-type circles around \( \Gamma \) point, which do not touch each other, and two electron-type co-centered ellipses around M point, which are degenerate along the M-X line. By first-principles calculations, here we show that additional degeneracy exists for the two electron-type FS, and the crucial role of F-doping and pressure is to enhance this orbital degeneracy. It is suggested that the inter-orbital fluctuation is the key point to understand the unconventional superconductivity in these materials.

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![Diagram](https://example.com/diagram.png)

FIG. 1: Upper panels: Schematic plots for the Fermi surfaces of LaOFeAs. The left panel is for pure LaOFeAs, while the right panel is for the case with about 20% F-doping. The large square (solid lines) is the BZ of one Fe cell, while the small diamond (dashed lines) is the BZ of two Fe cell. Please note the interchange of the orbital characters of two electron-type FS after F-doping. Lower panel: The projected orbital characters of states at FS, which is defined as \(|\langle \alpha |\Psi_k \rangle|\). Here \( \alpha \) are five local Fe-3d orbitals, \( \Psi_k \) are Bloch states around one of the ellipses, and angle \( \theta \) is defined in the inset.

The electronic structure of LaOFeAs is quasi two dimensional and very similar to typical semimetal. Namely there are three hole-type Fermi surfaces (FS) around the \( \Gamma-Z \) line, and two electron-type FS around the M-A line of the Brillouin zone (BZ). The existence of five FS makes the problem complicated, however the electronic structure around Fermi level can be qualitatively understood in a simple way using three orbitals per Fe site \( (d_{xy}, d_{xz}, d_{yz}) \). Here we define the local coordinates \( x \) and \( y \) to be 45° rotated from the \( a \) and \( b \) directions of the crystal lattice respectively.

Let’s focus on the \( k_z=0 \) plane. There are two co-centered circles around the \( \Gamma \) point, which are hole-type FS and mostly come from the \( d_{yz} \) and \( d_{xz} \) states of Fe. In addition, there are two co-centered ellipses around the \( M \) point, which are electron-type FS and mostly come from the \( d_{xy} \) and \( d_{yz/zz} \) states of Fe (see Fig.1). The anisotropy (or the shape) of the ellipses is related to the hybridization between \( d_{xy} \) and \( d_{yz} \) (or \( d_{xz} \)). The stronger the hybridization, the more distortion of the ellipses. The projected orbital characters of the electron-type FS are shown in Fig.1. One important fact to be noted here is that the two hole-type circles around \( \Gamma \) do not touch each other, however, the two electron-type ellipses around \( M \) are degenerate along the \( X-M \) line (see Fig.1), and this degeneracy is protected by the crystal symmetry of the system. However, we will show here that additional degeneracy exists for the two branches of electron-type FS, and the crucial roles of F-doping or pressure is to enhance this degeneracy.

As discussed recently by several papers, significant FS nesting exists between the hole and the electron type FS for pure LaOFeAs. After shifting the hole FS around \( \Gamma \) by a vector \( q=(\pi, \pi, 0) \), it will largely overlap with the electron FS around \( M \). This leads to spin-
density-wave (SDW) instability, and is the origin of the 150 K anomaly observed by transport, susceptibility, and optical measurements [14]. It is now realized that the SDW instability actually competes with superconductivity, and superconducting state can be realized only after the SDW transition is suppressed [2, 14]. Electron doping by F is an efficient way to suppress the nesting effect (the SDW instability), because the shifting of Fermi level enhances the mismatch between electron and hole FS (as shown in Fig.1). It is also true that the superconductivity was observed in LaONiAs [15], where nesting effect discussed above is irrelevant. All those information suggest that the nesting between the electron and hole FS can not be the key issue for the superconductivity.

Any role else played by F-doping in achieving high $T_c$ superconductivity? This is the main point we would like to address here, based on quantitative first-principles calculations. We use plane wave pseudo-potential method and the generalized gradient approximation (GGA) for exchange-correlation potential, the same approach as we reported before [12]. As discussed above, two hole-type FS are co-centered circles around Γ point. They have different size and do not touch each other. However, two electron-type FS are ellipses around M point. They have the same size, but are rotated by 90° from each other. As the result, they overlap (or degenerate) at special k-points along the X-M line of the BZ (see Fig.1 for schematic understanding). The size of the electron-type FS will increase with F-doping, however, most interestingly the shape of two ellipses is also significantly changed by F-doping, as shown in Fig.2. With the increment of F-doping, the anisotropy of ellipses is suppressed (i.e., they are more and more circle-like), as the result the orbital degeneracy right at the two electron-type FS is enhanced. By about 10% F-doping, the two ellipses become very close to circles and almost exactly overlap. However, with further F-doping, two ellipses are distorted again. 10%-F is about the optimal doping level found experimentally for this family of compounds, and our calculations show that at this doping level the orbital degeneracy in the momentum space is the highest.

More careful analysis about the band structure near the FS show that additional degeneracy exists at the two electron-type FS, which can be tuned by F-doping. This degeneracy can be understood from the calculated band
structure as shown in Fig.3(a). Looking at the M-Γ direct, there are two dispersive electron-type bands crossing the Fermi level. However, the two bands disperse at different velocity and they cross each other at about 85 meV above the Fermi level. It is this band-crossing which leads to the enhancement of FS degeneracy discussed above. This band-crossing is accidental, but it is guaranteed by the different dispersion velocities of the two bands, and it is a common feature as seen in this family of compounds [12]. One of the bands has mainly character of two-dimensional \( d_{xy} \) orbital, which is strongly dispersive in the plane; another one of the bands is the linear combination of one-dimensional orbitals \( d_{yz} \) and \( d_{zx} \) orbitals. The key point is that the low-lying \( d_{xy} \) band (at M point) disperses faster than the high-lying \( d_{yz/zx} \) band. By up-shift of the Fermi level (F-doping), the two electron-type FS will become more and more degenerate, however beyond 85 meV above the Fermi level, the two FS interchange the orbital character and start to deviate from each other (as shown in Fig.1 and Fig.2).

In the following we discuss the effect of pressure and point out that pressure can play a similar role as F-doping. For this purpose, we fully optimize the crystal structure (including internal coordinates) using the experimental space group P4/mmm for each fixed volume. Then the electronic structures are calculated using the optimized structure. Fig.4 shows the calculated total energies, \( c/a \) ratios, and internal coordinates as function of volume. The general tendency of lattice behavior under pressure is quite smooth and the calculated bulk modulus is about 90 GPa, suggesting that the compound is relatively easy to be compressed. Other details about the effect of pressure will be discussed elsewhere, here we concentrate on the electronic structure. Fig.3(b) shows the calculated band structure of LaOF_{e}As under pressure (about 30 GPa). It is clearly seen that the crossing between the two electron-bands (along M-Γ line) is shifted downward to be less than 1 meV above Fermi level. In the meanwhile, the size of the electron-type FS is enlarged. All these indicate the same tendency as discussed above for F-doping, namely the orbital degeneracy of two electron-type FS is enhanced by pressure. In addition to the uniform pressure, we also found that this degeneracy can be enhanced by uniaxial pressure along the \( c \) axis. As shown in Fig.3(c), the band crossing is shifted downward to be about 7 meV above Fermi level by 5% shorting of \( c/a \) ratio with fixed volume.

The high orbital degeneracy at the FS will lead to strong inter-orbital fluctuation and may lead to inter-orbital pairing. In such case, it will be very easy to understand why the \( T_c \) is enhanced initially by F-doping [1] and pressure [16], and is suppressed beyond the optimal doping level about 10%. Based on this inter-band pairing picture, the possible pairing symmetry has been discussed in our parallel paper [17]. Here we will show that the experimentally observed \( T_c \) versus F-doping phase diagram can be explained semi-quantitatively by our scenario. For this purpose, we construct a minimum two bands effective Hamiltonian to describe the electron-type FS.

As we have discussed in our parallel paper [17], the strong inter-orbital ferromagnetic fluctuation will induce an even parity, orbital singlet and spin triplet paring state. This tendency will be strongly enhanced by the large orbital degeneracy at the Fermi surface. Since the electron pairing happens in momentum space, the main contribution to the paring comes from the area near the FS. Therefore for the purpose of illustration, we can use a very simple two band model on the square lattice, which not only gives the right shape but also the density of states near the FS for different \( F \) doping. The Hamiltonian reads,

\[
H = \sum_{k\alpha\sigma} (\varepsilon_{k\alpha} - \mu) C_{k\alpha \sigma}^\dagger C_{k\alpha \sigma} - J_{k-k'} \sum_{k,k',m} \Delta_{km}^\dagger \Delta_{k'm}^\dagger (1)
\]

where \( \alpha = 1, 2 \) are orbital indices, and

\[
\varepsilon_{k,1} = t_1 \gamma_k + t_1 \gamma_k^{(1)} + t_2 \gamma_k^{(2)} ,
\]

\[
\varepsilon_{k,2} = t_2 \gamma_k^{(1)} + t_1 \gamma_k^{(1)},
\]

with \( \gamma_k = \cos k_x + \cos k_y, \gamma_k^{(1)} = \cos (k_x + k_y) \) and \( \gamma_k^{(2)} = \cos (k_x - k_y) \).

By tuning the hopping integrals \( t, t_1 \) and \( t_2 \), we can obtain very similar FS with the calculated results from first-principles for different doping. We then solve the above
Hamiltonian by mean field decoupling, as described in detail in our previous paper [17]. The spacial pairing symmetry is chosen to be s-wave and \( k \) dependence of \( J_k \) is also ignored for simplicity. For each doping, we first fit the FS to the GGA results by tuning the above hopping integrals and then calculate the superconducting gap by mean field approach. The results are plotted in Fig. 5. Although our calculation is very rough, it still indicate two important features of our theory. First, the superconductivity in the hole doped side and electron doped side is from the same origin. As pointed out previously [14], for the pure compound (i.e. without doping), there is an extra SDW instability due to the nesting effect between hole and electron FS, which kills the superconductivity. Both electron and hole doping will remove the FS nesting effect and superconductivity appears. Second the strongest superconductivity tendency appears on the electron doping side, with the doping concentration around 10%. Both of these predictions seem quite consistent with the current experimental data. On the other hand, care must be taken if both F-doping and pressure are applied. Our prediction is that \( T_c \) will be enhanced by pressure for samples below optimal F-doping (about 10%), however it is opposite for overdoped samples.

In summary, by first-principle calculation, we show that the crucial role played by either F-doping or pressure is to enhance the orbital degeneracy, which leads to strong inter-band fluctuation. Combining with experimental observations, we suggest that the inter-orbital pairing is the key to be considered for the mechanism of superconductivity in this compound. The same orbital degeneracy is also present in LaONiAs, and this will be discussed in our separated paper [19].

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