Magnetic softness in iron-based superconductors

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Abstract
We examine the relevance of several major material-dependent parameters to the magnetic softness in iron-based superconductors by means of first-principles electronic structure analysis of their parent compounds. The results are explained in the spin-fermion model where localized spins and orbitally degenerate itinerant electrons coexist and are coupled by Hund’s rule coupling. We found that the difference in strength of the Hund’s rule coupling term is the major material-dependent microscopic parameter for determining the ground-state spin pattern. The magnetic softness in iron-based superconductors is essentially driven by the competition between the double-exchange ferromagnetism and the superexchange antiferromagnetism.

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, high transition-temperature ($T_c$) superconductivity has been observed in a number of doped iron-based layer materials [1–4] near a static antiferromagnetic (AF) order [5–9] and with a spin resonance [10–12], a pattern exhibited previously by the layered cuprate high-$T_c$ superconductors. It has been generally believed that strong spin fluctuations in two-dimensional (2D) space is at the heart of the high-$T_c$ mechanism. A proper understanding of the magnetism in parent undoped materials thus becomes an essential first step towards understanding the high-$T_c$ mechanism. The undoped cuprates are universally described by the 2D Heisenberg model. The key character of this model is that a novel resonating-valence-bond spin-liquid state competes fiercely with the traditional Néel spin-solid state for being the ground state [13], a situation referred to as magnetic softness. Magnetic softness becomes even more apparent in the parent compounds of iron-based superconductors (FeSCs), since different ground-state AF spin patterns are truly realized—‘collinear’ C-type in iron pnictides (e.g., LaOFeAs and BaFe$_2$As$_2$ [5, 6]) and ‘bicollinear’ E-type in iron chalcogenides (e.g., FeTe$_{1-x}$Se$_x$ [7, 8]), as illustrated in figure 1—despite apparent similarity in crystal and electronic structures. To elucidate its nature, it is necessary to first identify what material-dependent parameter drives the difference in the magnetic pattern; this knowledge will put stringent constraints on minimum theoretical modeling of FeSCs.

In literature, the anion height from the iron plane ($z_{anion}$) and the ordered magnetic moment ($m$) have been considered as major material-dependent parameters [16, 17], since neutron diffraction experiments reported $z_{anion} = 1.31, 1.35,$ and 1.73 Å and $m = 0.36, 0.87,$ and 1.70 µB in LaOFeAs, BaFe$_2$As$_2$, and FeTe, respectively [5–8]. First-principles studies qualitatively reproduced these observations [18, 19] and further revealed that the C–E magnetic transition can be induced by tuning $z_{anion}$ in FeTe$_{1-x}$Se$_x$ [20]. Since varying $z_{anion}$ also varies $m$, it is unclear whether it is $m$ or something else that determines the C–E transition. Another interesting scenario is that the difference in the orbital ordering pattern determines the ground-state magnetic pattern: one of the initially degenerate Fe $d_{xz}$ and $d_{yz}$ orbitals gets more populated than the other in the C-type pnictides [21–24], and Fe $d_{yz} = (d_{xz} - d_{yz})/\sqrt{2}$ orbital was stipulated to be more populated than $d_{xz} = (d_{xz} + d_{yz})/\sqrt{2}$ in the E-type FeTe [25]. While the former was verified by first-principles calculations [22], the latter remains untested.

The purpose of this paper is to examine the relevance of $z_{anion}$, $m$, and orbital order to the magnetic softness in
2. First-principles analysis

We performed first-principles calculations in local spin-density approximation of density functional theory with full potential, all-electron, linearized augmented plane wave basis implemented in the WIEN2k software package [33]. We adopted an eight-Fe-atom unit cell for all the calculations and the $10 \times 10 \times 8$ mesh of $k$ points. The energy convergence is better than 1 meV per Fe atom.

In figure 2, we compare the total energies of the C-type and E-type AF states in BaFe$_2$As$_2$. First, the effect of $z_{\text{ion}}$ was investigated. Like in FeTe$_{1-x}$Se$_x$ [20], increasing $z_{\text{ion}}$ in BaFe$_2$As$_2$ also increases $m$ and drives the magnetic transition from C to E around $z_{\text{ion}} = 1.6$ Å. Then, to isolate the effect of $m$ from $z_{\text{ion}}$, we fixed $z_{\text{ion}}$ at the experimental position of 1.35 Å [2] and varied $m$ using the fixed-spin-moment method. We found that varying $m$ alone cannot drive the C–E transition.

To examine a possible orbital order in the E type, we performed first-principles Wannier function analysis [22, 34] on FeTe and got the following Fe density matrix:

$$
\begin{pmatrix}
3z^2 - r^2 & x^2 - y^2 & yz & xz & xy \\
3z^2 - r^2 & 1.44 & 0.00 & -0.04 & -0.04 & 0.03 \\
x^2 - y^2 & 0.00 & 1.31 & 0.04 & -0.04 & 0.00 \\
yz & -0.04 & 0.04 & 1.05 & 0.01 & 0.05 \\
xz & -0.04 & -0.04 & 0.01 & 1.05 & 0.05 \\
xy & 0.03 & 0.00 & 0.05 & 0.05 & 1.13
\end{pmatrix}
$$

where the $x$ and $y$ axes point to the nearest-neighbor (NN) Fe atoms. To compare with the orbital ordering pattern proposed in [25], the coordinate system needs to be rotated by 45° in
the Fe plane. The resulting density matrix is rewritten as

\[
\begin{pmatrix}
3z^2 - r^2 & 1.44 & 0.00 & 0.00 & -0.057 & 0.03 \\
XY & 0.00 & 1.31 & -0.057 & 0.00 & 0.00 \\
YZ & 0.00 & -0.057 & 1.04 & 0.00 & 0.00 \\
XZ & -0.057 & 0.00 & 0.00 & 1.06 & 0.071 \\
X^2 - Y^2 & 0.03 & 0.00 & 0.00 & 0.071 & 1.13 \\
\end{pmatrix}
\]

where the X and Y axes point to the next-nearest-neighbor (NNN) Fe atoms. Apparently, orbital polarization within the XZ and YZ orbitals is negligible. Therefore, site orbital ordering is not the driving force for the E-type spin order in FeTe.

Below we explain these results using the spin-fermion model that was shown to be capable of providing a unified picture for magnetic correlation and electronic transport in the parent compounds of FeSCs [14, 35, 36].

### 3. The spin-fermion model

The electrons in the degenerate Fe 3d_{xz} and 3d_{yz} orbitals are treated as itinerant electrons, and those in the rest Fe 3d orbitals as effective localized spins. This leads to an effective two-orbital double-exchange model [14, 26, 27]:

\[
H = \sum_{ij \gamma' \mu' \mu} \left( t_{ij}^{\gamma' \gamma} C_{ij \mu}^\dagger C_{ij' \mu'} + h.c. \right) - K \sum_{ij} \bar{\sigma}_{\mu \mu'} C_{ij \mu}^\dagger \bar{\sigma}_{\mu' \mu} C_{ij' \mu'} + \sum_i J_i \bar{S}_i \cdot \bar{S}_i, \tag{1}
\]

where \( C_{ij \mu}^\dagger \) 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, \( \bar{\sigma}_{\mu \mu'} \) is the Pauli matrix and \( \bar{S}_i \) is the localized spin whose magnitude is \( S \). \( K \) is the effective Hund’s rule coupling. \( J_i \) is the AF superexchange couplings between the localized orbitals; in particular, \( J \) and \( J' \) are respectively the NN and NNN ones. The filling of the itinerant electrons is on average \( n_\gamma \). The spin-fermion model is effective on average over the Fe-As-Fe plaquette, hybridizations via the Fe–As–Fe path give rise to comparable NN and NNN parameters.

To get a general and simple picture about the magnetic ordering of the model, we considered a variety of static spin orders, such as the ferromagnetic (FM) state and the AF states of C-type, E-type, and G-type (i.e., the Néel state where all NN spins are antiparallel), with the localized spins treated as Ising spins [14, 37]. Then, equation (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 \( \bar{S}_i \), respectively.

The resulting phase diagram of the model is presented in figure 3. Changing the spin moment \( S \) will lead to changing both \( KS \) and \( J'S^2 \). This direction of change, as marked by the red ray in figure 3, will not induce the C–E transition. On the other hand, we argued that changing \( z_{\text{anion}} \) corresponds to changing \( KS \), as marked by the black ray in figure 3: 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 effective Hund’s rule coupling term and suppress the nonlocal parameters \( t_{ij} \); therefore, \( J_iS^2 \) as a whole is much less material dependent than \( KS \). Hence, the effective Hund’s rule coupling term is decisive in determining the ground-state magnetic pattern. (Note that the enhancement of the on-site Coulomb and Hund’s rule interaction terms by increasing \( z_{\text{anion}} \) were also found in the Hubbard model of the 10-fold Fe 3d bands for FeSCs [38].) The results of the spin-fermion model agree well with those from first-principles presented in figure 2.

The Hund’s rule coupling brings in a blockade mechanism: the electron hopping to a neighboring site with opposite spin orientation suffers from the energy barrier whose height is of order of \( KS \). Hence, the larger \( KS \) is, the more likely the neighboring spins are aligned to the same direction. This is the so-called double-exchange ferromagnetism [31, 32], which has been studied intensively and extensively in the context of manganites for their colossal magnetoresistance phenomenon. In addition, comparable \( J \) and \( J' \) between the localized spins favor the C type. Hence, FeSCs contain intrinsic competition between the double-exchange ferromagnetism and the C-type superexchange antiferromagnetism in the localized-spins sector. The E type emerges in the intermediate regime as a compromise.

This model also reproduces the weak orbital polarization within the \( xz \) and \( yz \) (or \( XZ \) and \( YZ \)) orbitals in the E type because (i) the on-site occupation numbers are always the same in both the \( xz \) and \( yz \) orbitals in the E type from symmetry consideration, and (ii) the parameters that can mix these two orbitals to polarize in the \( XZ \) and \( YZ \) representation are negligibly small.
4. Discussion

The double-exchange ferromagnetism was employed in the previous proposal that the metallic bcc(110) antiferromagnetism in FeTe was driven by a site orbital ordering [25]. However, the double-exchange effect was treated as being secondary to the YZ ferro-orbital order and the AF spin order along the Y direction; it was used to introduce weak FM ordering of those AF Y chains along the X direction. This way actually decoupled the whole Fe planar lattice into two interpenetrating sublattices with each one exhibiting the C-type AF order on its own. This means that the NN exchange coupling strength is weak. On the contrary, in the spin-fermion model equation (1) for the E-type FeTe $K_S \simeq 0.8$ eV is the leading energy scale; to gain Hund’s rule energy is so important that the NN Fe–Fe bonding along the zigzag FM chain (see figure 1) is strong. This means that if one has to fit the magnetic energy surface of FeTe to the Heisenberg model, the resulting NN exchange coupling on average is strong and FM, in agreement with neutron scatter data on FeTe [39].

The spin-fermion model equation (1) appears in form similar to that used to describe the manganites. These two classes of materials do share some common features, such as magnetic softness and large normal-state resistivity. We emphasize two differences between FeSCs and manganites. Firstly, the Jahn–Teller distortion energy in FeSCs [22] is one order of magnitude smaller than in manganites [34] because the layered structure of edge-sharing anion tetrahedra surrounding Fe atoms is much less flexible than the network of corner-sharing octahedra surrounding Mn atoms. As a result, unlike in the manganites where the orbital degree of freedom is often frozen into an orbital order via the cooperative Jahn–Teller effect, there lacks such a locking mechanism in FeSCs. A small change in $K_S$ could lead to a dramatic change in the orbital order status and thus would substantially affect the fit to the Heisenberg model. In fact, neutron scattering data on Ca$_{2}$Fe$_{2}$As$_{2}$ [40] and FeTe [39] reported that the C and E types were surprisingly well separated in the Heisenberg model parameter space, with the leading NN exchange interaction being AF and FM, respectively. This implies that while the Heisenberg model is still reasonable for describing magnetic linear response near one particular ground state, it cannot capture the essential orbital physics and is problematic for describing the general magnetic softness in FeSCs. Secondly, $K_S \simeq 2$ eV in manganites is much larger, driving the system into the FM regime, as shown in figure 3. With a moderate $K_S$, FeSCs are located near the C–E phase boundary and the FM phase becomes an irrelevant high-energy state, providing a necessary environment for the formation of singlet superconductivity where the paired electrons have opposite spins.

Regarding superconductivity, this magnetic softness is actually a two-blade sword. On the one hand, with its strong ability to undertake electronic reconstruction, the system may on the one hand manage to efficiently screen direct electron–electron Coulomb interaction and generate appropriate bosonic excitations to glue electron pairs in order to form superconductivity. The magnetic softness also implies a large scattering rate for electron transport and the observed large resistivity in the normal state. This is a favorable feature, according to Home’s law that $T_c$ is proportional to both the superfluid density and the normal-state resistivity [41]. On the other hand, a too correlated system may find ways to satisfy the competing non-superconducting players first. For example, the $C_x E_{1-x}$ region, a mixed C-type and E-type AF, could be formed in accord with the change in doping level [15, 42]. Only until none of these players can be adequately satisfied could superconductivity show up to relieve the high entropy—likely with a low superfluid density. While the high-$T_c$ mechanism of superconductivity in both FeSCs and cuprates remains to be discovered, the present results suggest that FeSCs, though closer kin to the manganites than the cuprates in terms of their magnetism, can exhibit a quantum phase transition to superconductivity instead of ferromagnetism.

5. Summary

We examine the relevance of the anion height from the iron plan, the ordered magnetic moment, and the orbital ordering pattern to the magnetic softness in iron-base superconductors by first-principles electronic structure analysis of their parent compounds. We conclude that the anion height is an effective tuning parameter and the magnetic moment alone is not, while a site orbital order is absent in the E-type and present in the C-type AF states. These results are shown to be compatible with a recently proposed spin-fermion model where localized spins and orbitally degenerate itinerant electrons coexist and are coupled by Hund’s rule coupling. This implies that the difference in the strength of the Hund’s rule coupling term is the major material-dependent microscopic parameter for determining the ground-state spin pattern, and that the magnetic softness in iron-based superconductors is essentially driven by the competition between the double-exchange ferromagnetism and the superexchange antiferromagnetism.

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