Orbital-selective magnetism in FeAs-based superconductors

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We report first-principles studies of lanthanide-series (Ln) iron oxypnictides LnFeAsO (Ln=La, Ce, Pr, Nd, Sm, and Gd) which show two competing orbital-selective magnetic phases in small-Fe-moment regime: an in-plane \( d_{xy} \) magnetic phase, itinerantly driven by orbital selection of Fermi-surface nesting, and an out-of-plane \( d_{yz} \) magnetic phase, driven by local interactions. The Fe magnetic moments in the two phases show different coupling strengths to Fermi-surface electrons orbital-selectively, suggesting different roles in superconductivity and in antiferromagnetism, and making orbital characters of the moment resolvable by measuring the electronic structures. These results show that orbital sensitivity is a key factor in the magnetic properties of FeAs-based materials.

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LaFeAsO\(_{1-x}\)F\(_x\) [1] and related compounds show unconventional superconductivity (SC) in the vicinity of antiferromagnetism (AFM) [2,10]. Among various families of iron pnictides and chalcogenides, lanthanide-series (Ln) iron oxypnictides LnFeAsO reach the highest superconducting transition temperature \( T_c \) with doping. Reported \( T_c \) in doped LnFeAsO increases dramatically from 26 K up to 55 K with Nd or Sm substitution for La and then \( T_c \) decreases slightly in doped GdFeAsO [1,2,8,11–13]. With this strong variation of \( T_c \), LnFeAsO is suited for studying material dependence of \( T_c \). Since FeAs-based materials are featured with multiple Fermi surfaces (FSs) with strong orbital characters, many studies have been done on FS nesting, local-moment interactions, and orbital orderings [12,21]. However, no specific feature has been pinpointed in electronic and magnetic properties correlated with material dependence of \( T_c \) except for As positions and their effect on FS.

In this Letter, we report, for the first time, orbital-selective magnetic phases in FeAs-based materials found by first-principles density functional theory (DFT) calculations. Two phases are identified with distinctive orbital characters of Fe magnetic moments, \( d_{xy} \) and \( d_{yz} \), which originate from FS nesting and local interactions, respectively. The two phases, while competing with each other, show different electronic band structures caused by orbital-selective coupling strengths between Fe magnetic moments and FS electrons. Our results suggest that spin or magnetic interactions for unconventional SC should have strong orbital sensitivity in FeAs-based materials.

Our calculations are based on \textit{ab initio} norm-conserving pseudopotentials and the Perdew-Burke-Enzerhof-type generalized gradient approximation, as implemented in the SIESTA code [28]. During self-consistent iterations, constraints are imposed on the electron spin density to reduce the size of the Fe magnetic moment \( (m_{Fv}) \) to specific values smaller than unconstrained results. We assume an oxidation state of +3 for all considered Ln elements, treating their \( 4f \) orbitals as core orbitals [29,30]. Experimental lattice constants and atomic positions at the high-temperature tetragonal phase are used for the calculations [3,4,9,10,17,31].

An intriguing new finding in our present work is Ln-dependent distinctive \( d \)-orbital characters of the Fe magnetic moment in LnFeAsO in small \( m_{Fv} \) regime. Figure 1 shows two prototypical cases of LaFeAsO and SmFeAsO. For \( m_{Fv} \) of 0.15 Bohr magneton \( (\mu_B) \) per Fe atom, LaFeAsO shows out-of-plane \( d_{yz} \) character, but SmFeAsO shows in-plane \( d_{xy} \), character. In previous studies, the main concern was not \( d_{xy} \) versus \( d_{yz} \), but \( d_{yz} \) versus \( d_{xx} \), regarding symmetry lowering from tetragonal to orthorhombic structures. In our work, symmetry
is lowered by imposing the single-stripe-type AFM, yet \(d_{xy}\) character is predominant in SmFeAsO.

For systematic study, we analyze orbital contributions to the Fe magnetic moment in LnFeAsO in function of \(m_{Fe}\). We find that either \(d_{xy}\) or \(d_{yz}\) character is dominant, switching abruptly at a critical value of \(m_{Fe}\) in each compound. The critical \(m_{Fe}\) is 0.014 \(\mu_B\) in LaFeAsO and increases to 0.23 \(\mu_B\) in GdFeAsO. Except for GdFeAsO, the \(d_{xy}\) (\(d_{yz}\)) character appears at smaller (larger) \(m_{Fe}\) than the critical value. In LaFeAsO, the critical \(m_{Fe}\) is so small that the \(d_{yz}\) character is dominant [Fig. 2(a)]. In GdFeAsO, unlike other compounds, the \(d_{yz}\) character is larger than the \(d_{xy}\) character at \(m_{Fe}\) smaller than the critical moment [Fig. 2(f)].

The overall increase of the critical \(m_{Fe}\) from LaFeAsO to GdFeAsO is correlated most strongly with the increase of the As height from the Fe plane among various structural parameters [Fig. 2(g)], and correlated with experimentally reported \(T_c\) [Fig. 2(h)]. This suggests that the \(d_{xy}\) magnetic moment is closely related with measured \(T_c\) in the doped LnFeAsO for Ln from La to Sm, while GdFeAsO shows different and more complicated orbital features possibly because GdFeAsO is beyond an optimal chemical composition for \(T_c\) [1, 2, 11, 13].

To understand the origin of the orbital-distinctive magnetic moments, we analyzed orbital characters of FS in nonmagnetic LnFeAsO. As a prototype, SmFeAsO has three cylindrical hole pockets [\(a\) , \(\beta\), and \(\gamma\) in Figs. 3(a)-(c)] and two electron pockets [\(\delta\) and \(\epsilon\) in Figs. 3(a)-(c)] at the Fermi energy \((E_F)\). Orbital analysis shows that the \(a\), \(\gamma\), and \(\delta\) pockets are derived from Fe \(d_{yz}\) and \(d_{zx}\) character at
orbits, the \( \beta \) pocket is from \( d_{xy} \), and the \( \epsilon \) pocket is from \( d_{yx}, d_{yz}, \) and \( d_{zx} \) [Figs. 3(a)-(c)]. For FS nesting, we consider six pairs of hole and electron pockets: \( \alpha-\delta, \beta-\delta, \gamma-\delta, \alpha-\epsilon, \beta-\epsilon, \) and \( \gamma-\epsilon \). Among these, \( \alpha-\delta \) nesting is not significant because the two pockets have quite different pocket areas in all LnFeAsO [Figs. 3(d) and (e)], and \( \beta-\delta \) nesting is not effective because orbital difference of the two pockets degrades effects of nesting greatly. In addition, \( \gamma-\delta \) and \( \alpha-\epsilon \) nesting effects should be very weak because of orbital mismatch due to out-of-phase alternations of \( d_{x^2-y^2} \) and \( d_{xz} \) characters around the pockets. Thus, we need to examine only \( \beta-\epsilon \) and \( \gamma-\epsilon \) nesting regarding the orbital character of the Fe magnetic moment.

Since the \( \beta \)-hole pocket is derived from the \( d_{xy} \) orbital, \( \beta-\epsilon \) nesting may induce Fe magnetic moment of \( d_{xy} \) character. Similarly, \( \gamma-\epsilon \) nesting may induce Fe magnetic moment of \( d_{yz} \) or \( d_{zx} \) character. Calculated FS pocket areas as a function of Ln elements [Figs. 3(d) and (e)] show that the \( \beta \)-hole pocket area is sensitive to Ln elements, approaching the \( \epsilon \)-electron pocket area for heavier Ln elements, while the \( \gamma \)-hole pocket area is almost insensitive to Ln elements and close to the \( \epsilon \)-electron pocket area. This indicates that \( \beta-\epsilon \) FS nesting is a key factor in the electronic structures in LnFeAsO which changes the orbital character of the Fe magnetic moment.

Although it is not involved in the FS nesting, the area of the \( \delta \)-electron (\( d_{yz} \) and \( d_{zx} \)) pocket also depends sensitively on Ln elements [Figs. 3(d) and (e)]. With heavier Ln elements, the \( \beta \)-hole (\( d_{xy} \)) band moves upward in energy and the \( \delta \)-electron band moves downward in energy, resulting in electron transfer from the \( d_{xy} \) orbital to the \( d_{yz} \) and \( d_{zx} \) orbitals. Since the \( \delta \)-pocket is not related with FS nesting, the increased \( d_{yz} \) and \( d_{zx} \) electrons can contribute to magnetic moments only by non-FS-nesting mechanism, e.g., local-moment interactions \([7, 10]\). Therefore, while the enhanced \( d_{xy} \) magnetic moment from LaFeAsO to SmFeAsO is due to better \( \beta-\epsilon \) FS nesting, the enhanced \( d_{yz} \) magnetic moment in GdFeAsO is due to increased \( d_{yz} \) electrons in the \( \delta \)-pocket which favor non-FS-nesting mechanism.

To find out effects of different orbital characters of Fe magnetic moments on the electronic structures, we obtained orbital-resolved band structures and projected density of states (PDOS) in SmFeAsO, as a prototype of LnFeAsO, in nonmagnetic and magnetic phases (Fig. 4). With zero \( m_{Fe} \), energy bands have distinct orbital characters along high-symmetry lines, yielding PDOS slowly varying near \( E_F \) [Figs. 4(a) and (b)].

With the \( d_{xy} \) magnetic moment, strong anti-crossing occurs between \( d_{xy} \) bands, opening orbital-dependent energy gaps at \( E_F \) [Fig. 4(c)]. In the \( \Gamma X \) line, \( d_{xy} \) and \( d_{zx} \) bands repel each other at \( E_F \) and at -260 meV. In the \( \Gamma Y \) line, \( d_{xy} \) bands open a large energy gap near \( E_F \) [marked with \( \Delta_{xy} \) in Fig. 4(c)], while \( d_{zx} \) bands are intact. Except for anti-crossing at -100 meV in the \( \Gamma Y \) line, \( d_{yz} \) bands are almost unchanged. The \( d_{xy} \) PDOS is greatly modified with a partial-gap opening at \( E_F \) and a huge peak right above \( E_F \) [Fig. 4(d)]. The \( d_{yz} \) PDOS also shows a reduction near \( E_F \) because of coupling to \( d_{xy} \) [Fig. 4(d)]. Despite these large effects of the \( d_{xy} \) magnetic moment on the electronic structures near \( E_F \), deformation of bands is mostly near the crossing points, with no shift of original band edges [Fig. 4(c)]. This confirms that the origin of the \( d_{xy} \) magnetic moment is due to FS nesting.

In contrast, with the \( d_{yz} \) magnetic moment, \( d_{yz} \) bands are deformed in the whole Brillouin zone much more greatly than anti-crossing of bands [Fig. 4(e)]. Whole
upper part of \(d_{yz}\) bands and whole lower part of \(d_{xz}\) bands are expelled from each other [Fig. 4(e)], so even the top of the \(d_{yz}\) hole band is pushed up by 100 meV and the bottom of the \(d_{yz}\) electron band is pushed down by 100 meV. This change of \(d_{yz}\) bands in the whole Brillouin zone indicates that the driving mechanism for the \(d_{yz}\) magnetic moment is not FS nesting (local in k-space) but lowering of the total energy of electrons by formation of local magnetic moments (local in real space). Despite the large change in the \(d_{yz}\) bands, all the other bands are almost unchanged except for some anti-crossings.

Since different orbital characters of the Fe magnetic moment result in orbital-dependent difference in electronic structures, the orbital characters of the Fe magnetic moment can be distinguished by, e.g., angle-resolved photoemission spectroscopy of detwinned samples [27, 62]. As established by previous studies, DFT electronic band structures are qualitatively consistent with experimental results in FeAs-based materials although the DFT results overestimate experimental bandwidths by a factor of 2 to 3 near \(E_F\). Thus, detailed comparison of our band structures with experimental results will reveal orbital characters of the Fe magnetic moment, and thereby their roles in AFM.

As shown above, the \(d_{xy}\) magnetic moment is driven by orbital-selective FS nesting, while the \(d_{yz}\) magnetic moment is related with spatially localized interactions such as local-moment interactions. Thus, the competition of \(d_{xy}\) and \(d_{yz}\) magnetic moments in LnFeAsO is itinerant versus local-moment magnetisms. In addition, when \(m_{Fe}\) is increased to 1.0 \(\mu_B\) and higher, the Fe magnetic moment evolves gradually to an almost spherical shape with no specific orbital characters. Thus, the orbital-distinctive magnetic moments and their effects appear with different strengths in various iron pnictides and chalcogenides for the wide range of reported \(m_{Fe}\).

In conventional SC, electron-phonon interactions depend on phonon polarizations, and too large interactions may induce structural changes that suppress SC. Likewise, the Fe magnetic moment in LnFeAsO may have different roles in SC and AFM depending on its orbital character. Since our results show that the \(d_{yz}\) character couples more strongly to electrons than the \(d_{xy}\) one, a possibility is that the former drives AFM while the latter mediates SC. Another possibility is that only the \(d_{xy}\) character is significant in both AFM and SC, which could be relevant if the \(d_{yz}\) character has much weaker coupling to electrons in real samples than our results due to, e.g., fluctuations. An opposite scenario is that only the \(d_{yz}\) character is significant in AFM and SC, which is less likely according to our result that SmFeAsO, having much higher \(T_c\) than LaFeAsO when doped, shows the strong \(d_{xy}\) character while LaFeAsO shows the \(d_{yz}\) one.

In conclusion, we have found that Fe magnetic moment in LnFeAsO (Ln = La to Gd) has distinctive orbital character, \(d_{xy}\) or \(d_{yz}\), depending on Ln and \(m_{Fe}\). With orbital analysis of electronic structures, we have shown that the origins of the \(d_{xy}\) and \(d_{yz}\) orbital characters of the Fe magnetic moment are FS nesting and local interactions, respectively. These orbital characters have different coupling strength to FS electrons, so they can be identified by orbital-sensitive measurement of electronic structures and they may have different roles in SC and AFM. These results pave the way for understanding the role of spin or magnetic interactions in FeAs-based superconductors.

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