Electron-hole asymmetry and quantum critical point in hole-doped \( \text{BaFe}_2\text{As}_2 \)

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**Abstract** – We show, from first-principles calculations, that the hole-doped side of Fe-As–based compounds is different from its electron-doped counterparts. The electron side is characterized as an itinerant metal with Fermi surface nesting, and SDW-to-NM quantum critical point (QCP) is realized by doping. For the hole-doped side, on the other hand, orbital-selective magnetic ordering develops together with checkboard anti-ferromagnetic (AF) ordering without lattice distortion. A unique SDW-to-AF QCP is achieved, and the \( J_2 = J_1/2 \) criterion (in the approximate \( J_1\&J_2 \) model) is satisfied at a hole-doping level of about \( z=0.7 \). The observed superconductivity is located in the vicinity of QCP for both sides.

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The superconductivity found in Fe-As–based compounds \([1]\) is attractive and challenging not only because it is the only non-cuprate system which shows superconductivity beyond 40 K \([2]\), but also because of the magnetic nature of Fe, and of the multi-band character of the system. Initial studies concentrated on the electron-doped compounds, such as \( \text{Re}(\text{O}_{1-x}\text{F}_x)\text{FeAs} \) \([1]\) or \( \text{ReO}_{1-x}\text{FeAs} \) \([3]\). For the parent compound \( \text{LaOFeAs} \), it was first pointed out by Singh et al. \([4]\) and G. Xu et al. \([5]\), based on first-principles calculations, that magnetic instabilities play crucial roles for the understanding of superconductivity, and \( \text{LaOFeAs} \) is located at the border line of both anti-ferromagnetic (AF) and ferromagnetic (FM) instabilities. Soon it was realized that significant Fermi surface nesting exists between the hole and the electron Fermi surfaces (FS) connected by a \( q = (\pi, \pi) \) vector \([6,7]\). Based on transport and optical measurements and detailed first-principles calculations, J. Dong et al. \([7]\) proposed that a stripe-type spin-density-wave (SDW) state should be stabilized at low temperature, and the essential physics to be discussed here is the competing orders between the SDW and the superconducting states. The predicted SDW state was confirmed by neutron experiment, and the stripe-type spin ordering pattern was observed \([8]\). The success of LDA or GGA-type calculations \([9,10]\) for the present systems are in sharp contrast to the failure when the same calculations were applied to cuprates. Although the electron correlation may play certain important roles \([11]\), it is clear that \( \text{LaOFeAs} \) is located at the metallic side, as suggested by the metallic nature of the SDW state. The experimentally observed small ordered moment \([8]\) (compared with first-principles calculations based on LDA or GGA) remains to be a difficult issue, however it was demonstrated by recent careful studies \([9,10,12]\) that the discrepancy can be much reduced if an optimized structure is used.

Recent interests however move to the hole-doped \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) or \( \text{Sr}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) with \( T_c \) up to 38 K \([13]\), because very large single crystal can be synthesized \([14]\). For the parent compound \( \text{BaFe}_2\text{As}_2 \), the SDW instability similar to \( \text{LaOFeAs} \) was observed \([15]\), and it was demonstrated by first-principles calculations \([16]\) that \( \text{BaFe}_2\text{As}_2 \) is electronically similar to \( \text{LaOFeAs} \). However, as we will show in this paper, the situation is true for the parent compounds, but the physics at the hole-doping side is quite different with the un-doped or electron-doped side.

We performed systematic first-principles calculations for both hole-doped \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) and electron-doped \( \text{LaO}_{1-x}\text{F}_x\text{FeAs} \), using the virtual crystal approximation for the doping. We used the experimental lattice parameters with the optimized internal coordinates of

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Fig. 1: The magnetic ordering patterns of two kinds of anti-ferromagnetic states. The checkboard ordering is called AF1, and the stripe-type SDW state [7] is called AF2 here. Two exchange coupling constants, $J_1$ and $J_2$, are defined for the nearest-neighbor and next-nearest-neighbor interactions, respectively.

As, as suggested by previous studies [12]. Two different anti-ferromagnetic ordered structures (as defined in Fig. 1) are considered in the present study.

**Parent compound BaFe$_2$As$_2$.** – Figure 2 and Fig. 3 show the calculated electronic properties of BaFe$_2$As$_2$ in the non-magnetic (NM) solution. Similar to LaOFeAs, there are two circle-like hole-type FS around the $\Gamma$ point, and two ellipse-like electron-type FS around the $X$ point. Because BaFe$_2$As$_2$ has a body-centered tetragonal structure, the $X$ point of BaFe$_2$As$_2$ Brillouin Zone (BZ) corresponds to the $M$ point (labeled as $M'$ hereafter) in the BZ of LaOFeAs. On the other hand, differently from LaOFeAs, the band dispersion of BaFe$_2$As$_2$ along the $z$-direction is stronger. In particular, as shown in Fig. 3(a)–(c), for the $k_z = 0$ ($k_z = \pi$) plane, the size of hole pockets is smaller (larger) than the electron pockets, and only for the $k_z = \pi/2$ plane the size of the two are almost equal. This suggests the enhanced three-dimensionality in BaFe$_2$As$_2$. The fact that the ellipse-shaped electron pockets have different orientations for different $k_z$ plane can help us to understand the ARPES results, and indeed the calculated FS shape can be well compared with the recent ARPES measurement [17], again suggesting the quality of first-principles calculations.

In addition to the FS characters, we calculated the Lindhard response function $\chi_0(q)$ as shown in Fig. 3(d)–(e). Also similar to LaOFeAs, we found significant FS nesting for the $q = (\pi, \pi)$ vector, and the nesting can be suppressed by either electron or hole doping. As a result, the stripe-type SDW state (called AF2 as shown in Fig. 1) similar to LaOFeAs is stabilized as the ground state (see Fig. 4 for the stabilization energy). The calculated moment is about 1.6$\mu_B$/Fe, again larger than the measured moment of 0.8$\mu_B$/Fe [15]. All these facts suggest that the BaFe$_2$As$_2$ is very similar to LaOFeAs except the enhanced three-dimensionality.

**Effect of doping.** – The electron- and hole-doped compounds are however quite different as will be addressed in this part. Figure 4 shows the calculated total energies of AF1 and AF2 with respect to the NM solution, and the corresponding magnetic moment for both Ba$_{1-x}$K$_x$Fe$_2$As$_2$ and La$_{1-x}$F$_x$FeAs. The qualitative behavior as a function of doping is definitely very different. We start the discussion from the LaOFeAs side. The ground state of LaOFeAs is AF2 as suggested before [7] and confirmed by neutron [8], in the presence of Fermi surface nesting. By electron doping, the nesting effect is suppressed and the stabilization energy of AF2 is reduced. It is also shown
in fig. 4 that the size of the ordered moment is reduced by electron doping. If the doping \( x \) is approaching 0.2, the AF2 state and its moment will be totally suppressed, and the AF2-to-NM quantum critical point (QCP) is realized [18].

Although BaFe\(_{2}\)As\(_{2}\) itself is quite similar to LaOFeAs, however, with hole doping the system behaves quite differently. First, the energy gains of both AF1 and AF2 relative to the NM state are substantial and they are not suppressed significantly by hole doping. Second, the calculated moments for both AF states are almost constant and do not reduce with doping. What is even more interesting is that the AF1 and AF2 states become degenerate at about \( x = 0.7 \), and the AF1 state is more stable than AF2 beyond this doping. The AF1-to-AF2 QCP is therefore realized by hole doping in sharp contrast to the electron-doped side. The constructed ground-state phase diagram is shown in fig. 4. The electron- and the hole-doped sides are asymmetric, and they are physically quite different: 1) the AF2-to-NM QCP is realized for the electron-doped side, while AF2-to-AF1 QCP is realized for the hole-doped side; 2) the electron-doped side can be understood from FS nesting, however the hole-doped side behaves more or less like competing AF orders (between AF1 and AF2).

The first question to be answered at this stage is why the hole-doped side behaves so differently from the electron-doped side? A simple understanding is provided by looking at the density of state (DOS) of parent compounds as shown in fig. 2a (and see ref. [5] for the DOS of LaOFeAs), which is asymmetric around the Fermi level \( E_f \). It is characterized as a strong peak and high DOS below \( E_f \), however as dispersive bands (mostly \( xy \)) and low DOS above \( E_f \). By electron doping the electron pockets formed by the wide \( xy \) band (hybridized with \( yz, zx \) orbital) dominate, and the system becomes more and more itinerant. On the other hand, by hole doping, the \( E_f \) is shifted into the narrow band region with high DOS peak. In addition, we should also notice that the number of \( d \) electrons, which is 6/Fe for undoped compounds, is reduced to be more close to 5/Fe (half-filled) by hole doping.

The second question is what is the difference between the AF1 and the AF2 states? The simple answer is that orbital-selective magnetic ordering develops in the AF1 state. For this purpose, we plot in fig. 5 the calculated magnetic moment decoupled to each orbital of Fe. For the AF2 solution, the magnetic moment is nearly uniformly distributed to each orbital. (The difference between \( yz \) and \( zx \) orbital is due to the stripe ordering, which breaks the four-fold rotational symmetry.) However, the AF1 solution is unique: one of the orbitals, \( 3z^2-r^2 \), which forms a narrow band below \( E_f \), contributes to the magnetic moment dominantly. Clearly the multi-orbital physics and the orbital degrees of freedom play a crucial role here. Finally, at \( x = 1.0 \), the AF1 state is stabilized with mostly the magnetic ordering of \( 3z^2-r^2 \) orbital. With hole doping, it is therefore realized that the orbital-selective magnetic transition is the essential physics.
and lower panels: the calculated magnetic moments for each 3d orbital for AF1 and AF2 states, respectively. 

The positive sign is defined for AF coupling. From the mean-field solution of this model, the total energy of the AF1 state is given as $E_{\text{AF1}} = -J_1/2 - J_2$. Therefore if $J_2 = J_1/2$, the two ordered state will be energetically degenerate, and a strong quantum fluctuation will be expected near this critical point. Such model has been suggested to describe the physical properties of LaOFeAs, however, first-principles calculations [9,10] suggest that the electron-doped LaOFeAs system is actually far away from degeneracy, namely $J_2 \gg J_1/2$. On the other hand, here we show that the quantum degeneracy can be actually realized in the hole-doped side. Of course, our system is still away from the fully localized insulating region (therefore the use of $J_1$-$J_2$ model here is not rigorously justified). However, we can borrow the simple idea of the $J_1$-$J_2$ model and qualitatively understand the physics. We map the calculated total energy to this model, and estimate the $J_1$ and $J_2$ coupling constants as shown in fig. 5. (The spin $S=1$ is used as suggested from the calculated magnetic moment.) Indeed, the $J_2 = J_1/2$ criteria is realized at $x = 0.7$, and the stabilization of the AF1 state as a function of hole doping can be understood from the doping-dependent modification of the $J_1$ and $J_2$ coupling strength.

**Discussions.** – We would like to address some important issues here:

1) The proposed AF1 solution for large hole-doping side does not break the 4-fold rotational symmetry. It is therefore expected that the lattice distortion associated with the AF2 solution (the SDW state in LaOFeAs, which break the 4-fold rotational symmetry) should not occur for the AF1 phase region. In other words, on the electron-doped side, the structure transition and the SDW share the same symmetry breaking pattern in AF2. Therefore it is difficult to disentangle them and find which one is the driving force. Now in the new AF1 phase, the 4-fold symmetry does not break, therefore the magnetic and structural transition can be separated and it will be very important to study the nature of the possible structural transitions experimentally.

2) In the mean-field theory, the quantum phase transition between AF1 and AF2 happens at $J_1 = 2J_2$. For a pure 2D system, however, the spatial quantum fluctuation will completely destroy the long-range order in the AF2 phase, because of the absence of effective locking terms between two different sub-lattices [19]. On the other hand, the long-range order in the AF1 state will survive under the quantum fluctuation. Therefore beyond mean field, the AF1 to AF2 transition predicted here is actually replaced by AF1 to quantum disorder transition. Turning on the inter-layer coupling will stabilize the long range order for both AF1 and AF2 phases in finite temperature. Due to the different behaviors of the quantum fluctuation in AF1 and AF2 phases, the AF1 phase will be more classical with a larger order parameter, while there will be still a strong quantum fluctuation in the AF2 phase, which greatly reduces the order parameter and also may stabilize the superconducting phase around the phase boundary. This scenario is also supported by the fact that the observed ordered moment in BaFe$_2$As$_2$ (0.8$\mu_B$) is larger than that in LaOFeAs (0.3$\mu_B$), and closer to the calculated one from DFT, because of the enhanced 3-dimensionality in BaFe$_2$As$_2$. Nevertheless, it should be kept in mind that the usage of the $J_1$-$J_2$ model is just approximate, and also it is not clear yet how the on-site multi-orbital physics (inter-orbital fluctuation) may modify the story.

3) For both the electron- and hole-doped sides, the observed superconductivity phase region [13] is located around the QCP, although two QCPs are physically

![Graph showing exchange (meV) as a function of hole-doping x](image_url)
electron-hole asymmetry and quantum critical point in hole-doped BaFe$_2$As$_2$

different. This fact indicates that the magnetic fluctuations play a crucial role in Fe-As-based superconductors.

4) To justify our theory experimentally, the direct detection of the AF1 magnetic ordering in pure KFe$_2$As$_2$ by neutron scattering is desirable. Actually at least, the AF1 ordered insulating state has been suggested in further hole-doped samples (such as LaOMnAs) as studied by both experiment [20] and theoretical calculations [5]. Therefore, although the predicted critical point of $x = 0.7$ for hole doping may not be so rigorous, the tendency that hole doping favors the AF1 state should be correct. It will be also important to have a systematical measurement of spin susceptibility as a function of hole doping for high-quality single crystals.

In summary, by first-principles calculations, we show that the hole-doped side of FeAs-based compounds is very different from its electron-doped side. For the hole-doped side, we predict that the checkerboard-type AF1 state should be stabilized with orbital-selective magnetic ordering but without lattice distortion. A unique AF2-to-AF1 QCP is realized with hole doping, in sharp contrast to the electron-doped side.

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