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Orbital selective spin excitations and their impact on superconductivity of $\text{LiFe}_{1-x}\text{Co}_x\text{As}$

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We use neutron scattering to study spin excitations in single crystals of $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$, which is located near the boundary of the superconducting phase of $\text{LiFe}_{1-x}\text{Co}_x\text{As}$ and exhibits non-Fermi-liquid behavior indicative of a quantum critical point. By comparing spin excitations of $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$ with a combined density functional theory (DFT) and dynamical mean field theory (DMFT) calculation, we conclude that wave-vector correlated low energy spin excitations are mostly from the d_{xy} orbitals, while high-energy spin excitations arise from the d_{yz} and d_{xz} orbitals. Unlike most iron pnictides, the strong orbital selective spin excitations in LiFeAs family cannot be described by anisotropic Heisenberg Hamiltonian. While the evolution of low-energy spin excitations of $\text{LiFe}_{1-x}\text{Co}_x\text{As}$ are consistent with electron-hole Fermi surface nesting condition for the d_{xy} orbital, the reduced superconductivity in $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$ suggests that Fermi surface nesting conditions for the d_{yz} and d_{xz} orbitals are also important for superconductivity in iron pnictides.

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Superconductivity in iron pnictides occurs near the vicinity of an antiferromagnetic (AF) instability [1–5]. One exception is LiFeAs , which exhibits superconductivity at $T_c = 18$ K without an AF ordered parent compound [6–8]. Although magnetism is generally believed to play a central role in the superconductivity of iron pnictides [4, 5], the unique nature of LiFeAs has raised considerable debates concerning whether magnetism is indeed fundamental to the superconductivity of iron-based superconductors. There are two important issues to be addressed. The first is whether magnetism and superconductivity in LiFeAs can arise from quasiparticle excitations between hole and electron nested Fermi surfaces similar to other iron pnictide superconductors [9–11]. The second concerns the impact of orbital degrees of freedom on the superconductivity of LiFeAs [12, 13].

In most iron pnictides, Fe ions are in a d^6 configuration with five same-spin electrons in the e_g and t_{2g} orbitals, and one remaining opposite-spin electron fluctuating among all the d orbitals, due to the large Hund's rule coupling, although there is a considerable (but smaller) crystal-field splitting between the e_g and t_{2g} orbitals [14–20]. The t_{2g} electrons near the Fermi level occupy the d_{xy} and degenerate d_{xz}/d_{yz} orbitals. In the undoped state, low-energy spin excitations in LiFeAs are trans-

versely incommensurate from the AF ordering wave vector of iron pnictides such as BaFe_2As_2 [Fig 1(a) and Fig. 1(b)] [3], consistent with nested Fermi surfaces from either the large d_{xy} or small d_{yz}/d_{xz} hole pocket near Γ point in reciprocal space to electron pockets near M points [Fig. 1(c) and Fig. 1(e)] [21–23]. When Co is doped into LiFeAs to form $\text{LiFe}_{1-x}\text{Co}_x\text{As}$, superconductivity is gradually suppressed with increasing Co doping and vanishes near $x = 0.14$ [24], and the system becomes paramagnetic for higher Co-doping levels [Fig. 1(a)] [25]. From angle resolved photoemission spectroscopy (ARPES) [26, 27], it was found that Co-doping introduces electrons to LiFeAs , reduces the size of the d_{xy} hole Fermi surface, moves the small d_{yz}/d_{xz} hole pockets below the Fermi surface, and enlarges the electron pockets [Fig. 1(d)]. While the hole-electron Fermi surface nesting condition is improved for the d_{xy} orbitals near $x = 0.12$, Fermi surface nesting is no longer possible for the d_{yz}/d_{xz} orbitals [Fig. 1(d)]. Since transport, optical spectroscopy, and nuclear magnetic resonance measurements on $\text{LiFe}_{1-x}\text{Co}_x\text{As}$ find enhanced low-energy spin fluctuations near $x = 0.12$ with non-Fermi liquid behavior, these results were taken as evidence that spin fluctuations due to enhanced Fermi surface nesting can give rise to the observed non-Fermi liquid behavior, but are

not important for superconductivity of LiFeAs [25].

In this Letter, we present inelastic neutron scattering study and a combined density functional theory (DFT) and dynamical mean field theory (DMFT) calculation of spin excitations in LiFe_{0.88}Co_{0.12}As. While low-energy spin excitations in LiFe_{0.88}Co_{0.12}As indeed become commensurate consistent with improved electron-hole Fermi surface nesting condition for the d_{xy} orbitals [Fig. 1(d)], the absence of the hole Fermi pockets near the Γ point prevents the electron-hole nesting between the d_{yz}/d_{xz} orbitals. Since our DFT+DMFT calculations suggest a strongly correlated d_{xy} orbital with much reduced magnetic bandwidth and effective exchange coupling (Fig. 2, 3, 4), the improved nesting condition in LiFe_{0.88}Co_{0.12}As, while sufficient to induce the observed non-Fermi liquid behavior [25] and increased magnetic excitations near the AF wave vector, is insufficient to cause superconductivity due to increased incoherent electronic state of the d_{xy} band in Co-doped LiFeAs [26]. Similarly, we find that spin excitations at higher energies with much steeper dispersion arise mostly from electron-hole quasi-particle excitations of the d_{yz}/d_{xz} orbitals with much larger magnetic bandwidth and effective exchange coupling compared with NaFeAs (Fig. 4) [28]. Therefore, spin excitations in the LiFeAs family are highly orbital selective. While spin waves in many iron pnictides can be well described by an anisotropic Heisenberg Hamiltonian [5], the spin excitations in the LiFeAs family cannot be satisfactorily explained by such a model. Our results thus suggest that the occurrence of superconductivity in LiFe_{1-x}Co_xAs requires Fermi surface nesting of the d_{xz}/d_{yz} orbitals.

Our inelastic neutron scattering measurements on LiFeAs and LiFe_{0.88}Co_{0.12}As were carried out at the wide Angular-Range Chopper Spectrometer (ARCS) and Cold Neutron Chopper Spectrometer (CNCS) at Spallation Neutron Source, Oak Ridge National Laboratory. Single crystals of LiFeAs (3.95-g) and LiFe_{0.88}Co_{0.12}As (7.58-g) are grown using flux method with ⁷Li isotope. We define the momentum transfer \mathbf{Q} in three-dimensional reciprocal space in \AA^{-1} as $\mathbf{Q} = H\mathbf{a}^* + K\mathbf{b}^* + L\mathbf{c}^*$, where H , K , and L are Miller indices and $\mathbf{a}^* = \hat{\mathbf{a}}2\pi/a$, $\mathbf{b}^* = \hat{\mathbf{b}}2\pi/b$, $\mathbf{c}^* = \hat{\mathbf{c}}2\pi/c$ with $a = b \approx 5.316 \text{ \AA}$, and $c = 6.306 \text{ \AA}$ for both samples. In this notation, the AF Bragg peaks for magnetically ordered compound NaFeAs should occur at $\mathbf{Q}_{AF} = (\pm 1, 0, L)$ ($L = 0.5, 1.5, \dots$) positions in reciprocal space [Fig. 1(e) and 1(f)] [30]. Samples are co-aligned in the $[H, 0, L]$ scattering plane with mosaic less than 3° and incident beam ($E_i = 20, 35, 80, 250, 450 \text{ meV}$) parallel to the c -axis of the crystals [31].

We first compare low energy spin excitations in pure LiFeAs ($T_c \approx 18 \text{ K}$) and LiFe_{0.88}Co_{0.12}As ($T_c \approx 4 \text{ K}$). Figure 2(a) shows image of the $E = 7 \pm 1 \text{ meV}$ excitations near \mathbf{Q}_{AF} for LiFeAs obtained on ARCS. Consistent with earlier work [21–23], the data reveals clear transverse incommensurate spin excitations away from

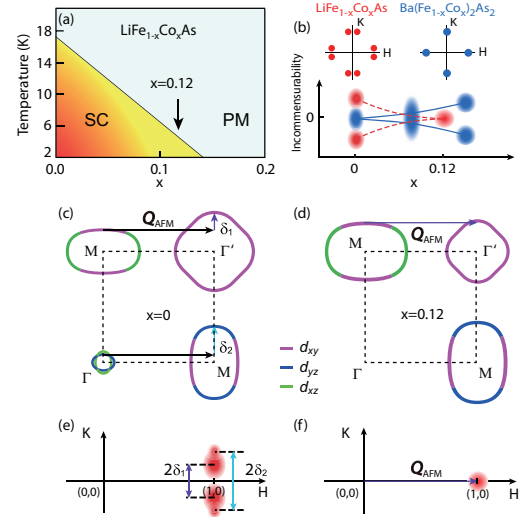


FIG. 1: (Color online) (a) Electronic phase diagram of LiFe_{1-x}Co_xAs. The superconductivity (SC) is suppressed by Co-doping and the system is in paramagnetic (PM) phase above T_c . The arrow indicates the doping level of $x = 0.12$ in our experiment [26, 27]. (b) Evolution of the low energy spin excitations in reciprocal space with electron doping for LiFeAs and BaFe_{2-x}Ni_xAs₂. Red spots indicate positions of low energy spin fluctuations in LiFe_{1-x}Co_xAs and Blue ones are for BaFe_{2-x}Ni_xAs₂ [32]. Schematics of the Fermi surfaces for LiFeAs (c) and LiFe_{0.88}Co_{0.12}As (d) [26]. Based on ARPES measurements, the mismatched hole and electron Fermi surfaces should result in the incommensurate spin excitations at δ_1 and δ_2 . (e) Positions of transverse incommensurate spin excitations of LiFeAs at $E = 10 \text{ meV}$ seen in the neutron scattering measurements [23]. (f) Commensurate spin excitations of LiFe_{0.88}Co_{0.12}As at $E = 10 \text{ meV}$.

\mathbf{Q}_{AF} as shown in the $[1, K]$ cut of Fig. 2(b). The incommensurate peaks may arise from nesting of the outer hole or inner hole Fermi surface to the electron Fermi surfaces, which give slightly different incommensurability δ_1 and δ_2 , respectively, as seen in the experiment [Fig. 1(c) and 1(e)] [22, 23]. Figure 2(c) shows identical image of constant energy ($E = 7 \pm 1 \text{ meV}$) excitations for LiFe_{0.88}Co_{0.12}As. A constant energy cut along the $[1, K]$ direction reveals that spin excitations are well defined at the commensurate wave vector \mathbf{Q}_{AF} [Fig. 2(d)]. Figure 2(e) shows the dispersion of commensurate spin excitations obtained on CNCS. The rod like feature at \mathbf{Q}_{AF} below 10 meV confirms the commensurate nature of spin excitations in LiFe_{0.88}Co_{0.12}As. To determine if weak superconductivity at $T_c = 4 \text{ K}$ has an impact on low-energy spin excitations, we show in Fig. 2(f) temperature difference plot between 2 K and 10 K . The absence of the temperature difference scattering in Fig. 2(f) below and above T_c suggests that the weak superconductivity has negligible effect on the low-energy spin excitations. Based on data in Fig. 2, we summarize in Fig. 1(b) the Co-doping evolution of the low-energy spin excitations in LiFe_{1-x}Co_xAs. Different from BaFe_{2-x}Ni_xAs₂,

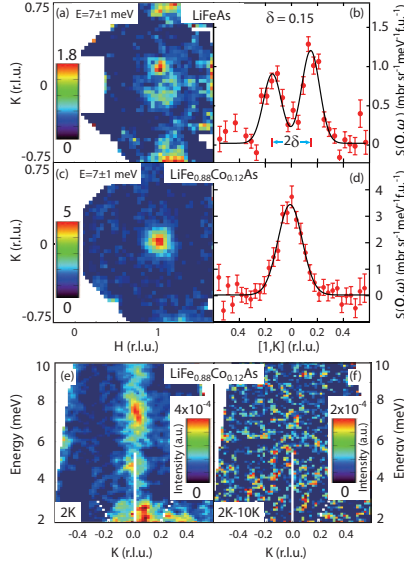


FIG. 2: (Color online) (a,c) Two-dimensional constant-energy images of spin excitations in the $[H, K]$ plane at $E = 7 \pm 1$ meV and 5 K for LiFeAs and LiFe_{0.88}Co_{0.12}As, respectively. The high scattering intensity near $(1, \pm 0.75)$ in (a) is due to phonons, but becomes less obvious in (c) due to different intensity scale. (b,d) Constant-energy cuts of spin excitations along the $[1, K]$ direction for LiFeAs and LiFe_{0.88}Co_{0.12}As at $E = 7 \pm 1$ meV, respectively. The solid lines are fits to two Gaussians for LiFeAs and a single Gaussian for LiFe_{0.88}Co_{0.12}As [31]. The intensity is in absolute units by normalizing a vanadium standard. (e) Energy-momentum plots of spin excitations along the $[1, K]$ direction integrated from $H = 0.9$ to 1.1 for LiFe_{0.88}Co_{0.12}As. The commensurate spin excitations form a vertical rod of scattering centered at $\mathbf{Q}_{AF} = (1, 0)$ point. (f) The temperature difference scattering between 2 K and 10 K.

where the low-energy spin excitations becomes transversely incommensurate with increasing Ni-doping [32], Co-doping in LiFeAs changes transversely incommensurate spin excitations to commensurate as shown in Fig. 1(b), Fig. 1(e) and 1(f). The differences in the electron doping evolution of the low-energy spin excitations between LiFe_{1-x}Co_xAs and BaFe_{2-x}Ni_xAs₂ can be understood within the Fermi surface nesting picture as due to the differences in Fermi surfaces of LiFeAs [26, 27] and BaFe₂As₂ [33]. A unique feature of the Fermi surfaces in LiFeAs is the large d_{xy} orbital hole pocket at $(1, 1)$ [Fig. 1(c)] [34]. Upon Co-doping to introduce additional electrons to LiFeAs, the large d_{xy} hole pocket shrinks and results in a better nesting with the electron pocket at $(0, 1)$, while the small d_{yz}/d_{xz} hole pocket sinks below the Fermi level [Fig. 1(c) and 1(d)]. For LiFe_{0.88}Co_{0.12}As, the observed commensurate spin excitations are consistent with this picture, and suggest that low-energy spin excitations are mostly driven from the d_{xy} orbitals. This is consistent with the random phase approximation (RPA) calculations using ARPES deter-

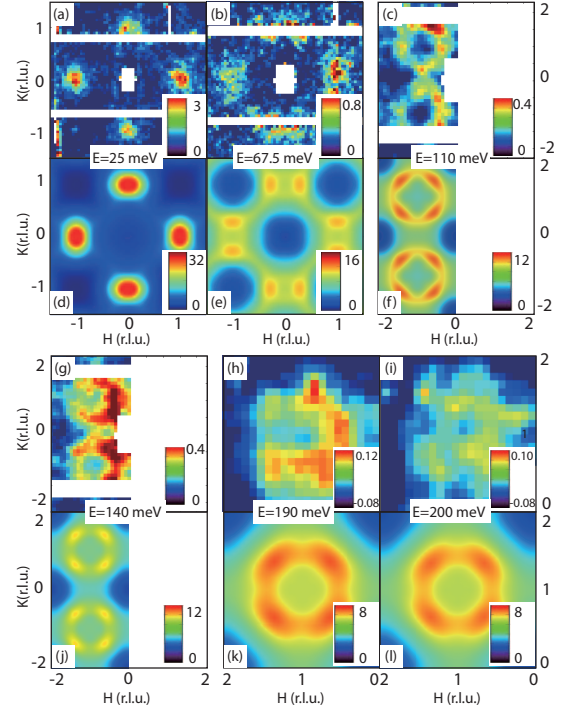


FIG. 3: (Color online) (a-c),(g-i) Constant-energy scattering images in the $[H, K]$ zones for LiFe_{0.88}Co_{0.12}As at energy transfers of $E = 25 \pm 5$ meV ($E_i = 80$ meV), 67.5 ± 7.5 meV ($E_i = 250$ meV), 110 ± 10 meV, 140 ± 10 meV, 180 ± 10 meV, and 200 ± 10 meV ($E_i = 450$ meV). The scattering intensity is obtained after subtracting a radial background and has two-fold [(c),(g)] or fourfold symmetry [(h),(i)]. (d-f), (j-l) Corresponding constant-energy slices of dynamic magnetic structure factor $S(\mathbf{Q}, E)$ obtained from DFT+DMFT calculation. All data are taken at $T = 5$ K.

mined Fermi surfaces, where the low-energy spin excitations for Co-doped LiFeAs involve mostly the d_{xy} - d_{xy} character (Fig. S3) [31]. Similarly, spin excitations from the d_{yz} - d_{yz} channel are considerably reduced with the suppression of superconductivity.

Figure 3 summarizes the two-dimensional images of spin excitations at different energies and their comparison with DFT+DMFT calculations for LiFe_{0.88}Co_{0.12}As. Below $E = 25$ meV, spin excitations occur at $\mathbf{Q}_{AF} = (1, 0)$ and $(0, 1)$ positions similar to spin waves in NaFeAs [Fig. 3(a)] [28]. On increasing energy to $E = 67.5 \pm 7.5$ meV, spin excitations begin to split vertically from $(1, 0)$, again similar to spin waves of NaFeAs [Fig. 3(b)]. However, at energies above $E = 100$ meV, spin excitations in LiFe_{0.88}Co_{0.12}As form rings of scattering centered around $(\pm 1, \pm 1)$ which shrink slowly with increasing energy and persist up to $E = 200$ meV [Figs. 3(c), 3(g), 3(h), and 3(i)]. This is significantly different from NaFeAs, where spin waves reach the band top near 100 meV [28]. Since high-energy spin excitations in LiFeAs behave similarly [35], we conclude that spin excitations of LiFe_{1-x}Co_xAs have larger band width than that of NaFeAs [28], are

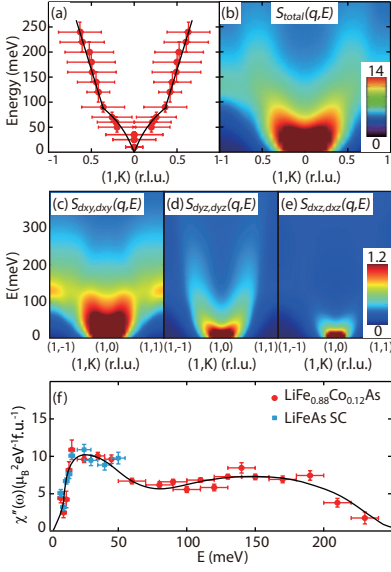


FIG. 4: (Color online) (a) The dispersion of spin excitations from time-of-flight neutron scattering data as seen in Fig. S2. The points represent the peak positions fitted with Gaussians. The errors in energy are the energy integration range and the \mathbf{Q} -errors come from the fitted peak width. (b) The corresponding total dynamic spin susceptibility calculated by DFT+DMFT. (c-e) The diagonal components of the dynamic magnetic structure factor $S_{xy,xy}(\mathbf{q}, E)$, $S_{yz,yz}(\mathbf{q}, E)$, and $S_{xz,xz}(\mathbf{q}, E)$ which originate from the d_{xy} , d_{yz} and d_{xz} orbitals, respectively. (f) Energy dependence of the measured local dynamic spin susceptibility for $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$ and superconducting LiFeAs at $T = 5$ K.

similar to that of $\text{BaFe}_{2-x}\text{Ni}_x\text{As}_2$ [37, 38]. Given the similar crystal structure and superconducting transition temperatures of $\text{LiFe}_{1-x}\text{Co}_x\text{As}$ [24] and $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ [36], one would expect similar electron correlations and spin excitations band width in these two families of materials [39, 40].

To determine the spin excitation dispersions of $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$, we made a series of cuts on images of spin excitations in Fig. 3 along the $[1, K]$ direction at different energies (Fig. S2) [31] and extracted the dispersion as shown in Fig. 4(a). Compared with dispersions of spin waves in NaFeAs [28] and spin excitations in $\text{BaFe}_{2-x}\text{Ni}_x\text{As}_2$ [37, 38], dispersion of $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$ has distinctive features around 100 meV [Fig. 4(a)]. Figure 4(b) shows the DFT+DMFT calculated total dynamic spin dynamic susceptibility, which reveals clear two component structure similar to spin excitations in Fig. 4(a). Figures 4(c), 4(d), and 4(e) are dynamic spin susceptibility corresponding to the d_{xy} - d_{xy} , d_{xz} - d_{xz} , and d_{yz} - d_{yz} intra-orbital scattering channels between the hole and electron Fermi surfaces, respectively. Along the $(1, K)$ direction, spin excitations from the d_{xy} orbital reach zone boundary around $E = 130$ meV [Fig. 4(c)], while excitations from the d_{yz} orbital extend to energies well above $E = 200$ meV [along the $(K, 1)$ direction,

it would be the d_{xz} orbital component due to the four fold symmetry]. The similarities in Figures 4(a) and 4(b) strongly suggest that the upper and lower branches of the observed spin excitations have different orbital origins. In Figure 4(f), we compare the estimated local dynamic spin susceptibility for $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$ and LiFeAs at $T = 5$ K. The total fluctuating moment of $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$ is $\langle \mathbf{m}^2 \rangle = 1.5 \pm 0.3 \mu_B^2/\text{Fe}$. This is similar to superconducting LiFeAs [21–23], but is somewhat smaller than those of NaFeAs ($\langle \mathbf{m}^2 \rangle \approx 3.2 \mu_B^2/\text{Fe}$) [28] and BaFe_2As_2 ($\langle \mathbf{m}^2 \rangle \approx 3.6 \mu_B^2/\text{Fe}$) [41, 42]. This means that the total fluctuating moments for LiFeAs family of materials are smaller than those of NaFeAs and BaFe_2As_2 iron pnictides.

In iron pnictide such as BaFe_2As_2 , spin wave dispersions can be well described by an anisotropic Heisenberg Hamiltonian [41]. However, the two branch feature of the spin excitation dispersion in $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$ clearly cannot be satisfactorily fitted by this anisotropic Heisenberg model. Our neutron scattering experiments and DFT+DMFT calculations suggest that orbital selective quasiparticle excitations may account for the energy and wave vector dependence of spin excitations in $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$. This indicates that the superexchange spin interactions are different for different orbitals.

It is well known that electronic correlations in iron pnictides depend sensitively on the Fe pnictogen distance owing to the kinetic frustration mechanism of the Fe $3d$ electrons, and are strongly enhanced with increasing Fe-pnictogen distance [39, 40, 43]. Together with the large Hund's rule coupling and strong on-site Coulomb repulsion, the kinetic frustration mechanism also gives rise to the strong orbital differentiation of the electronic correlation strength [15, 39]. Orbital selective electronic correlation has been found in $\text{FeTe}_{1-x}\text{Se}_x$, where the effective mass of bands dominated by the d_{xy} orbital character decreases with increasing selenium as compared to the d_{xz}/d_{yz} bands [44]. In the case of LiFeAs , charge transfer from the d_{xy} to d_{xz}/d_{yz} orbitals can account for the Fermi surface topology of LiFeAs as the consequence of orbital dependent band renormalization [39, 45]. As shown in Fig. S6 [31], the increased pnictogen height in LiFeAs compared with NaFeAs narrows the electronic bandwidth of the d_{xy} orbital, which in turn transfers electrons from the d_{xy} to the d_{xz}/d_{yz} bands. The observed Co-doping dependence of low-energy spin excitations results from the d_{xy} - d_{xy} orbital dependent Fermi surface nesting. The narrow electronic bandwidth of the d_{xy} also leads to narrow bandwidth of spin excitations, and weak effective magnetic exchange coupling.

Since the d_{xy} orbital dominated Fermi surface nesting becomes better for $\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$, low-energy spin excitations become commensurate with enhanced spectral weight compared to incommensurate spin excitations in LiFeAs [Fig. 1(b) and 1(d)]. This is consistent with NMR measurements [25] and RPA/DFT+DMFT calculations

(Figs. S3 and S4) [31]. The observed non-Fermi liquid behavior near $x = 0.12$ is then due to vanishing Fermi surface pocket associated with d_{yz}/d_{xz} orbitals as the Lifshitz transition is approached from the underdoped side [46]. In principle, an increased spin-fluctuation spectral weight should provide a larger electron pairing strength, and thus higher T_c within the spin-fluctuation mediated superconductivity scenario [4]. However, since Co-doping to LiFeAs also induces large incoherent electron scattering [26] and narrows the magnetic bandwidth in the d_{xy} orbital [Fig. 4(c)], superconductivity associated with the d_{xy} orbital may be prohibited due to reduced effective magnetic exchange coupling associated with the d_{xy} orbitals [29]. Similarly, in spite of the large magnetic bandwidth associated with the d_{xz}/d_{yz} orbitals, the poor Fermi surface nesting of these orbitals suppresses low energy spin excitations, which is also bad for superconductivity [29]. Therefore, superconductivity in iron pnictides can only occur with appropriate orbital selective low-energy spin excitations coupled with reasonable large magnetic exchange coupling.

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