Anisotropy, Itineracy, and Magnetic Frustration in High-T$_C$ Iron Pnictides

Myung Joon Han$^1$, Quan Yin$^*$, Warren E. Pickett, and Sergey Y. Savrasov
Department of Physics, University of California, Davis, California 95616, USA
(Dated: March 9, 2009)

Using first-principle density functional theory calculations combined with insight from a tight-binding representation, dynamical mean field theory, and linear response theory, we have extensively investigated the electronic structures and magnetic interactions of nine ferropnictides representing three different structural classes. The calculated magnetic interactions are found to be short-range, and the nearest ($J_{1a}$) and next-nearest ($J_2$) exchange constants follow the universal trend of $J_{1a}/2J_2 \sim 1$, despite their itinerant origin and extreme sensitivity to the $z$-position of As. These results bear on the discussion of itineracy versus magnetic frustration as the key factor in stabilizing the superconducting ground state. The calculated spin wave dispersions show strong magnetic anisotropy in the Fe plane, in contrast to cuprates.

Recent discovery of the new high-temperature superconductor, LaO$_{1-x}$F$_x$FeAs with a transition temperature ($T_C$) of $26K$ [1] has triggered tremendous research activities on iron pnictides. Rare-earth (RE) doping increases $T_C$ up to $55K$ for Sm [2,3]. Replacing RE-O layers with Li produces an intrinsic superconductor LiFeAs with $T_C$ of 18K [4]. The 122 ferropnictides, ALFe$_2$As$_2$ ($AL$: Ca, Sr, Ba, K), span another structural class with $T_C$ up to $38K$ [5,6]. More recently, arsenic-free FeSe$_{1-\delta}$ and Fe(Se$_{1-x}$,Te$_x$)$_{1-\delta}$ without any interlayer between Fe-(Se,Te) planes were found to be superconducting at $T_C$ as high as $27K$ under pressure [11,12,13,14]. In spite of the accumulating reports of both experiments and theories, the nature of the superconductivity and magnetism is still far from clear. After several works have ruled out the electron-phonon coupling [15,16], and the coexistence of magnetic fluctuation and superconductivity being confirmed by $\mu$SR [17,18], intensive investigations have been focused on the magnetic properties of these systems [19]. Using first-principle linear response calculations [27,28], we provide the data of in-plane magnetic exchange couplings for several Fe-based superconductors, and discuss their spin wave dispersions. The data bear on the question of whether the values of exchange constants indicates magnetic fluctuations play an important role. A total of nine materials have been studied: $RE$ FeAsO ($RE$: La, Ce, Pr, Nd), ALFe$_2$As$_2$ ($AL$: Ca, Sr, Ba, K), and LiFeAs. Exchange interactions of these systems are found to be short-range despite the metallic density-of-states (DOS), and the calculated interaction strengths follow the universal behavior of $J_{1a} \approx 2J_2$ for all materials, a relation that arises independently in the frustrated magnetic picture [21,22,23]. Considering not only the variety of the materials studied here but also the high sensitivity of the Fe moment to the $z$-position of As atom [29,30], this universal behavior of the exchange interactions is impressive. The calculated spin-wave dispersion shows an anisotropic spin interaction which is different from the cuprates.

There have been several published tight-binding (TB) parametrizations of the electronic structure of prototypical LaOFeAs in the vicinity of the Fermi level using fits based either on Wannier functions or atomic basis sets [31,32,33,34]. However the current situation still looks complicated because the projected DOS deduced from electronic structure calculations are based on the spherical harmonic projectors within the atomic spheres that may not be very well suited for the extended Fe and As orbitals presented here. Due to these complications even the crystal field splitting of Fe $d$ level appears to be controversial in the current literature [31,32,33,34].

To better understand the complicated electronic structure around Fermi level, we performed TB analysis by considering $d_{xz}$ and $d_{yz}$ orbitals of Fe $t_{2g}$ manifold hybridizing with the arsenic $p_z$ and $p_y$, respectively. As shown in Fig. 1, the separation between the energy levels...
of Fe-$t_{2g}$ and As-$p_{z,y}$ states is about 1.6eV. Accounting for the hybridization matrix element between $d_{xz}$-$p_x$, $d_{yz}$-$p_y$ states, which is of the order of 1.8eV, produces bonding and antibonding bands, both having the bandwidth of 2.8eV with the Fermi level falling into the antibonding part of the spectrum (approximately 1eV above the Fe $t_{2g}$ level). We also take into account the $d_{xy}$ state of Fe which hybridizes with itself (hopping integral is approximately 0.3eV), which produces an additional bandwidth of 2.2eV. The resulting bandwidth of Fe $d$-electron character near the Fermi level becomes $2.8 + 2.2/2 = 3.9$eV as exactly seen in the LDA calculation. The coordinate system used for this TB description is the original crystallographic lattice where the spin alternates in the $(\pi, \pi)$ direction. In this picture, the $\Gamma$-centered hole pockets (small circle in Fig. 1) are mostly of $d_{xy}$ character, and the $M$-centered pockets (large circle) are of $d_{xz}$, $d_{yz}$ character. This picture can be fine-tuned further by including the $d_{x^2-y^2}$ state which lies 0.3eV below the Fermi level and hybridizes primarily with As-$p_{z,y}$ states (hopping integral is about 0.8eV) as well as hybridization between $d_{xz,yz}$ orbitals with As $p_z$ states (hopping integral is about 0.4eV). Note that in this picture the Fe $d_{z^2-1}$ orbital becomes unoccupied and lies 1eV above the Fermi level.

Now we discuss the exchange interactions. To calculate the interactions between Fe moments, we used linear response theory based on first-principle density functional theory (DFT) calculations, which has been successfully applied to the 3$d$ transition-metal oxides and the 5$f$ actinides metallic alloys. We used the full potential linearized muffin-tin orbital (LMTO) as the basis set and local spin density approximation (LSDA) for the exchange-correlation (XC) energy functional. The LSDA is fairly good to describe the itinerant Fe 3$d$ states in these materials as shown in the previous studies and comparisons with angle resolved photoemission. In the calculations of REOFeAs compounds, we used the LSDA+DMFT method in which the RE 4$f$ orbitals are treated as the localized ones within Hubbard I approximation. $U = 6$eV and $J_H = 0.86$eV were used as the on-site Coulomb repulsion and Hund’s rule exchange parameter. Lattice constants are taken from experiments, and we performed the calculations at various $z$(As), including experimental $z$(As)$_{exp}$ and LDA optimized $z$(As)$_{LDA}$.

Fig. 2 shows the spin structure of the Fe plane which is common to all these materials. From here on we use the $(\pi,0)$ striped AFM coordinate system, which is convenient to discuss the spin wave dispersions. Magnetic interactions between Fe moments are governed by two dominating AFM couplings $J_{1a}$ and $J_2$, and the FM nearest-neighbor exchange $J_{1b}$ is small. We found the exchange couplings $J(q)$ can be expressed in terms of short-range exchange constants. This character suggests pursuing a comparison with local moment models with AFM spin interactions. The short range couplings do not conflict with the itinerant magnet picture because although the Fe 3$d$ orbital has finite DOS at the Fermi level, the magnetic interactions can still remain short range, which possibly reflects the bad metallicity and some correlation effects.

The calculated Fe magnetic moments and exchange interactions are summarized in Table I. We use the convention that positive $J$ means AFM couplings. The calculated moments are consistent throughout the materials. The calculations done at experimental $z$(As)$_{exp}$ are known to predict the moments about twice as large as experimental values, while at optimized $z$(As)$_{LDA}$ they give smaller moments. The cases in which DFT overestimates magnetic moments are rare, and the cause is still under debate for Fe oxypnictides. Although some theorists suggest it is due to the frustrated magnetic struc-
between the J has so far not been measured nor calculated. According around unity, demonstrating that this universal behavior Note that the calculated ratios shown in Table I are all here. The connection between itinerant AFM and super-

| System     | Moment | $J_{1a}$ | $J_2$ | $J_{1b}$ | $J_{1a}/2J_2$ | $J_{1a} + 2J_2$ |
|------------|--------|----------|-------|----------|---------------|----------------|
| LaFeAsO    | 1.69   | 47.4     | 22.4  | -6.9     | 1.06          | 92.2           |
| CeFeAsO    | 1.79   | 31.6     | 15.4  | 2.0      | 1.03          | 62.4           |
| PrFeAsO    | 1.76   | 57.2     | 18.2  | 3.4      | 1.57          | 93.6           |
| NdFeAsO    | 1.49   | 42.1     | 15.2  | -1.7     | 1.38          | 72.5           |
| CaFe$_2$As$_2$ | 1.51 | 36.6     | 19.4  | -2.8     | 0.95          | 75.4           |
| SrFe$_2$As$_2$ | 1.69 | 42.0     | 16.0  | 2.6      | 1.31          | 74.0           |
| BaFe$_2$As$_2$ | 1.68 | 43.0     | 14.3  | -3.1     | 1.51          | 71.5           |
| KFe$_2$As$_2$ | 1.58 | 42.5     | 15.0  | -2.9     | 1.42          | 72.5           |
| LiFeAs     | 1.69   | 43.4     | 22.9  | -2.5     | 0.95          | 89.2           |

TABLE I: Calculated Fe moments (in $\mu_B$) and in-plane exchange interactions (in meV), using experimental $z(As)$. conductivity has been discussed previously \[43\].

Another important quantity is $|J_{1a} + 2J_2|$ which determines the spin wave velocity in the $(\pi, 0)$ direction, and can be directly probed by neutron scattering experiments. The available experimental data are in general agreement with our calculation. For SrFe$_2$As$_2$ calculation shows $|J_{1a} + 2J_2| = 74meV$, not much smaller than the $100 \pm 20meV$ measured by neutron scattering \[9\]. Also, for CaFe$_2$As$_2$ our calculated $|J_{1a} + 2J_2| = 75meV$ is slightly smaller than the measured $95\pm16meV$ \[26\] (derived from the observed spin wave velocity, see eq. (2) below). Especially our result for BaFe$_2$As$_2$ is in good agreement with recent experiment by Ewings et al. \[44\]: One of their best fits shows that $J_{1a} = 36meV$, $J_2 = 18meV$, and $J_{1b} = -7meV$.

As an example, Fig. 3 shows the $z(As)$-dependence of the magnetic moments and interactions of SrFe$_2$As$_2$. The moment is a simple monatomic function of $z(As)$ ranging from $0.35\mu_B$ to $2.23\mu_B$. The three $J$’s have different behaviors. $J_{1a}$ increases rapidly with $z(As)$ at the beginning, saturates in the middle, and eventually turns down. This behavior is a result of the hybridization between Fe $d_{xz,yz}$ and As $p_{x,y}$ orbitals, as we discussed in the tight-binding representation. Due to the shape and orientation of the Fe $d_{xz,yz}$ and As $p_{x,y}$ orbitals, there is a certain $z(As)$ that gives the maximum overlapping, and hence largest $J_{1a}$. Note that $J_{1b}$ changes sign at $z(As)_{exp}$, and eventually surpasses $J_2$. Also, $J_{1a}$ and $J_2$ plateau in the small region around $z(As)_{exp}$. Similar behaviors are also found in other materials. The $J_{1a}/2J_2$ and $|J_{1a} + 2J_2|$ values presented in Table I are robust against the small deviations in $z(As)$ around the experimental values. From the data one can also calculate $J_{1a}/2J_2$ vs. $z(As)$, which reveals the existence of
FIG. 4: The calculated spin wave dispersion of SrFe$_2$As$_2$ along high-symmetry lines, the exchange constants are given in Table I.

The “sweet spot” where the optimal ratio $J_{1a}/2J_2 = 1$ is achieved independent of any Heisenberg model assumption. In the case of SrFe$_2$As$_2$ it is $z(As) = 0.357$ (the inset of Fig. 3).

The calculated spin wave dispersion gives more intuitive information about the magnetic interaction and anisotropy of these systems [9, 25]. The dispersion relation of the 2D striped-AFM lattice reads

$$\omega(q) = S \sqrt{(J_0 + J_{1b}(q))^2 - (J_{1a}(q) + J_2(q))^2}. \quad (1)$$

Using the calculated magnetic exchange constants, we plot the spin wave dispersion of SrFe$_2$As$_2$ in Fig. 4, whose $S = 0.94$ is taken from experiment [8]. The non-symmetric dispersions in (0, 0) – (0, $\pi$) and (0, 0) – (0, $\pi$) directions indicate in-plane magnetic anisotropy, which is a major difference from cuprates. At small $q$ near (0, 0), the spin wave velocity in the ($\pi$, 0) direction is

$$v_\perp = 2aS |J_{1a} + 2J_2|, \quad (2)$$

which is the relation used to experimentally determine $|J_{1a} + 2J_2|$, such as for SrFe$_2$As$_2$ [9]. The difference in $J_{1a}$ and $J_{1b}$, a direct consequence of the QM-AFM ordering that breaks in-plane symmetry, accounts for the anisotropy in ($\pi$, 0) and (0, $\pi$) directions. These anisotropic spin waves can be directly probed by neutron scattering experiments on single crystals.

To conclude, we have studied magnetic exchange interactions in various Fe-based high $T_C$ superconductors using first-principle based linear response calculations. From the nine different materials, the magnetic interactions are short-range and can be well described by the first and second nearest-neighboring interactions. Importantly $J_1/2J_2$ is close to unity for all the cases, just as would be the case for the frustration limit of a local moment model. Calculated spin wave dispersions show the magnetic anisotropy and the roles of the three in-plane exchange interactions. Our result strongly suggests the magnetic fluctuation as the pairing mechanism for the superconducting ground state.

The authors would like to thank Elihu Abrahams (Rutgers Univ.) and Rajiv Singh (UC Davis) for helpful discussions on the spin wave dispersion. The authors acknowledge support from NSF Grants DMR-0606498 (S.Y.S) and DMR-0421810 (W.E.P), and collaborative work supported by DOE SciDAC Grants SE-FC0206ER25793 and DE-FC02-06ER25794.

* These authors have contributed equally to this paper.

[1] Y. Kamihara et al., J. Am. Chem. Soc. 130, 3296 (2008).
[2] X. H. Chen et al., Nature 453, 761 (2008).
[3] Z. A. Ren et al., Chinese Phys. Lett. 25, 2215 (2008).
[4] J. H. Tapp et al., Phys. Rev. B 78, 060505(R) (2008).
[5] C. Krellner et al., Phys. Rev. B 78, 100504(R) (2008).
[6] A. Jesche et al., arXiv:0807.0632 (2008).
[7] A. I. Goldman et al., Phys. Rev. B 78, 100506(R) (2008).
[8] J. Zhao et al., Phys. Rev. B 78, 140504(R) (2008).
[9] J. Zhao et al., Phys. Rev. Lett. 101, 167203 (2008).
[10] L. Zhao et al., arXiv:0807.0398 (2008).
[11] F. -C. Hsu et al., PNAS 105, 14262 (2008).
[12] M. H. Fang et al., Phys. Rev. B 78, 224503 (2008).
[13] K. -W. Yeh et al., Europhysics Lett. 84, 37002 (2008).
[14] Y. Mizuguchi et al., Appl. Phys. Lett. 93, 152505 (2008).
[15] L. Boeri, O. V. Dolgov and A. A. Golubov, Phys. Rev. Lett. 101, 026403 (2008).
[16] K. Huale, J. H. Shim and G. Kotliar, Phys. Rev. Lett. 100, 226402 (2008).
[17] A. J. Drew et al., Phys. Rev. Lett. 101, 097010 (2008).
[18] W. Bao et al., arXiv:0809.2058 (2008).
[19] J. I. Pulikkotil, M. van Schilfgaarde, and V. P. Antropov, arXiv:0809.0283 (2008).
[20] F. Ma et al., arXiv:0809.4732 (2008).
[21] Q. Si and E. Abrahams, Phys. Rev. Lett. 101, 076401 (2008).
[22] C. Fang et al., Phys. Rev. B 77, 224509 (2008).
[23] C. Xu, M. Müller, and S. Sachdev, Phys. Rev. B 78, 020501 (2008).
[24] J. Wu, P. Phillips, and A. H. Castro Neto, Phys. Rev. Lett. 101, 126401 (2008).
[25] G. S. Uhrig et al., arXiv:0810.3068 (2008).
[26] R. J. McQueeney et al., Phys. Rev. Lett. 101, 227205 (2008).
[27] A. Georges et al., Rev. Mod. Phys. 68, 13 (1996).
[28] G. Kotliar et al., Rev. Mod. Phys. 78, 865 (2006).
[29] Z. P. Yin et al., Phys. Rev. Lett. 101, 047001 (2008).
[30] T. Yildirim, Phys. Rev. Lett. 101, 057010 (2008).
[31] K. Kuroki et al., Phys. Rev. Lett. 101, 087004 (2008).
[32] C. Cao, P. J. Hirschfeld, and H.-P. Cheng, Phys. Rev. B 77, 220506 (2008).
[33] K. Nakamura, R. Arita, and M. Imada, J. Phys. Soc. Jpn. 77, 093711 (2008).
[34] E. Manousakis et al., arXiv:0806.3432 (2008).
[35] D. J. Singh and M.-H. Du, Phys. Rev. Lett. 100, 237003 (2008).
[36] A. I. Liechtenstein et al., J. Magn. Magn. Mater. 67, 65 (1987); P. Bruno, Phys. Rev. Lett. 90, 087205 (2003).
[37] X. Wan, Q. Yin, and S. Y. Savrasov, Phys. Rev. Lett. 97, 266403 (2006).
[38] M. J. Han, X. Wan, and S. Y. Savrasov, Phys. Rev. B
[39] S. Y. Savrasov, Phys. Rev. B 54, 16470 (1996).
[40] D. H. Lu et al., Nature 455, 81 (2008).
[41] I. I. Mazin and M. D. Johannes, Nature Physics doi:10.1038/nphys1160 (2008).
[42] A. V. Chubukov, D. Efremov and I. Eremin, Phys. Rev. B 78, 134512 (2008).
[43] T. Moriya, Proc. Jpn. Acad. Ser. B 82, 1 (2006).
[44] R. A. Ewings et al., Phys. Rev. B 78, 220501 (R) (2008).
[45] Where $J_{1a}(q) = 2J_{1a} \cos q_x$, $J_{2}(q) = 2J_{2}[\cos(q_x + q_y) + \cos(q_x - q_y)]$, $J_{1b}(q) = 2J_{1b} \cos q_y$, and $J_0 = 2J_{1a} + 4J_2 - 2J_{1b}$. 
