

# Microscopic origin of magnetism and magnetic interactions in ferropnictides

M.D. Johannes, I.I. Mazin

Code 6393, Naval Research Laboratory, Washington, D.C. 20375

(Dated: Printed on April 24, 2009)

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 these materials are strongly or at least moderately correlated, the electrons are considerably localized and close to a Mott-Hubbard transition, with the local magnetic moments interacting via short-range superexchange. In this paper 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.

PACS numbers: Pacs Numbers:

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 "stripe-order" transition plays 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 this[2]). 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 calculations (where it is called the Stoner  $I$ .) Indeed, the local density approximation (LDA) correctly predicts the particular antiferromagnetic and structural ground state of undoped ferropnictides, 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 density functional theory will reflect the actual physics of these systems. Given the heated (but largely devoid of solid facts) discussion of whether antiferromagnetism in pnictides is due to Fermi surface nesting or to second neighbor superexchange (See Ref. [3] for a review), a clear understanding of, at least, the message that LDA calculations send seems highly necessary.

In this paper, 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 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  $\text{eV}^{-1}$ , 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 fer-

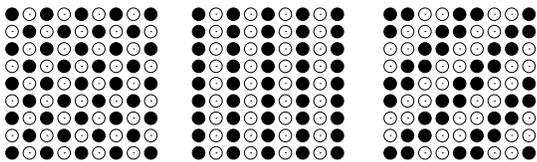


FIG. 1: (color online) Top-down view of the a) checkerboard b) stripe and c) doublestripe magnetic patterns for a single FeAs or FeTe layer. The light colored sites have majority up spin and the darker sites have majority down spin.

ropernictides 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 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 AF 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  $\chi_0$  is directly related to Fermi surface nesting, being defined, in the constant matrix elements approximation, as  $\sum_{ij} \int \delta(\varepsilon_{\mathbf{k}i}) \delta(\varepsilon_{\mathbf{k}+\mathbf{Q},j}) d\mathbf{k}$ , 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. [4]).

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[5], 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 quasi-nesting wave vector in some cases, it is not always true, as exemplified by the case of FeTe that we discuss later.

It should be noted that while quasi-nesting is not particularly relevant for the long-range ordering in the undoped crystals, it does define the low-energy excitations in non-magnetic 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

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

|                                   | checkerboard | stripe  | double stripe |
|-----------------------------------|--------------|---------|---------------|
| BaFe <sub>2</sub> As <sub>2</sub> | 16 meV       | 94 meV  | 0.6 meV       |
| FeTe                              | -            | 207 meV | 230 meV       |

structure for the 122 systems, but not for FeTe. We use BaFe<sub>2</sub>As<sub>2</sub> as an example, but the results for LaFeAsO are very similar. Our calculations were performed using an all-electron, full-potential LAPW package WIEN2k, in the Generalized Gradient Approximation, similar to Ref. [8]. All structures were fully relaxed (except where stated otherwise) using the Vienna Ab-Initio Simulation Program (VASP) [9], with the PAW formulation [10] and also using GGA. In Table 1 we show the magnetic stabilization energies of the three different antiferromagnetic structures.

In Fig. 2a,b,c, we show the DOSs for BaFe<sub>2</sub>As<sub>2</sub> in 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 doublestripe 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 state [11] should be taken *cum grano salis*. However, as Table 1 shows, it is definitely the stoichiometric ground state in density functional calculations, and this is the only thing that matters for our analysis [12]. 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.

Table I indicates that for FeTe, as opposed to BaFe<sub>2</sub>As<sub>2</sub>, the energies of the single and double stripe

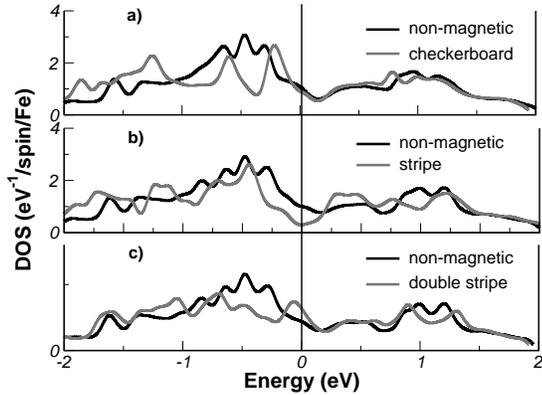


FIG. 2: (color online) The densities of states for  $\text{BaFe}_2\text{As}_2$  in the non-magnetic configuration in comparison to a) checkerboard magnetic pattern b) stripe (ground state) magnetic pattern and c) double stripe magnetic pattern

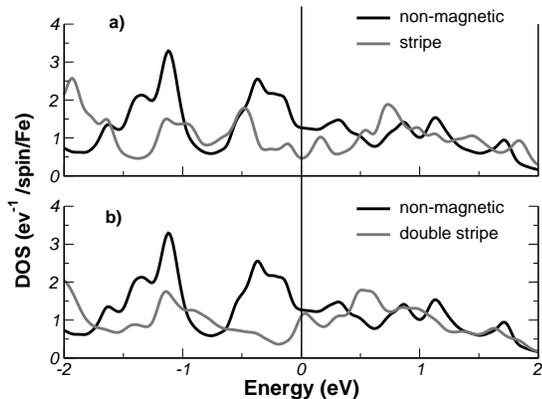


FIG. 3: (color online) The densities of states for  $\text{FeTe}$  in the non-magnetic configuration in comparison to a) stripe magnetic pattern and b) double stripe magnetic pattern.

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 Fig. 3a,b where a large downward shift of spectral weight is visible for both patterns. Interestingly, the nonmagnetic Fermi surfaces in  $\text{FeTe}$  are extremely similar to those in the 122 and 1111 materials, whereas nonmagnetic DOS and the magnetic electronic structure are quite different. This reinforces that FS nesting, which would be nearly identical for  $\text{BaFe}_2\text{As}_2$  and  $\text{FeTe}$ , 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 anti-aligned 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  $\text{FeTe}$  system, however, both  $J_1$  and  $J_2$  cancel, leaving only  $J_3$  to establish the ordering. Considering the remarkably strong stability (compared to non-magnetic) calculated for double stripe order (See Table I), this is hard to rationalize. Furthermore, the energy term for stripe is  $J_2 - J_3$  (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 paths" 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, in fact, to be expected since superexchange is not efficient when the bandwidth is much larger than the energy cost of flipping an electron's spin, which is precisely the case here.

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[6].
- (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. [6] 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  $K \sim J$ . [7]

We now switch our attention to the structural transition observed simultaneously with the magnetic one in the 122 systems. Density functional calculations very accurately reproduce the experimentally observed distor-

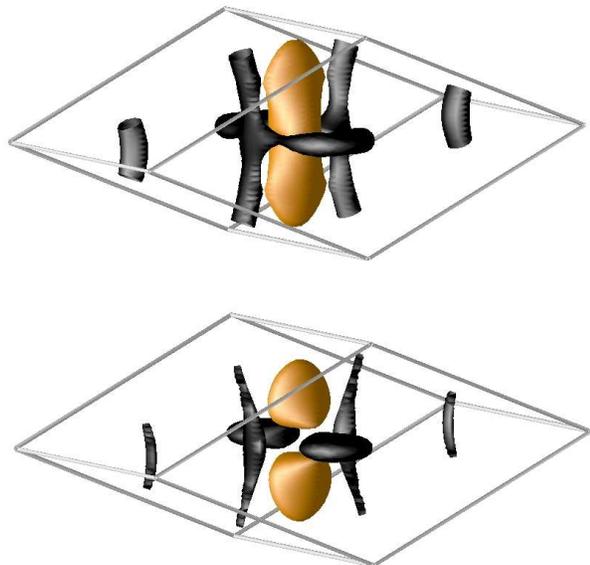


FIG. 4: The Fermi surfaces of stripe-ordered  $\text{BaFe}_2\text{As}_2$ . Top panel shows the 'reverse distortion' in which the Fe-Fe distance is lengthened along the like spin direction and shortened along the unlike spin direction. The bottom panels shows the fully relaxed calculation which reproduces the experimentally observed distortion (to within a few percent).

tion in which Fe ions along the stripe direction are closer to one another than Fe atoms belong to adjacent stripes [13, 14]. 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 of spectral weight to lower energies, though small shifts of the order of 0.05 eV did occur and these were within 0.5 eV of the Fermi energy (for comparison see the heavy restructuring of the DOS in Figs. 2 and 3). 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 a 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.

We thank H. Eschrig, K. Koepernik and T. Yildirim for useful and engaging discussions related to this work. We acknowledge funding from the Office of Naval Research.

- 
- [1] T. Kroll, S. Bonhommeau, T. Kachel, H.A. Duerr, J. Werner, G. Behr, A.Koitzsch, R. Huebel, S. Leger, R. Schoenfelder, A. Ariffin, R. Manzke, F.M.F. de Groot, J. Fink, H. Eschrig, B. Buechner, M. Knupfer, Phys. Rev. B **78**, 220502 (2008); F. Bondino, E. Magnano, M. Malvestuto, F. Parmigiani, M. A. McGuire, A. S. Sefat, B. C. Sales, R. Jin, D. Mandrus, E. W. Plummer, D. J. Singh, N. Mannella; Phys. Rev. Lett. **101**, 267001 (2008); E. Z. Kurmaev, R. G. Wilks, A. Moewes, N. A. Skorikov, Yu. A. Izyumov, L. D. Finkelstein, R. H. Li, X. H. Chen, Phys. Rev. B **78**, 220503(R) (2008); V. I. Anisimov, E. Z. Kurmaev, A. Moewes, I. A. Izyumov, Physica C (Special Issue), to be published; T.D. Devereaux et al, to be published.
  - [2] V. I. Anisimov, Dm. M. Korotin, M. A. Korotin, A. V. Kozhevnikov, J. Kuneš, A. O. Shorikov, S. L. Skornyakov, S. V. Streltsov, J. Phys.: Condens. Matter **21**, 075602 (2009); T. Miyake, L. Pourovskii, V. Vildosola, S. Biermann, A. Georges, J. Phys. Soc. Jpn. **77**, Supplement C, 99 (2008).
  - [3] I.I. Mazin and J. Schmalian, Physica C (Special Issue), to be published.
  - [4] M.D. Johannes and I.I. Mazin, Phys. Rev. **B77**, 16535 (2008).
  - [5] M.A. Korotin, S.V. Streltsov, A.O. Shorikov, and V.I. Anisimov, JETP **107**, 649 (2008).
  - [6] K.D. Belashchenko, V.P. Antropov, Phys. Rev. **B78**, 212505 (2008); T. Yildirim, Physica C (Special Issue), to be published.
  - [7] A. N. Yaresko, G.-Q. Liu, V. N. Antonov, O.K. Andersen, arXiv:0810.4469.
  - [8] I. I. Mazin, M. D. Johannes, L. Boeri, K. Koepernik, D. J. Singh, Phys. Rev. **B78**, 085104 (2008).
  - [9] G. Kresse, J. Furthmuller, Phys. Rev. B **54**, 169 (1996).
  - [10] P. E. Blochl, Phys. Rev. B **50**, 953 (1994).
  - [11] S. Li, C. de la Cruz, Q. Huang, Y. Chen, J.W. Lynn, J. Hu, Y-L. Huang, F-C. Hsu, K-W. Yeh, M-K. Wu, P. Dai, Phys. Rev. B **79**, 054503 (2009).
  - [12] We are interested in how the double stripe structure manifests in stoichiometric FeTe within LDA. We can-

not make meaningful comparisons with experiment and we therefore do not fully relax the FeTe structure, but only relax the internal positions. As before, relaxations are done separately for magnetic and nonmagnetic cases. We also neglect the checkerboard case as being of only secondary interest for this system.

[13] T. Yildirim, arXiv:0805.2888 (2008).

[14] A. Jesche, N. Caroca-Canales, H. Rosner, H. Borrmann, A. Ormeci, D. Kasinathan, K. Kaneko, H. H. Klauss, H. Luetkens, R. Khasanov, A. Amato, A. Hoser, C. Krellner, C. Geibel, Phys. Rev. B **78**, 180504R (2008)