Solid State Communications 150 (2010) 62–65

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Is the nature of magnetic order in copper-oxides and in iron-pnictides different?

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ARTICLE INFO

Article history:
Received 9 July 2009
Received in revised form
11 September 2009
Accepted 5 October 2009 by S. Miyashita
Available online 8 October 2009

PACS:
75.10.-b
74.25.Ha
74.25.Jb

Keywords:
A. Magnetically ordered materials
D. Electronic band structure
D. Exchange and superexchange

ABSTRACT

We use the results of first-principles electronic structure calculations and a strong coupling perturbation approach, together with general theoretical arguments, to illustrate the differences in super-exchange interactions between the copper-oxides and iron-pnictides. We provide a possible explanation for the two magnetic ground states within the same theoretical foundation. Contrary to the emerging view that magnetic order in the iron-pnictides is of itinerant nature, we argue that the observed magnetic moment is small because of frustration introduced by the electrons of the Fe orbitals as they compete to impose their preferred magnetic ordering.

1. Introduction

The copper-oxide layers present in the high-Tc superconducting families are turned into superconductors by introducing dopants that create electrons or holes in these otherwise antiferromagnetic (AF) insulating layers [1]. The proximity of antiferromagnetism to superconductivity has led to the general view that this form of magnetic order is intimately related to the mechanism of superconductivity in these materials [2]. In the recently discovered iron-pnictide-based superconductors [3–8], which exhibit superconductivity at relatively high-Tc, the copper-oxide layer is replaced by an iron-pnictide layer. Interest in the new materials, reminiscent of that seen when the cuprates were discovered more than two decades ago, is due to the fact that many unsuccessful attempts were made to replace the copper-oxide layer in high-Tc materials to facilitate practical applications. The parent compounds of these iron-pnictide materials, like the copper-oxide parent materials, show a spin-density-wave order [9,10] illustrated in Fig. 1(a). Unlike the copper-oxides, the parent compounds in the iron-pnictides, such as the pure LaOFeAs, are metallic, but are magnetically ordered and non-superconducting and they become superconductors by doping with electrons or holes. The copper-oxide parent compounds are well described as spin-1/2 Heisenberg quantum antiferromagnets [2]. Furthermore, it is widely believed that superconductivity in copper-oxides arises when, by doping the quantum antiferromagnet, the carriers (holes or electrons) form a strongly correlated Anderson–Mott-type system with the spin–spin correlations playing a fundamental role in the superconductivity mechanism. After the discovery of the iron-pnictide superconductors, there is an emerging view that the magnetism in these compounds is of itinerant type [11–17] and that these systems are different from the cuprates and in fact weakly correlated. This is an important issue to settle, because any further theoretical analysis of other properties of this new family of materials, including the still unknown superconductivity mechanism, depends on it.

Here we focus on this issue and seek a broader framework to reconcile the different forms of magnetic order and to explain the magnetic properties in both families of materials with the same approach. Our arguments are inspired by the results of Ref. [18], where first-principles electronic structure calculations based on density functional theory (DFT) were combined with a strong coupling expansion to obtain an effective low-energy Hamiltonian which describes the electrons occupying the five Fe orbitals. The values of the on-site coupling repulsion on the Fe d-orbitals as well as the other parameters, such as hopping matrix elements and spin-exchange interactions, differ depending on the first-principles calculation employed [19–21] and, thus, there is no clear

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doi:10.1016/j.ssc.2009.10.005

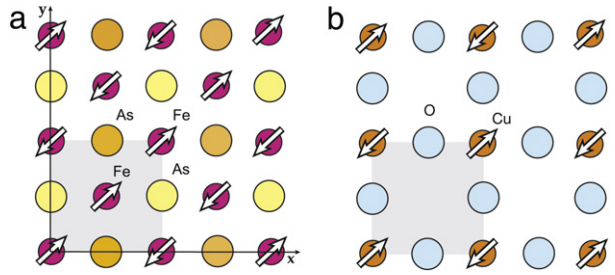

Fig. 1. (a) The spin-density-wave order (columnar antiferromagnetic) as observed by neutron diffraction. The Fe magnetic moments along the (1, 1) direction are aligned, while two nearest neighboring such chains are antiferromagnetically aligned. (b) The familiar antiferromagnetic ordering of the cuprous-oxides. The shaded square denotes the unit cell. With the mapping Fe → Cu, As → O, the CuO_2 unit cell differs from the Fe_2As_2 one by a magnetic atom missing from the center.

justification for the application of the strong coupling expansion. In the present work, however, we address the nature of the magnetic order in the iron-pnictide and the copper-oxide-based materials using a more general scheme based on symmetry arguments, which may be qualitatively correct independently of the conditions of validity and the details of the calculation presented in Ref. [18]. We show that the origin and nature of magnetism in these two families of materials is the same and both families should be treated within the same theoretical foundation. Specifically, if Mott physics is operative in the copper-oxides it should also be operative in the iron-pnictides, and if the magnetism in the copper-oxides is of the Anderson–Mott type it should be of the same type in these newly discovered materials.

2. Spin interaction in copper-oxides and iron-pnictides

First, we discuss the difference in the structure and magnetic order between the iron-pnictide layer and the copper-oxide layer as shown in Fig. 1. By removing the "extra" magnetic ion (i.e., Fe) from the center of the square unit cell of the iron-pnictide layer we obtain not only the same structure, but identical magnetic order with the copper-oxide layer. The only important difference, which will be addressed below, is that the magnitude of the observed magnetic moment [9] per Fe site is significantly reduced from its calculated value [11,22–24].

Fig. 2 schematically illustrates the qualitative origin of the well-known Anderson super-exchange interaction. These types of processes give rise to a super-exchange contribution to the spin-exchange interaction, $J_\nu^{(1)}$, between two electrons occupying two nearest neighbor (NN), or $J_\nu^{(2)}$, between two next nearest neighbor (NNN) Fe orbitals of a given flavor (where ν labels the five Fe or Cu d-orbitals: x^2-y^2, xz, yz, or z^2). The effective spin–spin interaction Hamiltonian for a particular flavor ν is:

$$\hat{H}_\nu = J_\nu^{(1)} \sum_{<ij>} \mathbf{S}_{i,\nu} \cdot \mathbf{S}_{j,\nu} + J_\nu^{(2)} \sum_{\ll ij \gg} \mathbf{S}_{i,\nu} \cdot \mathbf{S}_{j,\nu}, \quad (1)$$

where the $\mathbf{S}_i$ is a three component vector of a spin-1/2 quantum spin operator and $< ij >$ and $\ll ij \gg$ stand for NN and NNN pairs of magnetic ion sites. Here we have assumed that the particular Fe d-orbital is singly occupied. The case in which an orbital is occupied by two electrons is discussed separately. Other models in the literature, as in Refs. [25,22,23], are similar to ours with the very important difference that our Hamiltonian, Eq. (1), treats differently the various Fe d-orbitals labeled by ν. The condition for quantum- Néel (checkerboard) ordering (shown in Fig. 5(b)) is

$$J_\nu^{(1)} > 2J_\nu^{(2)}; \quad (2)$$

if the coupling between spins of electrons occupying the orbital ν do not satisfy the above condition, the SDW order of Fig. 1(a) is energetically favorable against the checkerboard order (Fig. 5(b)).

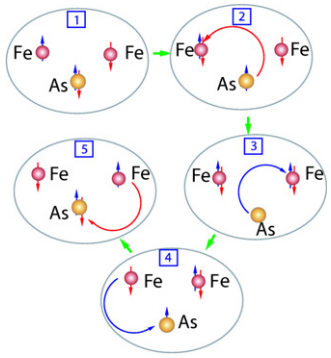

Fig. 2. Super-exchange between two nearest neighbor (NN) or next nearest neighbor (NNN) Fe atoms through electron-hopping (hybridization) process between any Fe d-orbital and any p or s orbital of an intervening As atom. One of the As spin-up electrons (shown as red) hops to a singly occupied Fe d-orbital (process 2), then the spin-down electron (shown as blue) from the same As orbital hops to a NN or NNN Fe d-orbital (process 3). With two successive hops (processes 4 and 5) the other electrons that were initially occupying the same two Fe d states, hop to the same As site, restoring its doubly occupied status. The initial configuration 1 differs from the final configuration 5 by the spin orientation on the two Fe orbitals. Such processes lead to AF spin–spin interaction between electron spins occupying any two d-orbitals belonging to NN or NNN Fe atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

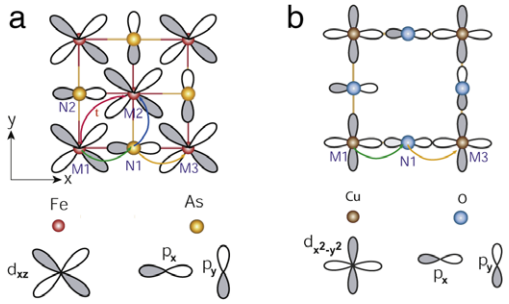

Fig. 3. (a) An example of the paths that contribute to the spin-exchange interactions $J_\nu^{(1)}$ and $J_\nu^{(2)}$ between NN and NNN Fe atoms for $\nu = d_{xz}$ and through the p_x or p_y orbital of the intervening non-magnetic As atoms. (i) Contributions to $J_\nu^{(1)}$ of the NN Fe atoms indicated as M1 and M2: First, there is a contribution from direct hopping t between the magnetic ions as shown by the red path. Second, there is the super-exchange through the p_x or p_y orbital (only the p_x is drawn) of the intervening As atom N1 or N2. One of these is shown by the green–blue path. (ii) Contributions to $J_\nu^{(2)}$ for the NNN magnetic atoms M1 and M3 through the p_x or p_y orbital of the intervening As atom N1 shown as a green–yellow path. (b) The corresponding situation for the copper-oxide layer: There is no corresponding M2 magnetic atom and the spin–spin interaction between the NN Cu atoms M1 and M3 for this case occurs through the hybridization of the $d_{x^2-y^2}$ orbital of the Cu atom M1 or M3 and the p_x orbital of the intervening O atom N1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

By fitting the first-principles electronic structure results to a tight-binding model, we have established that, with the exception of the $d_{x^2-y^2}$ orbital, for any given Fe d-orbital, there is only one orbital of the intervening As (of s or p mixed character) with which the hybridization amplitude is most significant. Therefore, the most significant super-exchange processes involve the same intervening As orbital for both of the exchanged electrons. The super-exchange process illustrated in Fig. 2 requires four steps because two electrons, each occupying one of the two NN or NNN magnetic (Fe) ions, need to move through hopping to the intervening non-magnetic ion (As) and, thus, each electron has to make two steps. To obtain the total spin–spin interactions we need to consider also the direct hopping of electrons between these two neighboring Fe or Cu d-orbitals. The results of Ref. [18] show that

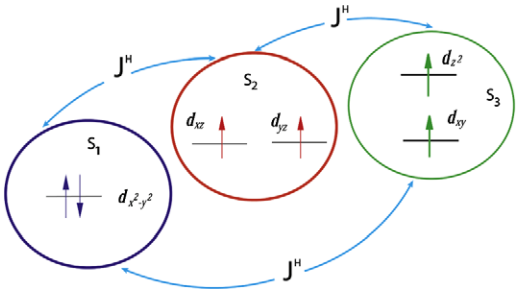

Fig. 4. The Hilbert space of the five Fe d-orbitals is divided into three subspaces (S_1 spanned by $d_{x^2-y^2}$, S_2 spanned by d_{xz}, d_{yz}, and S_3 spanned by d_{xy}, d_{z^2}). These subspaces are coupled through Hund's rule coupling J^H which is indicated by the blue arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

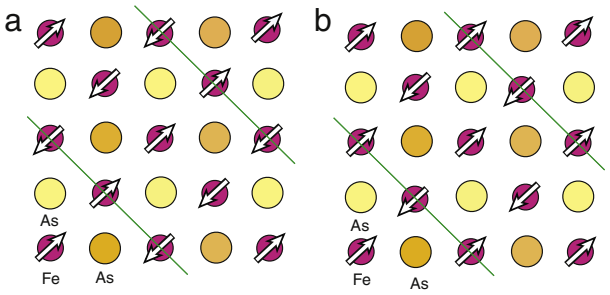

Fig. 5. (a) Illustration of the observed columnar AF order in the undoped iron-pnictides. This state is strongly favored by the S_2 subspace (spanned by d_{xz}, d_{yz}). (b) Illustration of the familiar checkerboard Néel ordering which is preferred by the S_1 subspace (spanned by $d_{x^2-y^2}$) and by the S_3 subspace (spanned by d_{xy}, d_{z^2}). Notice that the magnetic moments of the Fe atoms along the green lines are frustrated because their orientations in case (a) are opposite to their orientations in case (b).

the direct hopping matrix element between two NN Fe d-orbitals, indicated as t in Fig. 3, is smaller but not negligible. In the case of copper-oxides this direct process is non-applicable because two NN Cu atoms correspond to NNN Fe atoms in the Fe-pnictides.

Fig. 3 illustrates paths that give rise to the most significant contribution to $J_\nu^{(1)}$ and $J_\nu^{(2)}$, and compares the super-exchange interactions between the iron-pnictide layer and the copper-oxide layer through the intervening non-magnetic As or O atom respectively. For example, for iron-pnictides, $J_{xz}^{(1)}$ has two contributions: (i) one from the direct hopping t_{xz} between two NN Fe d_{xz} orbitals, (shown as the red path in Fig. 3), and (ii) a super-exchange contribution due to processes such as the one illustrated by the combined green–blue path in Fig. 3. The hybridization V_{xz}^x of the d_{xz} orbital of the Fe atom M1 and the p_x orbital of the As atom N1 is very large (∼1.4 eV), while its hybridization V_{xz}^y with the p_y orbital of the same atom N1 is negligible (∼0.1 eV). The reverse is true for the hybridization of the same Fe d-orbital with the p_x and p_y orbitals of atom in position N2 because of the 90° *relative orientation*. The contribution to $J_{xz}^{(1)}$ due to the green–red process illustrated in Fig. 4 is proportional to

$$J_{xz}^{(1)} \sim (V_{xz}^x V_{xz}^y)^2. \tag{3}$$

On the other hand, the contribution to $J_{xz}^{(2)}$ due to the green–yellow process illustrated in Fig. 4 is proportional to

$$J_{xz}^{(2)} \sim (V_{xz}^x)^4. \tag{4}$$

Therefore, $J_{xz}^{(1)}/J_{xz}^{(2)} \sim (V_{xz}^y/V_{xz}^x)^2 \sim 0.01$ and the super-exchange contribution to $J_{xz}^{(1)}$ is negligible as compared to that of $J_{xz}^{(2)}$ between NNN Fe atoms. Hence, we can conclude that in the subspace formed by d_{xz} and d_{yz}, $J_{xz}^{(1)}$ has contributions mainly through direct hopping while $J_\nu^{(2)}$ has significant super-exchange contributions similar to the copper-oxide case, as shown in Fig. 3(b).

On the other hand, the NN spin–spin interaction $J_\nu^{(1)}$, involving the other three Fe d-orbitals (yz,xy, or z^2), has contributions from super-exchange processes in which the intervening As orbital is the sp_z (a linear combination of the As 4s and $4p_z$). In these processes the magnitude of the hybridization of the yz, xy, or z^2 Fe d-orbitals with the sp_z-As orbital *does not change* with a 90° rotation which necessarily occurs in the red–green path. Therefore, for these three orbitals, $J_\nu^{(1)}$ is significantly larger than $J_\nu^{(2)}$, which implies that the condition (2) for checkerboard order is fulfilled.

3. Frustration and small local moment

Fig. 4 illustrates the fact that the Hilbert space spanned by all the Fe d-orbitals can be separated into three subspaces: S_1 spanned by $d_{x^2-y^2}$, S_2 spanned by (d_{xz}, d_{yz}), and S_3 spanned by (d_{xy}, d_{z^2}). These subspaces are mainly coupled through Hund's rule coupling J^H which tends to align the spins of the unpaired d electrons in the same Fe atom:

$$\hat{H} = \sum_{\nu=1}^{5} \hat{H}_\nu - J^H \sum_{i,\nu\neq\nu'} \mathbf{S}_{i,\nu} \cdot \mathbf{S}_{i,\nu'}. \tag{5}$$

The NN AF couplings $J_\nu^{(1)}$ in the subspaces S_1 and S_3 are greater than the NNN AF couplings $J_\nu^{(2)}$; however, in the subspace S_2 the NNN AF coupling $J_{xz}^{(2)}$ (and $J_{yz}^{(2)}$) is large, that is, the condition (2) is not satisfied for the arguments presented above. As a result the subspace S_2 alone prefers the observed SDW state illustrated in Fig. 5(a), while the other two subspaces prefer the checkerboard-type quantum-Néel order shown in Fig. 5(b). These two competing orders create a magnetic frustration illustrated in Fig. 5. Namely, in the two ordered states illustrated in Fig. 5, the magnetic moments of the electrons on the iron atoms along the alternating green lines in Fig. 5 are opposite. Hund's rule coupling, which is significantly stronger that the AF coupling between NN and NNN atoms, forces the electrons on these different subspaces to choose a common spin orientation. However, any such global choice within the same atom will minimize the energy in one subspace and at the same time frustrate the other subspaces as discussed in the caption of Fig. 5. In the case of the undoped material where there are six electrons occupying the five Fe d-orbitals, the S_1 subspace has zero spin; hence, the S_2 subspace competes with the S_3 subspace (which prefers the checkerboard AF order) only and because $J_{xz}^{(2)}$ is larger than the AF couplings in S_3, it imposes the observed SDW state. The local magnetic moment is expected to be small due to this frustration. As discussed in Ref. [26] the model of Eq. (5), for the case of two orbitals in which one is dominated by the NN AF coupling while the second is dominated by the NNN AF coupling, has a phase diagram with four different phases: (a) a region of the parameters where the (π, π) order is energetically favorable, (b) another region where the $(0, \pi)$ order is favored, (c) a region where a canted phase exists, and (d) a disordered phase. In particular, when the strength of the NN coupling is approximately twice the strength NNN coupling, the local moment associated with the sublattice magnetization should either be significantly reduced or the canted phase is preferred and in the limit of large Hund's rule coupling, the sublattice magnetization can be even zero. Therefore, the present analysis gives a natural explanation

for the observed small magnitude of the magnetic moment [9], while the calculations based on the itinerant picture [11,12,22–24] produce values for the Fe magnetic moment greater than $2\mu_B$.

From this analysis, we have shown that the different ordering in the iron-pnictides and copper-oxides can be understood within the same theoretical foundation. The observed small Fe magnetic moment arises from the fact that only the electrons occupying the subspace spanned by d_{xz}, d_{yz} prefer the observed SDW order (Fig. 5(a)), while the electrons occupying the other three Fe orbitals prefer a checkerboard ordering (Fig. 5(b)). This creates frustration and gives rise to large zero-point spin fluctuations. It was demonstrated in Ref. [26] that these frustrating effects lead to a significantly reduced local moment in agreement with neutron scattering experiments. The undoped Fe-pnictides are metallic and this fact has been used to argue that these are itinerant antiferromagnets. However, while the nature of the (π, π) order is to frustrate hole or electron motion, the $(\pi, 0)$ order does not frustrate the carrier motion along the direction in which the spins are aligned. Therefore, even at the undoped level, and in the strong coupling limit we expect the $(\pi, 0)$ order to be metallic.

Acknowledgements

We have benefited from discussions with C. Xu, E. Demler, S. Sachdev and B.I. Halperin.

References

[1] D. Vaknin, et al., Phys. Rev. Lett. 58 (1987) 2802–2805.
[2] E. Manousakis, Rev. Modern Phys. 63 (1) (1991).
[3] Y. Kamihara, et al., J. Am. Chem. Soc. 128 (2006) 10012.
[4] Y. Kamihara, et al., J. Am. Chem. Soc. 130 (2008) 3296.
[5] Z.A. Ren, et al., Chin. Phys. Lett. 25 (2008) 2215.
[6] X.H. Chen, et al., Nature 453 (2008) 761.
[7] G.F. Chen, et al., Phys. Rev. Lett. 100 (2008) 247002.
[8] H.H. Wen, et al., Europhys. Lett. 82 (2008) 17009.
[9] C. de La Cruz, et al., Nature 453 (2008) 899.
[10] H.-H. Klauss, et al., Phys. Rev. Lett. 101 (2008) 077005.
[11] D.J. Singh, M.-H. Du, Phys. Rev. Lett. 100 (2008) 237003.
[12] C. Cao, et al., Phys. Rev. B 77 (2008) 220506.
[13] S. Raghu, et al., Phys. Rev. B 77 (2008) 220503.
[14] I.I. Mazin, D.J. Singh, M.D. Du, Phys. Rev. Lett. 101 (2008) 057003.
[15] F. Wang, et al. arXiv:0805.3343 and arXiv:0807.0498.
[16] A.V. Chubukov, D.V. Efrenov, I. Eremin, Phys. Rev. B 78 (2008) 134512.
[17] K. Kuroki, S. Onari, H. Usui, Y. Tanaka, H. Kontani, H. Aoki, Phys. Rev. Lett. 101 (2008) 087004.
[18] E. Manousakis, J. Ren, S. Meng, E. Kaxiras, Phys. Rev. B. 78 (2008) 205112.
[19] K. Nakamura, R. Arita, M. Imada, J. Phys. Soc. Japan 77 (2008) 093711.
[20] V.I. Anisimov, Dm M. Korotin, M.A. Korotin, A.V. Kozhevnikov, J. Kunes, A.O. Shorikov, S.L. Skornyakov, S.V. Streltsov, J. Phys.: Condens. Matter 21 (2009) 075602.
[21] V. Vildosola, L. Pourovskii, R. Arita, S. Biermann, A. Georges, Phys. Rev. B 78 (2008) 064518.
[22] T. Yildirim, Phys. Rev. Lett. 101 (2008) 057010.
[23] F. Ma, et al. arXiv:0804.3370v2.
[24] K. Haule, J.H. Shim, G. Kotliar, Phys. Rev. Lett. 100 (2008) 226402.
[25] C. Xu, M. Mueller, S. Sachdev, Phys. Rev. B 77 (R) (2008) 020501.
[26] E. Manousakis, Phys. Rev. B 79 (R) (2009) 220509.