



Microscopic origin of magnetism and magnetic interactions in ferropnictides

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One year after their initial discovery, two schools of thought have crystallized regarding the electronic structure and magnetic properties of ferropnictide systems. One postulates that these are itinerant weakly correlated metallic systems that become magnetic by virtue of spin-Peierls-type transition due to near nesting between the hole and the electron Fermi-surface pockets. The other argues that these materials are strongly or at least moderately correlated and the electrons are considerably localized and close to a Mott-Hubbard transition, with the local magnetic moments interacting via short-range superexchange. In this Rapid Communication we argue that neither picture is fully correct. The systems are moderately correlated but with correlations driven by Hund's rule coupling rather than by the on-site Hubbard repulsion. The iron moments are largely local, driven by Hund's intra-atomic exchange. Superexchange is not operative, and the interactions between the Fe moments are considerably long range and driven mostly by one-electron energies of all occupied states.

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Ferropnictides are still attracting widespread attention from researchers both inside and outside the field of superconductivity. There is now a nearly universal agreement that magnetism and, specifically, proximity to an antiferromagnetic (AFM) “stripe-order” transition play a major role in the physics of these compounds. There is also growing evidence that the magnetic properties and correlation effects in this system are not controlled by the Hubbard U as in cuprates (spectroscopy tells us that Hubbard correlations are weak and the effective U is on the order of 1 eV,¹ smaller than the bandwidth; first-principles calculations of U support this²). On the other hand, the multiband character of Fe bands and the large intra-atomic (Hund's) exchange coupling in Fe suggest that the Hund's J may play the main role in the magnetism.

As opposed to the Hubbard U , the Hund's J is generally well accounted for in density functional theory (DFT) (where it is called the Stoner I .) Indeed, the local density approximation (LDA) correctly predicts the particular antiferromagnetic and structural ground state of undoped ferropnictides³⁻⁶ in striking contrast to the cuprates. In view of this, it is instrumental to trace down the origin of magnetism *within* LDA and to disentangle the nature of magnetic interactions captured by this approach. It is highly likely that the physics uncovered by DFT will reflect the actual physics of these systems. Given the heated discussion of whether antiferromagnetism in pnictides is due to Fermi-surface (FS) nesting or to second neighbor superexchange (see Ref. 7 for a review), a clear understanding of at least the message that LDA calculations send seems highly necessary.

In this Rapid Communication, we analyze the magnetic interactions and demonstrate that neither of the above two views (often presented as an axiomatic dilemma) is correct. The magnetism appears due to *local* Hund's rule coupling, while the particular ground state is selected by itinerant essentially one-electron interactions of which only a small part is played by the Fermi-surface nesting. We will also explain why conventional “Anderson-Kanamori” superexchange is not operative here and will show some striking examples

where calculations and experiment contradict both local superexchange and spin-Peierls pictures yet are perfectly understandable on the basis of one-electron energy balance.

We start with a qualitative analysis. The Hund's rule coupling energy in density functional theory is expressed as $E_H = -Im^2/4$, where m is the magnetization of an Fe ion and $I \approx 0.8$ eV is the Stoner factor for Fe [0.9 eV in generalized gradient approximation (GGA)]. Depending on the material, the self-consistent magnetic moment on Fe appears to be between $1.5-2\mu_B$ in LDA and $1.8-2.5$ in GGA. The corresponding energy gain even in LDA is 0.5 eV, which is remarkably large. In other words, every individual Fe wants to be strongly magnetic and the advantage of spin polarization should lead to a magnetic ground state at the mean-field level unless an unusually large kinetic energy penalty exists. However, this is exactly the case for the formation of a ferromagnetic configuration. To create a magnetization m on Fe, one needs to move approximately 1.15 (to account for the relative share of Fe- d orbitals at the Fermi level) spin-minority electrons into unoccupied spin-majority states, incurring an energy loss of $\approx (1.15m)^2/N_{\uparrow}(E_F)$. The density of states (DOS) per Fe, $N_{\uparrow}(E_F)$, varies between 1 and 1.5 eV⁻¹, depending on the system, creating an energy loss for $m = 1.5\mu_B$ of $0.5-0.8$ eV. This cost is about as large as the Hund's rule energy gain estimated above. This shows that the system is on the verge of a ferromagnetic instability but nothing more.

In low-DOS metals, magnetization without a large cost in kinetic energy is possible if some type of antiferromagnetic arrangement is formed (cf. metal Cr and Mn). For a broad band metal, this narrows the conductivity band, but as long as the exchange splitting is smaller than the bandwidth, the cost is small. Because in ferropnictides the calculated bandwidth is $5-6$ eV and the exchange splitting mI is at most 2 eV, this mechanism should be very favorable.

It is interesting to consider how the system determines which particular AFM arrangement is most profitable from the point of view of the one-electron energy (note that LDA calculations can be forced to converge to nearly any AFM

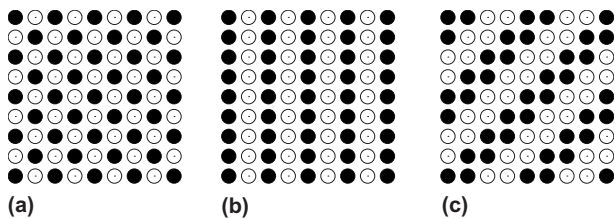


FIG. 1. Top-down view of the (a) checkerboard, (b) stripe, and (c) double-stripe magnetic patterns for a single FeAs or FeTe layer. The light colored sites have majority up spin, and the darker sites have majority down spin.

pattern but not to a ferromagnetic state). If the resulting magnetization is small, the answer is obvious: the second derivative of the total energy with respect to magnetization is defined by the noninteracting susceptibility at the AFM wave vector \mathbf{Q} , $\partial^2 E / \partial m^2 = -\chi_0^{-1}(\mathbf{Q})$ (with the small caveat that an actual spin density wave is not a single harmonic but includes all wave vectors $\mathbf{Q} + \mathbf{G}$, where \mathbf{G} is a reciprocal lattice vector). The imaginary part of χ_0 is directly related to Fermi-surface nesting being defined, in the constant matrix elements approximation, as $\sum_{ij} \int \delta(\epsilon_{\mathbf{k}_i}) \delta(\epsilon_{\mathbf{k}+\mathbf{Q},i}) d\mathbf{k}$, while the (actually relevant) real part collects information from all states and may or may not have any relation to the nesting conditions (for a detailed discussion see Ref. 8).

Geometrical nesting, as a property of the Fermi surface, becomes even more disconnected from a real instability in the strongly nonlinear regime, $m \gtrsim 1\mu_B$, which is the case for ferropnictides. Monitoring the evolution of the electronic bands with increasing spin polarization,⁹ one observes that at $m \sim 1\mu_B$ the resulting bands can in no way be described as anticrossing downfolded nonmagnetic bands with partial gapping of the Fermi surface. Rather, the entire Fe d band is fully restructured. Although the lowest-energy AFM state wave vector indeed coincides with the quasineesting wave vector in some cases, it is not always true, as exemplified by the case of FeTe that we will discuss later.

It should be noted that while quasineesting is not particularly relevant for the long-range ordering in the undoped crystals, it does define the low-energy excitations in nonmagnetic phases, and these can perfectly well mediate superconductivity.

Having established a general framework, we now address specific examples. First, we investigate checkerboard, stripe, and double-stripe magnetic structures (see Fig. 1) and show that the stripe order is lower in energy than either the checkerboard or the double-stripe structure for the 122 systems, but not for FeTe. We use the BaFe_2As_2 system as our primary example, but the results for other 122 systems and LaFeAsO are very similar. Our calculations were performed using an all-electron, full-potential linearized augmented planewave package WIEN2K, in the generalized gradient approximation, similar to Ref. 12. All structures were fully relaxed (except where stated otherwise) using the Vienna *ab initio* simulation program (VASP),¹³ with the projector augmented wave formulation¹⁴ and also using GGA. In Table I we show the magnetic stabilization energies of the three different antiferromagnetic structures.

In Figs. 2(a)–2(c), we show the DOSs for BaFe_2As_2 in

TABLE I. Stabilization energies for various magnetic configurations in the 122 and FeTe systems. All energies are per Fe atom.

	Checkerboard (meV)	Stripe (meV)	Double stripe (meV)
BaFe_2As_2	16	94	0.6
FeTe		207	230

each of the three magnetic configurations along with the nonmagnetic DOS. Compared to the nonmagnetic DOS, we see that the checkerboard pattern has a very similar spectrum at and near the Fermi energy and gains one-electron energy by shifting spectral weight from the region between -0.5 and -1.0 downward to the region between -1.0 and -2.0 . The double-stripe pattern actually incurs an energy penalty at and just below E_F but gains energy by shifting weight downward from between -0.2 and -0.7 to between -1.0 and -2.0 . The ground-state configuration, in contrast to the other two, gains energy all the way from E_F to -0.9 by shifting weight downward. This is accomplished through the opening of a large pseudogap (this terminology has no connection with the pseudogap in cuprates and simply signifies a depression in one-electron DOS around the Fermi level). Though all three magnetic configurations are stable with respect to a nonmagnetic state, it is visibly the case that the stripe ordering has the greatest one-electron energy advantage. This is reflected in the much larger gain in total energy (see Table I).

Let us now compare the results with the same calculations for FeTe. As indicated in a number of papers, FeTe is always formed with an excess Fe, so the fact that experiment gives the double-stripe structure as the low-temperature ground state¹⁵ should be taken *cum grano salis*. However, as Table I shows, it is definitely the stoichiometric ground state in density functional calculations, and this is the only thing that matters for our analysis.¹⁶ We note here that we do not fully relax the FeTe structure but only relax the internal positions. As before these relaxations are done separately for magnetic and nonmagnetic cases.

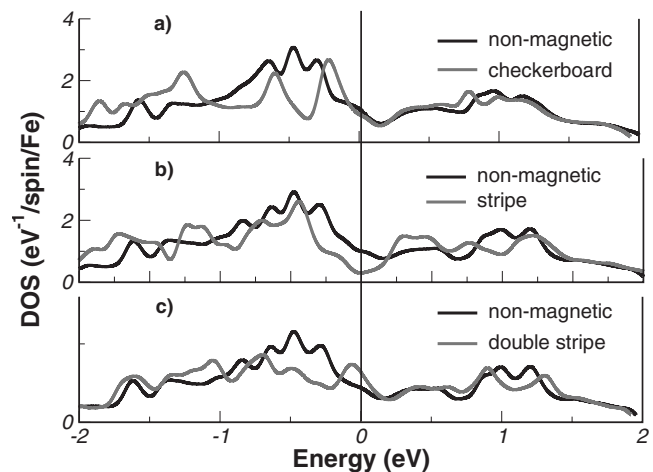


FIG. 2. The densities of states for BaFe_2As_2 in the nonmagnetic configuration in comparison to a) checkerboard magnetic pattern b) stripe (ground state) magnetic pattern and c) double-stripe magnetic pattern

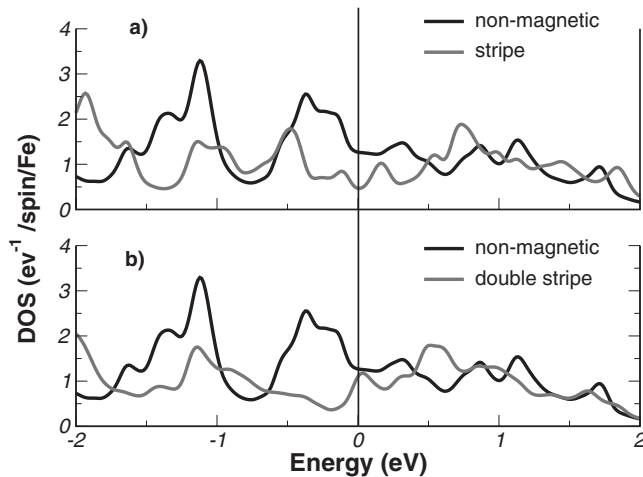


FIG. 3. The densities of states for FeTe in the nonmagnetic configuration in comparison to (a) stripe magnetic pattern and (b) double-stripe magnetic pattern.

Table I indicates that for FeTe, as opposed to BaFe_2As_2 , the energies of the single and double-stripe phases are relatively close. This suggests that the crude method of determining the ground state by looking at the DOS may not work here as the DOSs for the two AFM phases will probably be similar. Indeed, this is what we see in Figs. 3(a) and 3(b) where a large downward shift of spectral weight is visible for both patterns. Interestingly, the nonmagnetic Fermi surfaces in FeTe are extremely similar to those in the 122 and 1111 materials, whereas the nonmagnetic DOS and the magnetic electronic structure are quite different. This reinforces that FS nesting, which would be nearly identical for BaFe_2As_2 and FeTe, is not driving the magnetic order.

Our calculations also provide a strong argument against superexchange. Looking at the patterns in Fig. 1, it is easy to see that for both the stripe and double-stripe patterns, the first neighbor exchange, J_1 , does not contribute due to equal numbers of aligned and antialigned spins. The second neighbor exchange, J_2 , would have to be stronger than $J_1/2$ in order for the stripe pattern to be energetically favorable over the checkerboard pattern in a superexchange picture. It has often been argued that this situation is not unreasonable since the Fe-As-Fe paths available for J_1 and J_2 are similar. For double-stripe order in the FeTe system, however, both J_1 and J_2 cancel, leaving only J_3 to establish the ordering. Considering the remarkably strong stability (compared to nonmagnetic) calculated for double-stripe order (see Table I), this is hard to rationalize. Furthermore, the energy term for stripe is J_2J_3 (compared to J_3 alone for double stripe). For double stripe to stabilize, J_3 could be no smaller than $J_2/2$, but the “similar hopping path” is justification used for J_1 and J_2 and is not available: the third neighbor exchange path is more than twice as long as the second neighbor one and involves As-As hopping across a distance of a full lattice constant. Thus, the existence and stability of the double-stripe order severely strains the credibility of the superexchange picture. This is to be expected since superexchange is not efficient when the bandwidth is much larger than the energy cost of flipping an electron’s spin, as is the case here.

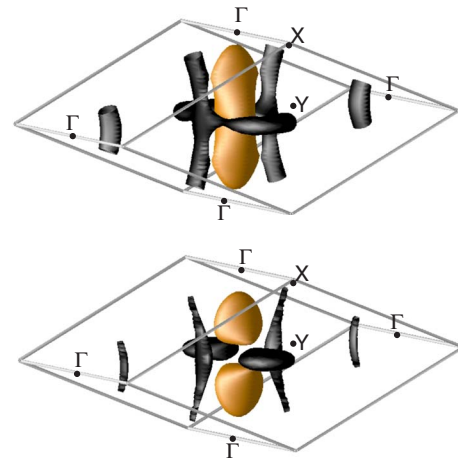


FIG. 4. (Color online) The Fermi surfaces of stripe-ordered BaFe_2As_2 . The primitive reciprocal zone with the high-symmetry directions of the conventional Brillouin zone designated. The Z point (along the c axis in real space) is in the very middle of the zone (not marked). Top panel shows the “reverse distortion” in which the Fe-Fe distance is lengthened along the like spin direction and shortened along the unlike spin direction. The bottom panels show the fully relaxed calculation (nearly the same as experiment).

This does not, however, mean that one cannot map the dependence of the total energy onto a suitable short-range exchange model. In fact, it is hard to imagine a case in which this would not be possible. Yet, in carrying out this procedure for ferropnictide systems, one should be aware of the following caveats:

(1) there is no microscopic justification (as for instance in the Hubbard model) for introducing any J - t (or J_1 - J_2 - t) Hamiltonian;

(2) there is no guarantee that this kind of mapping can be stopped at first or second neighbors. In fact, accurate calculations show that at least some of the exchange parameters in these mappings decay as $1/R^3$, just as in metal iron.¹⁰

(3) The resulting exchange parameters strongly and qualitatively depend on the long-range order established in the system. In particular, the parameters that can be used to describe the ordered state cannot be used to describe the spin fluctuations and vice versa. (see Ref. 10 and references therein.)

(4) In the absence of superexchange, there is no reason to believe that the total energy can be mapped onto a Heisenberg model, $\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$. In fact, direct calculations show that at least one biquadratic term needs to be added to map the total energy onto the mean-field Hamiltonian, $\sum K (\mathbf{S}_i \cdot \mathbf{S}_{i+1})^2$, where $K \sim J$.¹¹

We now discuss the structural transition observed simultaneously with the magnetic one in the 122 systems. Density functional calculations very accurately reproduce the experimentally observed distortion in which Fe ions along the stripe direction are closer to one another than Fe atoms belonging to adjacent stripes.^{5,6} We investigated whether the structural distortion, like the magnetic ordering, can be understood in terms of one-electron energies by calculating the DOS for a variety of small changes in the a and b lattice constants. In contrast to changing the magnetic pattern,

changing the structural distortion has very little effect on the DOS away from the Fermi energy. There were no large shifts in spectral weight to lower energies, though small shifts on the order of 0.05 eV did occur and these were within 0.5 eV of the Fermi energy. The distortion can therefore be treated as a linear perturbation with a one-electron energy lowering observable at (or very near) the Fermi energy. Specifically, we find that the lowest-energy structure corresponds to the smallest Fermi-surface area. As an example, in Fig. 4 we show the Fermi surface in the magnetic Brillouin zone of the fully relaxed (lowest-energy) structure and a “reverse distortion” in which the distances between like and unlike spins are reversed from the correct configuration. The change in the size of the Fermi surface is clearly visible. We were unable to engineer further minimization of the Fermi surface with any choice of in-plane distortions other than the optimal energy one.

In conclusion, we have shown that the relevant physics with respect to the magnetic ordering and structural distortion in the ferropnictides lies in the one-electron energies.

Our results resolve the superficially binary choice between superexchange and Fermi-surface nesting in favor of a third mechanism that is neither fully localized nor fully itinerant. One-electron energy is gained throughout an energy range of at least 1 eV below E_F , and the ground state is determined by which magnetic pattern most effectively exploits a downshift in spectral weight, not by fermiology. On the other hand, the Fermi surface itself is the operative feature for determination of the structural distortion. The energy minimum for an in-plane distortion corresponds to a simultaneous minimization of the Fermi-surface area.

Recently, we became aware of a study by Qiu *et al.*¹⁷ showing strong spin fluctuations derived from FS nesting in doped FeTe at a vector far away from the magnetic ordering vector. This is good evidence that nesting exists but does not drive the long-range magnetic order.

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