Unified Picture for Magnetic Correlations in Iron-Based Superconductors

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The varying metallic antiferromagnetic correlations observed in iron-based superconductors are unified in a model consisting of both itinerant electrons and localized spins. The decisive factor is found to be the sensitive competition between the superexchange antiferromagnetism and the orbital-degenerate double-exchange ferromagnetism. Our results reveal the crucial role of Hund's rule coupling for the strongly correlated nature of the system and suggest that the iron-based superconductors are closer kin to manganites than cuprates in terms of their diverse magnetism and incoherent normal-state electron transport. This unified picture would be instrumental for exploring other exotic properties and the mechanism of superconductivity in this new class of superconductors.

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Recently, high-temperature superconductivity has been observed in a number of doped iron-based layer materials near a static antiferromagnetic (AF) order [1–6] and with a spin resonance [7,8], a pattern exhibited previously by the copper oxides. Intriguingly, in contrast to the universal insulating checkerboard AF order in undoped copper oxides, the AF orders in this new class of superconductors are metallic and material-dependent: "collinear" [Fig. 1(a)] in undoped pnictides LaOFeAs and $BaFe_2As_2$ [4,5] and "bicollinear" [Fig. 1(b)] in undoped chalcogenide FeTe [6]. This newly unveiled magnetic diversity has greatly promoted the magnetic mechanism as a general route to high-temperature superconductivity [9]. It is thus essential to understand how these AF correlations developed in the first place [10].

The fact that all the iron-based superconductors have similar crystal structure, electronic structure, and Fermi-surface topology [11] suggests that their metallic magnetism has *a common origin*. This is further supported by the spin resonance in the superconducting state that appears to be universally collinearlike [7,8]. Moreover, it was shown [12] that FeTe could switch from bicollinear to collinear by decreasing the anion height from the Fe plane. These observations call for a unified picture that hosts a sensitive competition between the collinear and bicollinear AF orders.

However, previous model analyses did not reveal a close relationship between these two orders. The collinear order has been widely noted as a spin-density-wave state resulting from the nested Fermi-surface topology of itinerant electrons [9]. While doubts on its validity still remain [13], this scenario apparently does not work for the bicollinear order. On the other hand, direct data fitting with the Heisenberg model for local spin moments (in view of a Mott insulator [14]) revealed dramatic changes in the model parameters for these two orders [15], not to mention its difficulty to account for the metallicity.

The purpose of this Letter is to show that the unified microscopic understanding can be achieved with a model having both components, itinerant electrons and localized spins. It naturally possesses two competing magnetic effects: (i) the AF superexchange coupling J_{ij} between the localized spins and (ii) the double-exchange ferromagnetism [16] introduced by Hund's rule coupling K between the itinerant electrons and the localized spins. The competition results in the formation of antiferromagnetically coupled ferromagnetic (FM) chains in the iron plane. These FM chains can be *straight* [Fig. 1(a)] or *zigzag* [Fig. 1(b)]; the difference is small in energy but dramatic in the whole pattern—the collinear (C-type) or bicollinear (E-type) AF order. This magnetic softness is expected to strongly scatter charge carriers above the Néel temperature, where the system has not been frozen into a specific static order, leading to the observed rather incoherent normal-state electron transport [1,17].

We begin with the crystal structure, which suggests that Fe^{2+} is in an orbitally degenerate state, surrounded by the exceptionally polarizable anions As, Te, or Se.

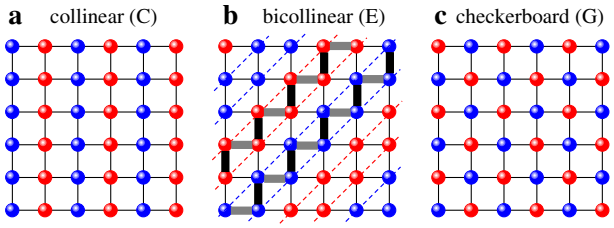

FIG. 1 (color online). The in-plane patterns of the spin-up (blue balls) and spin-down (red balls) iron atoms in (a) the collinear (C-type), (b) bicollinear (E-type), and (c) checkerboard (G-type) AF orders. Note that bicollinear means to follow the dashed lines for FM correlation, while a more insightful view is to follow the zigzag thick lines (black and gray stand for alternating electron hopping strengths) of the E type.

As such, the Coulomb repulsion energy U between the Fe $3d$ electrons is strongly solvated, whereas K remains nearly unchanged [18], and this is in agreement with x-ray data on both undoped and superconducting pnictides [19]. Furthermore, the solvation effect on U from the anions could be strongly orbital-dependent. A recent first-principles Wannier-function analysis [20] indicates that the influence of the anions on the Fermi-surface states, mainly of Fe d_{xz} and d_{yz} characters, is so substantial that the head-on "σ-bond" hopping becomes surprisingly small and the "π-bond" hopping becomes the leading one. It is likely that the U for the Fe d_{xz} and d_{yz} electrons is closer to the complete solvation. We thus assume that the Fe $3d$ electronic states separate into two different types: The d_{xz} and d_{yz} electrons are itinerant, and the rest form relatively localized spins. The double-exchange FM effect is thus introduced thanks to the energy barrier $\sim K$ for an itinerant electron to hop between two antiparallel localized spins [16]; to this extent, our proposal is supported by the spectroscopic imaging-scanning tunneling microscopy (SI-STM) data [21] on $CaFe_2As_2$ and neutron-scattering data [22] on $Fe_{1+\delta}Te_{1-x}Se_x$.

The minimum model considered is an effective orbital-degenerate double-exchange model [23]:

$$H = -\sum_{ij\gamma\gamma'\mu}(t_{ij}^{\gamma\gamma'}C_{i\gamma\mu}^{\dagger}C_{j\gamma'\mu} + \text{H.c.}) - \frac{K}{2}\sum_{i\gamma\mu\mu'}C_{i\gamma\mu}^{\dagger}\vec{\sigma}_{\mu\mu'}C_{i\gamma\mu'}\cdot\vec{S}_i + \sum_{ij}J_{ij}\vec{S}_i\cdot\vec{S}_j, \quad (1)$$

where $C_{i\gamma\mu}$ denotes the annihilation operator of an itinerant electron with spin $\mu =\uparrow$ or $\downarrow$ in the $\gamma = d_{xz}$ or d_{yz} orbital on site i. $t_{ij}^{\gamma\gamma'}$'s are the electron hopping parameters. $\vec{\sigma}_{\mu\mu'}$ is the Pauli matrix, and $\vec{S}_i$ is the localized spin whose magnitude is S. J_{ij} is the AF superexchange couplings between the localized spins; in particular, J and J' are, respectively, the nearest-neighbor (NN) and next-nearest-neighbor (NNN) ones. $KS \simeq 0.4$–0.8 eV [19] and $JS^2 \approx J'S^2 \approx 0.01$ eV. Our recent first-principles Wannier-function analyses on LaOFeAs [20] and FeTe suggest that to the y direction, the $d_{xz} - d_{xz}$ NN hopping integral $t_{\parallel} \simeq 0.4$ eV and the $d_{yz} - d_{yz}$ NN hopping integral $t_{\perp} \simeq 0.13$ eV; they are swapped to the x direction; by symmetry the NN interorbital hoppings are zero; the NNN intraorbital hopping integral $t' \simeq -0.25$ eV for both d_{xz} and d_{yz} orbitals, and the NNN interorbital hopping is ± 0.07 eV; farther hopping parameters and the interlayer ones are weak [20] and neglected and so are the farther superexchange parameters. We emphasize that, as demonstrated below, our conclusions are independent of the details of the parameters as long as the following two intrinsic features of the parameters hold: $t_{\parallel} \gg t_{\perp}$ and moderate $KS \sim t_{\parallel}$. Here one itinerant electron per site (denoted as $n = 1$) is considered to correspond to the parent compounds [24,25].

For the material dependence of the parameters, note that the anion height from the iron plane, z_{anion}, is the most significant local structural variation among the iron-based superconductors: $z_{\text{anion}} = 1.31$, 1.35, and 1.73 Å in LaOFeAs, $BaFe_2As_2$, and FeTe, respectively [4–6]. Since the iron atoms communicate with each other through the anions, the farther away the anions are, the more isolated the iron atoms are. The isolation of the Fe atoms would enhance the local parameters S and KS (in agreement with the ordered magnetic moments of 0.36, 0.87, and $1.70\mu_B$ in LaOFeAs, $BaFe_2As_2$, and FeTe, respectively [4–6]) but suppress the nonlocal parameters J_{ij}. Considering the cancellation of the z_{anion} effects on S and J_{ij}, $J_{ij}S^2$ as a whole is approximately material-independent. Hence, KS is decisive in distinguishing the bicollinear ordered FeTe ($KS \sim 0.8$ eV) from the collinear ordered LaOFeAs and $BaFe_2As_2$ ($KS \sim 0.4$ eV).

In Eq. (1), the itinerant electrons are actually strongly correlated via Hund's rule coupling to the quantum localized spins [26,27]. To give a general and simple picture elucidating that the model indeed conceives a strong magnetic phase competition, it suffices to compare a variety of static spin orders with the localized spins treated as Ising spins. The Ising approximation for the K term is supported by a recent numerical study in local-density approximation plus dynamical mean-field theory [13]. Then, Eq. (1) is reduced to a system of noninteracting electrons moving in an external potential that is $-KS/2$ and $KS/2$ at site i when the itinerant electron is spin parallel and antiparallel to $\vec{S}_i$, respectively.

The results shown in Fig. 2 indicate that a salient feature of Eq. (1) is the magnetic softness, namely, the close proximity of the collinear (C-type), bicollinear (E-type),

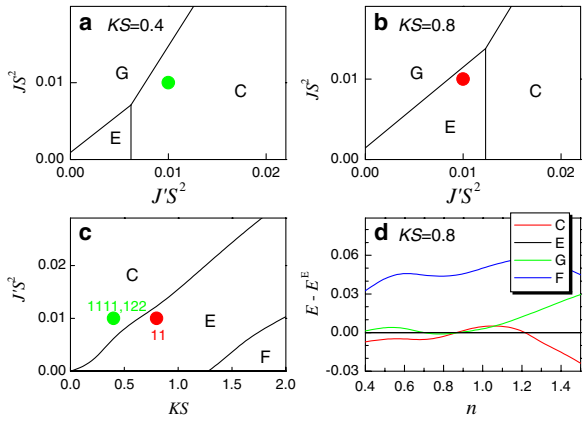

FIG. 2 (color online). Close proximity of AF orders. The shorthand notations [26] are G (checkerboard), C (collinear), E (bicollinear), and F (ferromagnetic). The $JS^2 - J'S^2$ phase diagrams for $n = 1$ with (a) $KS = 0.4$ eV and (b) $KS = 0.8$ eV. The green and red dots mark out $JS^2 = J'S^2 = 0.01$ eV. (c) The $J'S^2 - KS$ phase diagrams for $n = 1$. Also illustrated are the placements of FeTe ("11," red dot), LaOFeAs, and $BaFe_2As_2$ ("1111" and "122," respectively, green dot). $JS^2 = J'S^2$. (d) The total energy as a function of n with respect to that of the bicollinear order. $KS = 0.8$ eV and $JS^2 = J'S^2 = 0.01$ eV. The energy unit is eV.

and checkerboard (G-type) AF orders. This key point is robust, as it exists in a quite extended neighborhood of the realistic parameter values: $JS^2 \simeq J'S^2 \simeq 0.01$ eV [Figs. 2(a) and 2(b)], $KS = 0.4$–0.8 eV [Fig. 2(c)], and $n = 1$ [Fig. 2(d)]. It explains why a tiny change in chemical composition can induce a dramatic change in the magnetic structure. On the other hand, the FM (F-type) order is shown to be a rather high-energy and irrelevant state [Fig. 2(d)]. Hence, Eq. (1) with moderate KS warrants the overall in-plane AF correlations, providing a necessary environment for forming singlet superconductivity consisting of paired electrons with opposite spins.

Regarding the competition between the observed C-type and E-type AF orders, Figs. 2(a)–2(d) indicate that the C type is favored by larger $J'S^2$, smaller KS, or charge doping. Since the pure contribution of the localized spins to the total energy per iron is $-2S^2J'$ for the C type and zero for the E type, the case where the E type wins for $KS > 0.6$ eV [Fig. 2(c)] reflects the important role of the kinetic energy of the itinerant electrons. This is to be understood as follows. Let us first take the heuristic limit of $KS \rightarrow \infty$ and $t_{\|} \gg t_{\perp}$: The kinetic energy per iron is $-2t_{\|}/\pi \approx -0.64t_{\|}$ for the C type and $-t_{\|}[1 + \frac{2}{\pi}(\frac{|2t'|}{t_{\|}} \sin k_F - k_F)] \approx -1.07t_{\|}$ (where $\cos k_F = |t_{\|}/2t'| = 0.8$) for the E type; the difference is fairly enough to overcome $-2S^2J'$. Generally speaking, the larger KS is, the stronger confinement of electrons is within the ferromagnetic chain. This, together with the strong anisotropy in the first-neighbor hoppings, will make the electrons in one of the d_{xz} and d_{yz} orbitals tend to be not dispersive in the C type because of its straight FM chain structure. By contrast, in the E type, which has zigzag FM chains, both the d_{xz} and d_{yz} orbitals always equally contribute to the kinetic energy gain. In addition, the E type gains the kinetic energy mainly via a Peierls-transition-type [28] band splitting due to the doubling of the periodicity by the alternating first-neighbor hopping strengths [$t_{\|}$ versus $t_{\perp}$; black and gray thick lines in Fig. 1(b)] along the zigzag FM chain. The lower subbands are almost fully occupied at $n = 1$; thus, the E type benefits the most near $n = 1$ and is gradually disfavored by doping, in agreement with the neutron-scattering data [8,22] on $FeTe_{1-x}Se_x$. The above analysis is robust with respect to the electronic structure and the Fermi-surface topology because it requires only the intrinsic (symmetry-driven) strong anisotropy in the first-neighbor hoppings.

The *metallicity* of the four typical magnetic states is manifested in their band structures, as shown in Fig. 3. They are presented in the momentum space corresponding to one Fe atom per unit cell in order to explicitly illustrate the effects of broken periodicity: Additional gap openings and shadow bands can be clearly observed, whose intensity reflects the strength of the bands' coupling to the orders [29]. Note that the xz (blue) and yz (red) bands of the E, G, and F types have a symmetry with respect to the swap of k_x and k_y, whereas this symmetry is broken in the C type, indicating an accompanying ferro-orbital order.

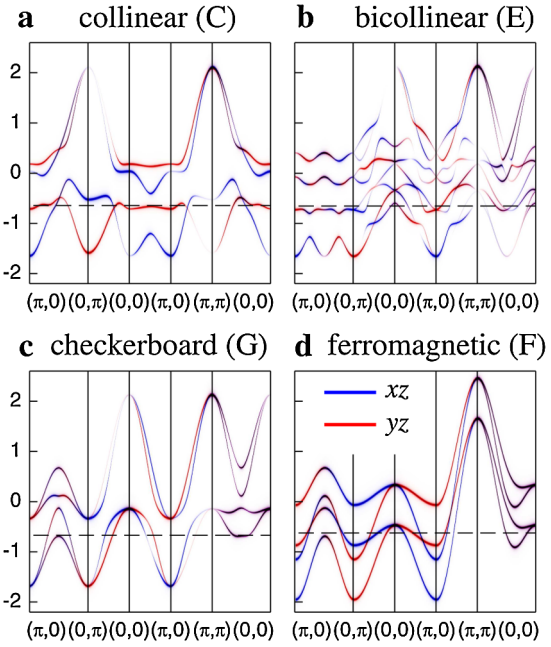

FIG. 3 (color online). Electronic structures of the itinerant electrons for the (a) collinear, (b) bicollinear, (c) checkerboard, and (d) ferromagnetic spin orders calculated with $KS = 0.8$ eV. The dashed lines are the Fermi level for $n = 1$. The energy unit is eV.

This agrees with our first-principles Wannier-function analysis of LaOFeAs [20] and FeTe. A close examination of the band structure of the C type [Fig. 3(a)] reveals that it is nearly dispersionless along the AF direction $[(0, 0) - (\pi, 0)]$ but strongly disperses along the FM direction $[(0, \pi) - (0, 0)]$, in agreement with the SI-STM measurement [21]. The same also holds for the E type [Fig. 3(b)], where the AF direction is along $(\pi, 0) - (0, \pi)$ and the FM direction along $(0, 0) - (\pi, \pi)$, and this is to be confirmed by future SI-STM measurements on FeTe.

It is interesting to point out that the zigzag view of bicollinear is nothing but the E-type AF order studied in the context of $RMnO_3$, where R is a rare-earth element [26]. $RMnO_3$ is known to be insulating due to the Peierls-transition-type gap opening; then, a critical question is why the E-type AF order of FeTe is metallic. The answer is that the iron-based superconductors have a considerably large NNN intraorbital hopping parameter t'. Comparable NN and NNN parameters are suggested by the crystal structure—the anions sit above or below the center of the Fe plaque. Besides, that the observed Fermi surface has a hole pocket around $(0, 0)$ and an electron pocket around $(\pi, 0)$ implies that $-2t' > t_{\|}$. This condition is found to warrant the overlap of the split subbands and the metallicity of the system. We verified that had $t' = 0$, the E type would be insulating. Moreover, since the G-type AF order [Fig. 1(c)] gains the kinetic energy mainly from the t' term, the large t' introduces the G type to the fierce phase competition.

Finally, it is noteworthy that the quantum nature of the localized spins is important to the spin excitations,

the self-energy correction to the itinerant electrons, the electron pairing via exchange of magnons, etc. For example, the full treatment of our model will inevitably yield rather incoherent normal-state electron transport. In fact, as temperature decreases, the undoped or underdoped compounds of the $FeTe_{1-x}Se_x$ or $FeTe_{1-x}S_x$ family exhibit an anomalous semiconductor behavior before getting into the metallic AF state or even the superconducting state [17]. Previously, the large normal-state electric resistivity was used as strong evidence for the proximity of the system to the Mott insulator like the cuprates [14], while the anomaly in $FeTe_{1-x}Se_x$ was attributed to scattering with excessive Fe atoms [17]. The present results imply that the phase competition among several distinct types of AF orders is the intrinsic driving force. The relatively more severe incoherence in $FeTe_{1-x}Se_x$ or $FeTe_{1-x}S_x$ owes its origin to a fiercer phase competition advocated by the E-type AF correlation and enhanced by the Fe impurities and the Te/Se/S disorder. Note that similar phenomena were observed in doped manganites, where phase separation, only enhanced by quenched disorder, has been demonstrated to be the decisive factor by using a double-exchange model [27] similar to Eq. (1). Our analysis indicates that K is crucial for the strongly correlated nature of the iron-based superconductors and suggests that they are closer kin to manganites than cuprates in terms of their magnetism and normal-state electron transport.

In summary, we have presented an orbital-degenerate double-exchange model that unifies the varying metallic antiferromagnetism in the iron-based superconductors, reproducing the essential conclusions from a number of experiments and first-principles band calculations. The KS (z_{anion}) and doping-induced switching of the AF orders manifests that the sensitive competition between the super-exchange antiferromagnetism and the orbital-degenerate double-exchange ferromagnetism is the decisive factor in the development of magnetic correlations. Our picture is anticipated to be instrumental for exploring other exotic properties in this new class of superconductors such as incommensurability, the mixed C_xE_{1-x}-type AF order, electron-magnon-phonon coupling (due to the strong z_{anion} dependence of KS), and ultimately the mechanism of high-temperature superconductivity.

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Note added.—After completing the present work, we became aware that Lv, Krüger, and Phillips [30] recently used a similar model to address the magnetic anisotropy and magnon dispersion in the collinear AF system.

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