Coexistence of orbital degeneracy lifting and superconductivity in iron-based superconductors


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We report the angle-resolved photoemission spectroscopy observation of the lifting of symmetry-protected band degeneracy, and consequently the breakdown of local tetragonal symmetry in the superconducting state of LiFe$_{1-x}$Co$_x$As. Supported by theoretical simulations, we analyze the doping and temperature dependences of this band splitting and demonstrate an intimate connection between ferro-orbital correlations and superconductivity.

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In contrast to conventional superconducting (SC) materials, superconductivity in high-temperature superconductors (HTSCs) usually emerges in the presence of other fluctuating orders with similar or higher-energy scales [1–4], thus instigating debates over their relevance for the SC pairing mechanism. Although spin fluctuations are widely believed to be crucial for unconventional superconductivity, orbital fluctuations in the multiorbital iron-based superconductors (IBSCs) are proposed to be directly responsible for the structural phase transition [5,6] and closely related to the observed giant magnetic anisotropy and electronic nematicity [7–13]. More recently, fluctuating orbital order has been proposed to lead to an attractive mechanism for pairing [14,15] and further raised the following question: Can superconductivity coexist with or even emerge from orbital fluctuations?

In the tetragonal phase without spin-orbital coupling (SOC), the $d_{xz}/d_{yz}$ orbitals are degenerate at the Brillouin zone center ($\Gamma$ point), which is guaranteed by point-group symmetry. Ferro-orbital (FO) order, which leads to unequal occupation of the $d_{xz}/d_{yz}$ orbitals, would lift the degeneracy at $\Gamma$, resulting in a band gap $\Delta_{\text{band}}$ that can be monitored directly by angle-resolved photoemission spectroscopy (ARPES). While FO fluctuations have been proposed as the origin of electronic nematicity [5,6] and can be closely related to the emergence of superconductivity [14,15], probing FO fluctuations directly in the absence of structural and magnetic phase transitions needs to be explored, and whether FO fluctuations coexist or compete with the SC order is still an open question.

In this Rapid Communication, we report the ARPES observation of the lifting of symmetry-protected band degeneracy, and consequently the breakdown of local tetragonal symmetry in the SC state of LiFe$_{1-x}$Co$_x$As. By analyzing the doping and temperature dependences of this band splitting and using theoretical simulations, we demonstrate that the splitting is caused by power-law decayed ferro-orbital correlations and prove its intimate connection with superconductivity.

Single crystals of LiFe$_{1-x}$Co$_x$As were synthesized by a self-flux method using Li$_3$As, Fe$_{1-x}$Co$_x$As, and As powders as the starting materials. The mixture was ground and put into alumina crucible and sealed in Nb crucibles under 1 atm of argon gas. The Nb crucible was then sealed in an evacuated quartz tube, heated to 1100 °C, and slowly cooled down to 700 °C at a rate of 3 °C/h. High-energy resolution ARPES data were recorded at the Institute of Physics, Chinese Academy of Sciences, using the He $\alpha$ ($h\nu = 21.2$ eV) resonance line of an helium discharge lamp. The angular and momentum resolutions were set to 0.2° and 3 meV, respectively. ARPES polarization measurements were performed at beamlines PGM and Apple-PGM of the Synchrotron Radiation Center (Wisconsin) equipped with a Scienta R4000 analyzer and a Scienta SES 200 analyzer, respectively. The energy and angular resolutions were set at 20 meV and 0.2°, respectively. All samples were cleaved in situ and measured in a vacuum better than 3 × 10$^{-11}$ Torr.

In addition to having a natural nonpolar cleaving surface preserving its bulk properties [16–18], LiFe$_{1-x}$Co$_x$As has neither structural nor magnetic phase transitions in its whole phase diagram [19], enabling us to study fluctuations in the absence of long-range orders. In Fig. 1, we compare the electronic band dispersion of LiFeAs and LiFe$_{0.88}$Co$_{0.12}$As at 20 K around the $\Gamma$ point. Our polarization analysis confirms that the $\alpha$ and $\alpha'$ bands, which are mainly composed of $d_{xz}/d_{yz}$ orbitals, have odd and even symmetries, respectively [20–22]. The extracted band dispersion [23] in LiFe$_{0.88}$Co$_{0.12}$As ($T_c = 4$ K) indicates that both the $\alpha$ and $\alpha'$ bands sink below $E_F$ and are exactly degenerate at the $\Gamma$ point, as required by symmetry. In contrast, the $\alpha$ band crosses $E_F$ at $k_F = 0.03\pi/a$ in the parent compound LiFeAs ($T_c = 18$ K), whereas the top of the $\alpha$ band lies about 12 meV below $E_F$, which means that the $d_{xz}/d_{yz}$ orbitals are split in LiFeAs without long-range magnetic and orbital orders. To precisely resolve the band splitting, we recorded very-high-energy ARPES intensity plots of LiFeAs and LiFe$_{0.88}$Co$_{0.12}$As, as shown in Fig. 1. From the high-resolution data, we evaluate the band gap to $\Delta_{\text{band}} \sim 14$ meV in LiFeAs by extrapolating the top of the $\alpha$ band using a parabolic fit, and we confirm the degeneracy of the $d_{xz}/d_{yz}$ bands in...
LiFe$_{0.88}$Co$_{0.12}$As. By zooming near $E_F$, we find that the $\alpha$ band further splits into two branches, as shown in Figs. 1(f) and 1(j). While one branch is the continuous extension of the high binding energy dispersion, the other one shows an inflection point at 14 meV binding energy. A similar effect is also observed on the electron band and, as discussed later, the observed fine structure is caused by twin domains and supports the observed band splitting is caused by FO fluctuations. For this material, we find that the band splitting might be related to superconductivity. Interestingly, there is at least one other IBSC for which a $d_{xz}/d_{yz}$ band splitting is clearly observed. Indeed, this observation has been reported for the FeTe$_{1-x}$Se$_x$ family of IBSCs [27,28]. Using the data from Miao et al. [27], reproduced in Fig. 2(e), we find that $\Delta_{\text{band}} = 18$ meV in FeTe$_{0.55}$Se$_{0.45}$, which is even larger than in LiFeAs. The observed band splitting in all the IBSCs studied here strongly suggests that the $d_{xz}/d_{yz}$ separation at the $\Gamma$ point has a fundamental origin.

We now focus on the temperature evolution of $\Delta_{\text{band}}$ in LiFeAs. For this purpose, we show in Fig. 3 high-energy resolution ARPES cuts across the $\Gamma$ point recorded between 50 and 250 K. The data are divided by the Fermi-Dirac function convoluted by the resolution function to reveal the band dispersion above $E_F$, which are obtained from parabolic fits. While the linewidths of the $\alpha'$ and $\beta$ bands broaden with temperature, their dispersions are unaffected. The $\alpha$ band, on the other hand, gradually shifts downward and its top almost merges with that of the $\alpha'$ band at 250 K. In Fig. 3(m), we show the evolution of $\Delta_{\text{band}}$ as a function of temperature by using different methods that all show that the $d_{xz}/d_{yz}$ splitting decreases gradually from nearly 0 at 250 K to about 14 meV at 50 K [22]. Interestingly, the splitting survives even below the SC phase transition at 18 K. As shown in Figs. 3(n)–3(p), the $\alpha$ band opens up a SC gap below $T_c$, whereas the $\alpha'$ band is barely changed. This observation proves that the band splitting coexists with superconductivity.

The observed degeneracy lifting by ARPES at the $\Gamma$ point reflects directly the difference in site energy of the $d_{xz}$ and $d_{yz}$ orbitals at low energies, which is a direct measurement of the ferro-orbital configuration, regardless of the origin of the mechanism driving the system into this configuration. In order to demonstrate that FO fluctuations can lead to the removal of a symmetry-imposed degeneracy, even in the absence of long-range ordering, we investigate a simple model of a quasi-one-dimensional (1D) electronic system (since $d_{xz}/d_{yz}$ orbitals have strongly anisotropic quasi-1D hopping integrals) under the influence of a spatially fluctuating local FO order parameter (represented by a diagonal Ising field) [21,22], and...
we display the results in Fig. 4. When the local order parameter has only short-range correlations (exponential decay), no clear indication of the fluctuating order is observed in the electronic structure other than the scattering of the particle that broadens the spectral function, as illustrated in the top row of Fig. 4. In contrast, when the spatial correlations of the local order parameter are long ranged (power-law decay), the quasiparticle peak splits in two and a pseudogap in the spectral function develops in between, as shown in Figs. 4(f)–4(h). This pseudogap corresponds to the splitting of the degenerate bands shown in Fig. 1. Although the spectral function exhibits features identical to those expected in the presence of a macroscopic long-range order, we emphasize that the system has not yet developed a true order, but only long-range spatial correlations. In other words, the one-particle Green’s function has gone ahead and reflects the underlying, almost ordered, electronic structure. Therefore, the experimentally observed doping-dependent splitting between the $d_{xz}/d_{yz}$ bands in the absence of FO order can be attributed to strong, slow-decaying, long-range FO correlations that cover a large region of the phase diagram and eventually support superconductivity at low temperature. We stress that although our minimal two-orbital model indicates that a fluctuating diagonal order parameter is capable of lifting a degeneracy required by symmetry, one should be cautious when comparing our models with realistic band structures. In real systems, the self-energy induced by the fluctuating ferro-orbital order parameter should be momentum, energy and orbital dependent, and thus exhibit rich variations.

Very recently, an electronic Raman scattering study of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [29], an ARPES study [9], and a combined study of magnetic torque and x-ray in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ [13] reported electronic nematicity in the absence of a magnetic phase transition. The observed nematic signal persists far above the SC and structural phase transitions, indicating the presence of a strong fluctuating orbital order, which is consistent with our doping- and temperature-dependent results, as well as with our theoretical interpretation. However, alternative mechanisms could also lead indirectly to the lifting of the band degeneracy. For example, although the C-type (collinear) antiferromagnetic (AF) correlations do not directly contribute to the observed band degeneracy lifting, they could do so when coupled to the orbital degree of freedom, as predicted by theoretical studies [5,6,30,31]. Nevertheless, in the present study, we find that superconductivity emerges...
Finally, we discuss the effect of SOC. In principle, SOC can lift the degeneracy of the $d_{xz}/d_{yz}$ orbitals at the $\Gamma$ point while maintaining global tetragonal symmetry [32]. However, since SOC is a local effect and barely changes with doping and temperature, our observation of $\Delta_{\text{band}}$ variations as a function of doping and temperature is inconsistent with this scenario. Moreover, we carefully extracted the electronic band structure near the $M$ point and found that the degeneracy between $d_{xz}$ and $d_{yz}$ at the $M$ point is lifted with a splitting gap $\Delta_M = 8 \text{ meV}$, which is smaller than the splitting at the $\Gamma$ point [22]. All the experimental facts support our assumption that the observed $d_{xz}/d_{yz}$ splitting at the $\Gamma$ point is caused by FO fluctuations instead of SOC. Although spin fluctuations have been widely studied and discussed, few experimental studies on the orbital fluctuations can be found in the literature. Our study provides evidence for strong, long-range FO correlations in IBSCs and demonstrates their intimate connection with superconductivity in LiFe$_{1-x}$Co$_x$As.

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