

Strong Correlations and Magnetic Frustration in the High T_c Iron Pnictides

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We consider the iron pnictides in terms of a proximity to a Mott insulator. The superexchange interactions contain competing nearest-neighbor and next-nearest-neighbor components. In the undoped parent compound, these frustrated interactions lead to a two-sublattice collinear antiferromagnet (each sublattice forming a Néel ordering), with a reduced magnitude for the ordered moment. Electron or hole doping, together with the frustration effect, suppresses the magnetic ordering and allows a superconducting state. The exchange interactions favor a d -wave superconducting order parameter; in the notation appropriate for the Fe square lattice, its orbital symmetry is d_{xy} . A number of existing and future experiments are discussed in light of the theoretical considerations.

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Introduction.—High T_c superconductivity has recently been discovered in the iron pnictides, with the F-doped LaOFeAs being the prototype [1]. Variations include P replacement for As, Ni replacement for Fe, and rare-earth replacements for La [2–6]. In addition, F substitution for O, which adds itinerant electron carriers to the system, could be replaced by, e.g., Sr substitution for La, which introduces hole doping [7].

Like the cuprates, the iron pnictides have a layered structure. The FeAs unit appears to contain all the electronic states near the Fermi energy, similar to the case of the CuO₂ layer in the cuprates. The electrons partially occupying the d orbitals of the iron sites can be strongly correlated, as are those on the copper sites in the cuprates. At the same time, there are also important differences between the two classes of materials. In this Letter, we consider the consequences of the unique aspects of the electronic states of the iron pnictides. We will frame our discussion in terms of the F-doped LaOFeAs family, and touch upon their cousin compounds where appropriate.

One basic question is whether the Mott insulating physics plays any significant role in LaOFeAs. The answer is not necessarily affirmative; there are, for instance, indications from band structure calculations that covalency is sizable not only in LaOFeP [8] but also in LaOFeAs [9]. Nonetheless, we argue that there are indirect evidences for the case that LaOFeAs is in proximity to a Mott insulator. First, the measured electrical resistivity is very large, $\rho \approx 5 \text{ m}\Omega \text{ cm}$ at room temperature [1]. This corresponds to a normalized mean free path $k_F l \approx hc/e^2 \rho \approx 0.5$ (where $c \approx 8.7 \text{ \AA}$ is the lattice constant along the normal to the FeAs plane, and $h/e^2 \approx 26 \text{ k}\Omega$ is the quantum resistance), which qualifies the system as a bad metal. Second, LaOFeP, which has a smaller lattice constant ($c = 8.5 \text{ \AA}$), thus a larger internal pressure, is expected to have a larger effective bandwidth W but a similar effective Coulomb interaction U compared to LaOFeAs. Our sug-

gestion that LaOFeP has a smaller U/W compared to LaOFeAs is consistent with the observation that LaOFeP is a better metal; it is $k_F l \approx 1$ at room temperature and, indeed, it is superconducting with $T_c \approx 4 \text{ K}$ [2]. These considerations are illustrated in Fig. 1. Additional evidence along this direction is provided by the lack of a Drude peak in both the measured optical conductivity of LaOFeAs [10], as well as the calculated one by the DMFT + DFT method [11]. Thus, our approach to LaOFeAs is motivated by important experimental observations: the very large resistivity and the small weight of a Drude peak. These are unlike a conventional metal and therefore are not likely to be accounted for without including correlation effects. They imply that most of the electronic excitations lie in the incoherent part of the spectrum. Even if LaOFeAs is not fully Mott insulating, it should not be far away from it. We therefore find it instructive to discuss these systems from a strong-coupling point of view.

Why is the magnetism so weak?—Within this strong coupling framework, the issue arises as to why the magnetism is so weak, both in the undoped and lightly doped iron pnictides. Consider first the undoped parent compound. Valence counting in LaOFeAs yields Fe²⁺, which contains six outermost-shell electrons partially filling the five $3d$ orbitals. The degeneracy of the latter is split by the crystal field.

One characteristic feature seen in the *ab initio* electronic structure calculations is that the splitting among the five $3d$ orbitals is relatively small. Reference [12] shows that the

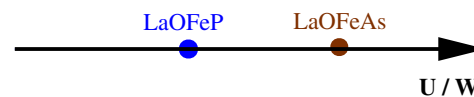


FIG. 1 (color online). Placing LaOFeAs and LaOFeP in terms of the control parameter U/W , where U is the on-site Coulomb interaction and W the effective bandwidth.

individual separations among the d levels is on the order of, or less than, 0.1 eV. Taking into account the typical Coulomb interactions U , of the order of 4–5 eV, and the Hund's coupling J_H , of the order of 0.7 eV [11], we expect the six outermost-shell electrons to occupy the $3d$ orbitals in the scheme depicted in Fig. 2(a). The associated Mott insulator has spin $S = 2$. The spin-orbit coupling is expected to be considerably weaker than J_H , so we shall focus on the spin magnetism. Even if the separations between the crystal levels were larger than J_H (but still smaller than U), there would still be a double degeneracy [13,14], leading in our consideration to an $S = 1$ Mott insulator.

Such a large-spin Mott insulator is expected to be strongly magnetic. Yet, a neutron scattering experiment [15] has shown that LaOFeAs is an antiferromagnet with a rather small ordered moment, on the order of $0.4\mu_B/\text{Fe}$.

The issue is even more acute in the doped cases. Electron doping will introduce additional states with spin $3/2$, as illustrated in Fig. 2(b). Since the relevant local states are all magnetic, it is surprising that a relatively small amount of doping (say 10% F doping for O) does not preserve the magnetic ordering.

Magnetic frustration.—We propose that the answer to these questions lies primarily in magnetic frustration. The key feature here is that in the FeAs unit, not only do the Fe atoms form a square lattice, but each As atom, away from the Fe plane, lies an equal distance from each of the four adjacent Fe atoms. Because our focus will be on the Fe plane, we find it convenient to use the symmetry classification appropriate for the Fe square lattice: we choose the x and y axes to be along the Fe-Fe bond direction; these are rotated by 45° from the notation used in recent papers.

Consider the superexchange interactions between the $3d_{x^2-y^2}$ orbitals of nearby Fe sites. Inspection of the orbitals suggest that the strongest channel of hybridization will be with the As $4p_{x-y}$ or $4p_{x+y}$ orbital.

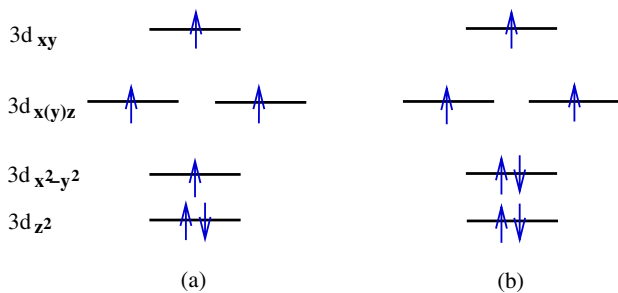


FIG. 2 (color online). (a) Spin-2 states relevant for the undoped LaOFeAs. The crystal levels are according to Ref. [12]. The x and y we use differ from the standard notation, adopted there, by a rotation of 45° ; see the main text. (b) Spin-3/2 states that become important when electron doping is introduced into the FeAs layer. Hole doping will lead to the analogous spin-3/2 states, corresponding to five electrons residing on the $3d$ orbitals.

For a pair of next-nearest-neighbor (NNN) Fe $3d_{x^2-y^2}$ spins, the lowest-energy intermediate state mediating the superexchange interaction corresponds to two electrons occupying the same $4p_{x-y}$ (or $4p_{x+y}$) orbital [Fig. 3(b)]. Since this intermediate state is a singlet state, the resulting exchange interaction is *antiferromagnetic*:

$$J_2 \approx 2 \frac{V_{x^2-y^2}^4}{(\epsilon_{p_{x-y}} - \epsilon_{d_{x^2-y^2}})^3}, \quad (1)$$

where $V_{x^2-y^2}$ is the hybridization matrix between the Fe $3d_{x^2-y^2}$ and As $4p_{x-y}$ orbitals.

For a pair of nearest-neighbor (NN) $3d_{x^2-y^2}$ Fe spins, the lowest-energy intermediate states correspond instead to two electrons occupying a pair of distinct $4p_{x+y}$ and $4p_{x-y}$ orbitals [Fig. 3(c)]. The resulting exchange interaction is ferromagnetic:

$$J_1 \approx -4V_{x^2-y^2}^4 \left[\frac{1}{(\epsilon_{p_{x-y}} - \epsilon_{d_{x^2-y^2}} + J_{H,p})^3} - \frac{1}{(\epsilon_{p_{x+y}} - \epsilon_{d_{x^2-y^2}})^3} \right]. \quad (2)$$

Here $J_{H,p} < 0$ is the Hund's coupling between the As $4p_{x-y}$ and $4p_{x+y}$ orbitals, which favors the triplet inter-

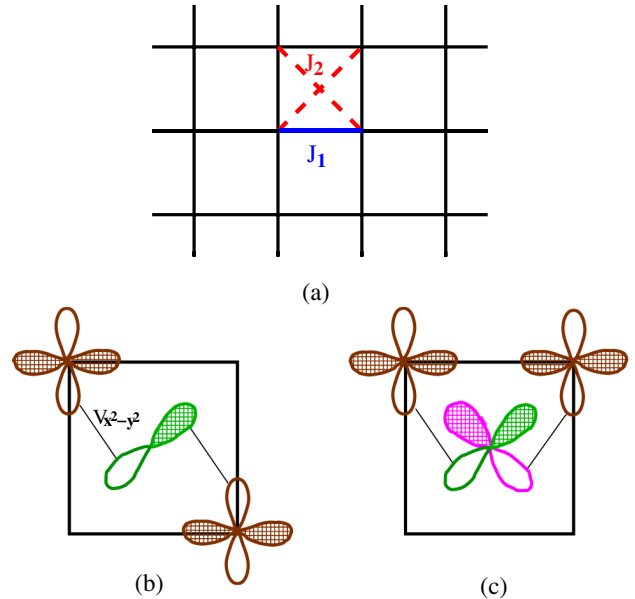


FIG. 3 (color online). (a) The dominant superexchange interactions are those between both a pair of nearest-neighbor Fe spins (J_1) and a pair of next-nearest-neighbor Fe spins (J_2). (b) The process contributing to the NNN superexchange interaction between a pair of $3d_{x^2-y^2}$ electrons. It involves the same $4p_{x-y}$ orbital, leading to an antiferromagnetic J_2 . (c) The process contributing to the NN superexchange interaction between a pair of $3d_{x^2-y^2}$ electrons. It involves two orthogonal $4p$ orbitals, leading to a ferromagnetic J_1 .

mediate state over the singlet one. Notice that $J_{H,p}$ is relatively small, we expect that the ferromagnetic term is small compared to the antiferromagnetic one.

The dominating matrix elements of the hybridization matrix have been given in Ref. [12]. The other relevant hybridizations involve the $3d_{x'z}$ and $3d_{y'z}$ orbitals. (Here a prime denotes the crystallographic axes, which are rotated by 45° from the Fe-square-lattice axes.) For the NNN interaction, the dominating antiferromagnetic terms [with appropriate replacements of the hybridization matrix elements in Eq. (1)] appear in the diagonal matrix elements $x'z - x'z$ and $y'z - y'z$, as well as in the off-diagonal matrix elements $x'(y')z - (x^2 - y^2)$. For the NN exchange J_1 , the dominating antiferromagnetic terms also appear in the diagonal matrix elements $x'z - x'z$ and $y'z - y'z$ and in the off-diagonal matrix elements $x'(y')z - (x^2 - y^2)$. Finally, the NNN exchange J_2 involves virtual processes associated with only one As atom, while the NN exchange J_1 picks up contributions from two As atoms. Taken together, we expect that the largest eigenvalues of both the J_2 matrix and the J_1 matrix correspond to antiferromagnetic interactions, with the former larger than half of the latter.

The result is the following general form for the spin Hamiltonian,

$$H_J = \sum_{ij} J_{ij}^{\alpha\beta} \mathbf{s}_{i,\alpha} \cdot \mathbf{s}_{j,\beta} + J_H \sum_{i,\alpha \neq \beta} \mathbf{s}_{i,\alpha} \cdot \mathbf{s}_{i,\beta}, \quad (3)$$

with mixed $J_{NN}^{\alpha\beta} = J_1^{\alpha\beta}$ but antiferromagnetic $J_{NNN} = J_2^{\alpha\beta}$. Here J_1 and J_2 are both matrices in the orbital basis, with matrix elements labeled by $\alpha\beta$. Again, whether the local states are spin 2 or spin 1, corresponding to α or $\beta = 1, 2, 3, 4$ or α or $\beta = 1, 2$, depends on whether the Hund's coupling J_H is large or small compared to the crystal level splittings.

Equation (3) specifies a frustrated spin system. In the $J_2 > |J_1|/2$ case here, the ground state is expected to be a two-sublattice collinear antiferromagnet (with each sublattice itself forming a Néel ordering) [16,17]. This spin pattern was first proposed for LaOFeAs based on a consideration of the Fermi-surface nesting within a spin-density-wave picture [10,18,19]. It has subsequently been shown to be consistent with the elastic neutron scattering experiment in LaOFeAs [15].

Frustration effects are also important to yield an ordered moment that is considerably smaller than the atomic value of order $2\mu_B$. The important point here is that it introduces J_2/J_1 as a tuning parameter, which allows for a reduction of the ordered moment. Indeed, as J_2/J_1 is decreased towards a critical value, the ordered moment is reduced to zero. The experimental value of the moment, as already mentioned, is about $0.4\mu_B/\text{Fe}$ in LaOFeAs [15].

According to Ref. [12], the $3d - 4p_x$ hybridization matrix elements and the corresponding energy level separations are of the order of 0.8 and 1.3 eV, respectively. The perturbative expression, Eq. (1), leads to an antiferromag-

netic component of the NNN exchange J_2 matrix of the order of 0.4 eV. While it is not expected to be quantitatively accurate, the result does suggest that the exchange interaction will be sizable.

For the doped case, the effective model is a matrix $t - J_1 - J_2$ Hamiltonian:

$$H_{IJ} = H_t + H_J. \quad (4)$$

The kinetic component of the Hamiltonian is

$$H_t = \sum_{ij} t_{ij}^{\alpha\beta} \tilde{c}_{i,\alpha}^\dagger \tilde{c}_{j,\beta}. \quad (5)$$

Here, the $\tilde{c}_{\alpha,i}$ describe constrained fermions, which connect the spin-2 and spin-3/2 configurations at the site i , while $t_{NN}^{\alpha\beta} = t_1^{\alpha\beta}$ and $t_{NNN}^{\alpha\beta} = t_2^{\alpha\beta}$ are the NN and NNN hybridization matrices. (Recall that α, β refer to the d orbitals.) The net result of H_t is to introduce transitions between the spin-2 and spin-3/2 states of the NN and NNN Fe sites.

Because the frustration in the superexchange interactions has already reduced the ordered moment in the undoped parent compound, the magnetic ordering can be readily suppressed in the doped materials. This further suppression occurs because the F doping for O induces a spin-3/2 (or spin-1/2) substitution of the spin-2 (or spin-1) states. Experimentally, the absence of magnetic ordering has been shown in $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$, with electron doping of $x \approx 8\%$ [15].

Superconductivity.—Frustration effects, while suppressing the magnetic ordering, accumulate entropy at low temperatures. The relief of this entropy can take the form of creating a superconducting order. Precisely how this happens is one of the challenging questions in strongly correlated electron systems. Still, there are some general considerations we can make on the superconductivity.

The proximity to a Mott insulator disfavors isotropic s -wave order parameter for the superconducting state. Given that the NNN antiferromagnetic exchange interaction plays a dominant role in the magnetic ordering at half filling, it is natural that the superconducting state has a d_{xy} orbital symmetry. [A mixed pairing state ($d_{x^2-y^2} + id_{xy}$) may also appear for certain range of J_2/J_1 [20].] To see this explicitly, we carry through a simplified analysis on a square plaquette. Our consideration parallels that of Ref. [21] for the cuprate case.

The square plaquette we consider is illustrated in Fig. 4. We will start from the spin-1/2 case. The four-electron ($N = 4$) ground state is well approximated by

$$|N = 4, gs\rangle \propto (c_{4,\uparrow}^\dagger c_{3,\uparrow}^\dagger c_{2,\downarrow}^\dagger c_{1,\downarrow}^\dagger + \text{S.R.})|0\rangle, \quad (6)$$

where $|0\rangle$ is the vacuum state, and S.R. denotes spin reversal.

The $N = 2$ ground state, at the same time, is well approximated by a Gutzwiller-projected Slater determinant of two electrons, which can be written in real space as

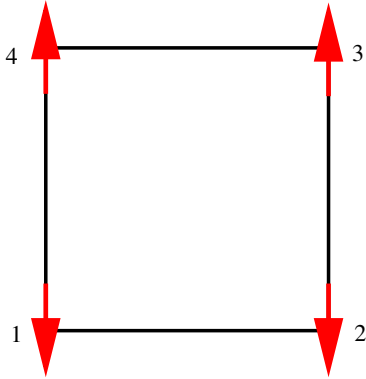


FIG. 4 (color online). A square plaquette showing a spin arrangement of the two-sublattice collinear antiferromagnet.

$$|N = 2, gs\rangle \propto P_G \sum_{i,i'=1}^4 c_{i,\downarrow}^\dagger c_{i',\uparrow}^\dagger |0\rangle, \quad (7)$$

where P_G eliminates any double occupancy of a site. It is straightforward to show that the pairing operator that has the maximum matrix element between $|N = 4, gs\rangle$ and $|N = 2, gs\rangle$ is the d_{xy} pairing operator,

$$\Psi_{xy} \propto \sum_{\mathbf{k}} (\sin k_x \sin k_y) c_{\mathbf{k},\uparrow} c_{-\mathbf{k},\downarrow}. \quad (8)$$

The construction of the exact $|N = 4, gs\rangle$ and $|N = 2, gs\rangle$ for the spin = 1/2 case, as well as the equivalent calculations for the higher spin cases, can be readily done numerically. The above suggests that the magnetic exchange interactions will promote the d_{xy} pairing, regardless of the specific mechanism with which the exchange interactions cause superconductivity.

Conclusion.—A complete analysis of the matrix $t - J_1 - J_2$ model that we have introduced could reveal the existence of other competing phases, such as inhomogeneous magnetic structures. The description of the phase diagram and its evolution with doping are thus interesting subjects. Such studies must await more accurate determinations from *ab initio* calculations and/or experiment of all the underlying matrix elements [e.g., Eqs. (1) and (2)] and are beyond the scope of this Letter.

A key test for our picture is to experimentally determine the relevant spin states in both the parent and doped systems, as well as to measure the exchange interactions from, say, the spin-wave spectra in the undoped parent compounds. Studying additional families of materials which, in the undoped case, can be placed along the U/W axis (Fig. 1) will allow a fuller exploration of the half-filled phase diagram and its doped counterpart. This is especially important for the parts of the phase diagram that are either deep inside the Mott insulating phase or well into the large- $k_F l$ nonsuperconducting metallic regime.

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Note added.—Immediately before this Letter was finalized, we learned of the work of Yildirim [22], who independently considered the frustration effect using *ab initio* calculations, and who, in contrast to many other density functional-based calculations, gave an ordered moment for the parent compound in the experimental range. While we believe that a consideration of correlation effects is essential to account for the “bad metal” properties described in the Introduction, there could be other routes to the existence of a small ordered moment itself.

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