Effect of hybridization on structural and magnetic properties of iron-based superconductors

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Abstract. We show that the strong hybridization between the iron 3d and the arsenic 4p orbitals, in the newly discovered iron-based high-$T_c$ superconductors, leads to an explanation of certain experimental observations that are presently not well understood. The existence of a lattice distortion, the smallness of the Fe magnetic moment in the undoped systems, and the suppression of both the lattice distortion and the magnetic order upon doping with fluorine, are all shown to result from this hybridization. We show that, as a result of hybridization, a tetragonal-to-orthorhombic distortion lowers the electronic energy of the Fe ions. The ground state of the Fe ions is shown to be a mixture of five states, four of which have zero magnetic moment, causing a large reduction in the average value of the magnetic moment per Fe site.

An interesting development occurred recently with the discovery of a new class of layered, iron-based, high temperature superconductors. Kamihara \textit{et al} \cite{1} reported a superconducting transition temperature $T_c = 26$ K in fluorine-doped LaFeAsO, and $T_c$ increased under pressure to 43 K \cite{2}. Replacement of lanthanum with other rare earth elements gave a series of superconducting compounds ReFeAsO$_{1-x}$F$_x$, where Re = Ce, Pr, Nd, or Sm, with transition temperatures close to or exceeding 50 K \cite{3}--\cite{6}. Oxygen-deficient samples were also fabricated and found to superconduct at 55 K \cite{7}. The parent compound, ReFeAsO, has a tetragonal unit cell with two ReFeAsO molecules, and it consists of a stack of alternating ReO and FeAs layers. The FeAs layer, in reality, consists of a square planar sheet of Fe atoms sandwiched between two sheets of As atoms, such that each Fe atom is tetrahedrally coordinated with four As atoms.

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Certain facts that emerged from neutron scattering measurements are not well understood:

1. A tetragonal-to-orthorhombic structural phase transition takes place in the undoped system at $T_S \sim 150 \text{ K}$, below which an antiferromagnetic (AFM) order is established [8]–[11]. It was suggested [12] that the tetragonal-to-orthorhombic distortion results from magnetic frustration. However, the magnetic order occurs more than 20 K below $T_S$ in LaFeAsO and PrFeAsO [8, 14], casting doubt on such an interpretation.

2. The measured magnetic moment of Fe is very small, $\sim 0.4–0.8 \mu_B$ [8]–[11], whereas calculations based on density functional theory (DFT) give $\sim 2 \mu_B$ [13]–[16].

3. It is observed that upon replacing a small fraction of the oxygen atoms in the ReO layer by fluorine atoms, the tetragonal-to-orthorhombic distortion is gradually suppressed, along with the AFM order [8]–[11].

In this paper, we present a scheme within which the above observations may be explained. It is based on the consequences of the strong hybridization between the Fe 3d and the As 4p orbitals. On the one hand, this hybridization gives rise to superexchange between different Fe atoms, leading to the establishment of the AFM order. On the other hand, the hybridization will have a strong effect on the states of any given Fe atom; it is this effect that we explore here, and show that it offers an explanation of the above observations.

In the tetragonal phase, and in the absence of hybridization, the crystal field at a given Fe site, produced by the four surrounding As ions, has $S_4$ symmetry, and it splits the otherwise degenerate Fe 3d levels into three nondegenerate levels and one doubly degenerate level [16] as shown in figure 1(a). Since DFT calculations indicate that an Fe site has a total spin 1, the six 3d electrons are taken to occupy orbitals as shown in figure 1; this occupation scheme was also suggested by Li [17] and Baskaran [18]. Another possible spin arrangement corresponding to $S = 2$ on the Fe site was also considered by Si and Abrahams [19]. Following Li [17], we assume that the energy splitting produced by the crystal field is sufficiently large to neglect the filled $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals and the empty $3d_{z^2-y^2}$ orbital in discussing the low energy behavior. A tetragonal-to-orthorhombic lattice distortion will lift the remaining degeneracy, and assuming that the lattice constant $a$ is larger than $b$, the energy level scheme of the d orbitals will be as shown in figure 1(b). If in figure 1(a) we set $\epsilon_{d_{xz}} = \epsilon_{d_{yz}} = \epsilon$, then in figure 1(b) we have $\epsilon_{d_{xz}} = \epsilon - \Delta \equiv \epsilon_1$ and $\epsilon_{d_{yz}} = \epsilon + \Delta \equiv \epsilon_2$. We consider a system comprising an Fe atom and

Figure 1. The occupation scheme of the Fe 3d levels in the (a) tetragonal and (b) orthorhombic structures of ReFeAsO, where Re is a lanthanide.
Figure 2. The state $|1\rangle$ along with the other four states that can be reached from it through hybridization of the Fe 3d and the As 4p orbitals.

an adjacent As atom, for which the Hamiltonian may be expressed as

$$H = H_0 + H', \quad H_0 = H_d + H_p,\tag{1}$$

$$H' = \sum_{\sigma} \alpha c_{p\sigma}^\dagger c_{d\sigma,\sigma} + \sum_{\sigma} \beta c_{p\sigma}^\dagger c_{d\sigma,\sigma} + \text{H.C.}\tag{2}$$

Here $H_d$ and $H_p$ are the Hamiltonians for the Fe and As atoms, respectively, $c_{p\sigma}^\dagger$ ($c_{p\sigma}$) is the creation (annihilation) operator for an electron in the As 4p orbital with spin $\sigma$, $c_{d\sigma,\sigma}^\dagger$ ($c_{d\sigma,\sigma}$) creates (annihilates) an electron with spin $\sigma$ in the Fe 3d orbital, with a similar definition applying to $c_{d\sigma,\sigma}^\dagger$ ($c_{d\sigma,\sigma}$), $\alpha$ and $\beta$ are hopping matrix elements, taken for simplicity to be constant and real, and H.C. stands for Hermitian conjugates of the first two terms in $H'$. The terms in $H'$ express the hybridization between the Fe 3d orbitals and the As 4p orbitals, in the form of electron hopping between these orbitals. We note that there is no need to consider the s states on the Fe sites; DFT calculations [20] indicate that states near the Fermi energy are dominated by contributions from the Fe 3d states. We also note that the model Hamiltonian considered here is, in essence, a simplified version of the Anderson model [21].

The states shown in figure 1 are eigenstates of $H_0$, but not $H$. Nonvanishing matrix elements connect the state $|1\rangle$ to other states shown in figure 2. State $|2\rangle$ can be reached from $|1\rangle$ by the spin-up electron in Fe 3d$_{yz}$ hopping to the As ion, followed by a spin-down electron hopping from the As ion to the Fe 3d$_{xz}$ orbital. Alternatively, a spin-down electron may hop first from the As ion to the Fe 3d$_{xz}$ orbital, followed by the electron in the Fe 3d$_{yz}$ orbital hopping to the As ion. The ground state of the Fe atom is now obtained by diagonalizing the Hamiltonian matrix in the subspace spanned by these five states.

The Hamiltonian is projected onto this five-dimensional subspace by a canonical transformation

$$H_T = e^{-S}He^S$$

$$= H + [H, S] + \frac{1}{2}[[H, S], S] + \cdots$$

$$= H_0 + H' + [H_0, S] + [H', S] + \frac{1}{2}[[H_0, S], S].\tag{3}$$

Choosing the operator $S$ such that $[H_0, S] = -H'$, and keeping terms to second order in $H'$, we obtain

$$H_T = H_0 + H_{\text{eff}},\tag{4}$$
where $H_{\text{eff}} = \frac{1}{2}[H', S]$. The matrix elements of $H'_{\text{eff}}$, connecting eigenstates of $H_0$, are given by
\[
\langle n | H'_{\text{eff}} | m \rangle = \frac{1}{2} \langle n | H'S - SH' | m \rangle = \frac{1}{2} \sum_k \left[ \langle n | H'| k \rangle \langle k | S | m \rangle - \langle n | S | k \rangle \langle k | H'| m \rangle \right].
\] (5)

Using $H' = -[H_0, S]$, we obtain
\[
\langle k | H'| m \rangle = \langle k | SH_0 | m \rangle - \langle k | H_0 S | m \rangle = (E_m - E_k) \langle k | S | m \rangle.
\] (6)

It follows that
\[
\langle k | S | m \rangle = \frac{\langle k | H'| m \rangle}{E_m - E_k}.
\] (7)

The matrix elements of $H'_{\text{eff}}$ may thus be written as
\[
\langle n | H'_{\text{eff}} | m \rangle = \frac{1}{2} \sum_k \left( \frac{1}{E_m - E_k} + \frac{1}{E_n - E_k} \right) H'_{nk} H'_{km}.
\] (8)

The eigenstates $| m \rangle$ of $H_0$ are in fact composite states comprising the $3d_{xz}$ and $3d_{yz}$ orbitals of the Fe atom, along with the $4p$ orbitals of As. We carried out DFT calculations on undoped LaFeAsO, along with Bader’s atoms in molecules (AIM) theory [23], and found that As has a charge of $-0.92e$ and Fe has a charge of $0.30e$, where $e$ is the charge of the proton. The charge transferred from LaO to the FeAs layer resides mainly on the As $4p_z$ orbital, which has an energy much lower than that of the As $4p_x$, or $4p_y$ orbital. Furthermore, by examining the projected density of states (PDOS) reported by Cao et al [16], we see that the DOS at the Fermi level is dominated by the Fe $3d_{xz}$ and $3d_{yz}$ states, while the DOS of the As p states has three peaks: one peak, which results from filled $4p_z$ bands, is 3–4 eV below the Fermi energy $E_F$, and two other peaks, one being about 0.5 eV below and the other 1 eV above $E_F$; these two peaks result from the $4p_x$ and $4p_y$ orbitals. Since there are two As atoms per unit cell, we can assume that there are two occupied $4p_z$ bands, 3–4 eV below $E_F$, two occupied bands with mixed $4p_x$ and $4p_y$ character, ~0.5 eV below $E_F$, and another two empty bands with mixed $4p_x$ and $4p_y$ character, ~1 eV above $E_F$. Considering any single As ion, we may assume that it has four electrons in the $4p$ orbitals, two of which occupy the $4p_z$ orbital, and the other two electrons occupy an orbital with mixed $4p_x$ and $4p_y$ character which, for convenience, we simply call p, and there is an empty orbital, also with mixed $4p_x$ and $4p_y$ character which we call p’. We ignore the filled, low energy $4p_z$ orbital, and we describe the state of the As atom by the occupation of the p and p’ orbitals. The eigenstates $|1\rangle$ and $|2\rangle$ of $H_0$ are written explicitly as
\[
|1\rangle = |\text{Fe; } d_{xz,\uparrow}, d_{yz,\uparrow} \rangle |\text{As; } p_{\uparrow}, p'_{\uparrow} \rangle.
\] (9)
\[
|2\rangle = |\text{Fe; } d_{xz,\downarrow}, d_{yz,\downarrow} \rangle |\text{As; } p_{\uparrow}, p'_{\downarrow} \rangle.
\] (10)

Note that $|2\rangle$ differs from $|1\rangle$ by having both d electrons in the $d_{xz}$ orbital and by a spin flip in the As p orbitals. In order to construct the matrix element $\langle 2 | H'_{\text{eff}} | 1 \rangle$ we need the intermediate states $|k\rangle$. As discussed earlier there are two such states,
\[
|k_1\rangle = |\text{Fe; } d_{xz,\uparrow} \rangle |\text{As; } p_{\uparrow,\downarrow}, p'_{\uparrow} \rangle,
\] (11)
\[
|k_2\rangle = |\text{Fe; } d_{xz} \uparrow, d_{yz} \uparrow \rangle |\text{As; } p_{\uparrow} \rangle.
\] (12)
Because of the onsite Coulomb repulsion on the d orbital, the state $|k_2\rangle$ has much higher energy than $|k_1\rangle$, and it will be ignored. We can then write

$$
(2|H'_{\text{eff}}|1) = 4 \times \frac{1}{2} \left[ \frac{1}{\epsilon_2 - \epsilon_{p'}} - J + \frac{1}{\epsilon_1 - \epsilon_p} \right] \alpha \beta = \gamma,
$$

(13)

where $J$ is the Hund’s exchange term in the d orbitals, $\epsilon_p$ ($\epsilon_{p'}$) is the energy of an electron in a p (p') orbital on the As atom, and Hund’s exchange term in the As 4p orbitals is ignored. The factor of 4 results from the fact that an electron on the Fe atom can hop to any of the four surrounding As atoms. In a similar way, we can construct the remaining matrix elements and diagonalize the Hamiltonian in the five-dimensional subspace spanned by the states $|1\rangle, \ldots, |5\rangle$.

It should be pointed out that the five states considered all have $S_z = 1$ and $S_z = -1$, so that our space will be ten-dimensional. However, since $H_{\text{eff}}$ does not change $S_z$, the $10 \times 10$ Hamiltonian matrix will split into two identical $5 \times 5$ blocks; consequently, the eigenvalues are not affected by such an enlargement of space. Nor is the expectation value of the magnitude of the magnetic moment on the Fe site affected. Moreover, in the antiferromagnetic phase, there is a spontaneous local breaking of time reversal symmetry [22]. Hence, we restrict our space to that spanned by the five states $|1\rangle$ to $|5\rangle$.

Needless to say, the expressions for the eigenvalues and eigenvectors of the $5 \times 5$ matrix are unwieldy. Instead, we diagonalize the matrix in the two-dimensional subspace spanned by $|1\rangle$ and $|2\rangle$, draw the necessary conclusions, and then extrapolate to the more general case.

Thus, assuming for the time being that only states $|1\rangle$ and $|2\rangle$ are mixed by the Hamiltonian, and noting that $(1|H_T|1) = \epsilon_1 + \epsilon_2 - J - 2\epsilon_p$ and $(2|H_T|2) = 2\epsilon_1 + \epsilon_p + \epsilon_{p'}$ we can express $H_T$ by a $2 \times 2$ matrix

$$
\begin{pmatrix}
\epsilon_1 + \epsilon_2 - J + 2\epsilon_p & \gamma \\
\gamma & 2\epsilon_1 + \epsilon_p + \epsilon_{p'}
\end{pmatrix}.
$$

The ground state energy is now given by the lower of the two eigenvalues of the $H_T$ matrix

$$
E_{gs} = \epsilon_1 + \epsilon_p + \frac{1}{2}(\epsilon_1 + \epsilon_2 + \epsilon_{p'} + \epsilon_{p'} - J) - \frac{1}{2} \sqrt{(\epsilon_1 - \epsilon_2 + \epsilon_{p'} - \epsilon_p + J)^2 + 4|\gamma|^2}
$$

(14)

and $E_{gs}$ is lower than the energy $E_1$ of state $|1\rangle$ by $\delta E$ given by

$$
\delta E = E_{gs} - E_1 = \frac{1}{2}((J - 2\Delta + 2\Delta_p) - \sqrt{(J - 2\Delta + 2\Delta_p)^2 + 4|\gamma|^2}),
$$

(15)

where $2\Delta_p = \epsilon_{p'} - \epsilon_p$. The unperturbed energy $E_1 = \epsilon_1 + \epsilon_2 - J + 2\epsilon_p = 2\epsilon + 2\epsilon_p - J$ is the same in both the tetragonal and orthorhombic phases, but $\delta E$ does depend on the crystalline phase. Since $\gamma$ depends only weakly on $\Delta$, we have

$$
\delta E_{\text{ortho}}^{(\text{e})} - \delta E_{\text{tetra}}^{(\text{e})} = \delta E(\Delta) - \delta E(\Delta = 0) = -\Delta - \frac{1}{2} \sqrt{(J - 2\Delta + 2\Delta_p)^2 + 4|\gamma|^2} + \frac{1}{2} \sqrt{(J + 2\Delta_p)^2 + 4|\gamma|^2} < 0,
$$

(16)

where the superscript ‘e’ stands for ‘electronic’. The above expression is negative for all values of $J$, $\Delta$ and $\gamma$. From our earlier discussion, we may take $\epsilon_d - \epsilon_p \sim 0.5$ eV, $\epsilon_d - \epsilon_{p'} \sim -1$ eV,
2\Delta_p \sim 1.5 \text{ eV}. The parameters $J$, $\alpha$, and $\beta$ are all estimated to be in the range $\sim$0.7–1 eV \cite{16, 17}; this gives $\gamma \sim 1.5$–3 eV. The above expression then reduces to

$$\delta E_{\text{ortho}}^{(e)} - \delta E_{\text{tetra}}^{(e)} = -\Delta \left( 1 - \frac{J + 2\Delta_p}{\sqrt{(J + 2\Delta_p)^2 + 4\gamma^2}} \right) + \mathcal{O}(\Delta^2),$$

which is negative. We thus conclude that a tetragonal-to-orthorhombic distortion lowers the electronic energy of the d state by a term proportional to $\Delta$ (ignoring the $\Delta^2$ term, being smaller than the linear term). The distortion takes place by a small increase in the lattice constant $a$ and a corresponding decrease in lattice constant $b$. Assuming this small distortion is $\delta x$, then $\Delta$ is proportional to $\delta x$, and we can write $\delta E^{(e)} = \xi \delta x$, where $\xi$ is some constant. On the other hand, this distortion raises the elastic energy by an amount $\delta E^L = \eta(\delta x)^2$, where $\eta$ is some constant. The value of the distortion $\delta x$ is found by minimizing

$$\delta E^{\text{total}} = \delta E^{(e)} + \delta E^L = -\xi \delta x + \eta(\delta x)^2$$

giving $\delta x = \xi/2\eta$ and $\delta E^{\text{total}} = -\xi^2/4\eta$. What we have just shown is that the hybridization between the Fe 3d states and As 4p states causes a greater downward shift in energy if the crystal distorts from tetragonal to orthorhombic, and seeking the lowest energy available, the crystal will indeed undergo such a distortion.

The qualitative results obtained so far remain unchanged. Qualitatively, the ground state will be a mixture of five states, in four of which the magnitude of the magnetic moment is zero. Therefore, we expect a further reduction in the expectation value of the Fe magnetic moment.

The ground state eigenket is obtained from the eigenvector corresponding to the ground state energy,

$$|\psi_{gs}\rangle = c_1|1\rangle + c_2|2\rangle,$$

where

$$\left| \frac{c_2}{c_1} \right| = \frac{1}{2|\gamma|} \left[ \sqrt{(J + 2\Delta_p - 2\Delta)^2 + 4\gamma^2} - (J + 2\Delta_p - 2\Delta) \right].$$

Using the values of the parameters given earlier, we find $|c_2/c_1|$ in the range $\sim$0.5–0.7. In the ground state the expectation value of the magnitude of the magnetic moment of the Fe atom is

$$\langle \mu \rangle = |c_1|^2 \langle \mu \rangle_1 + |c_2|^2 \langle \mu \rangle_2.$$

Since $\langle \mu \rangle_2$, the magnitude of the magnetic moment in state $|2\rangle$, is zero, it follows that $\langle \mu \rangle \sim 0.7\langle \mu \rangle_1$. In other words, the hybridization causes a large reduction in the value of the would be magnetic moment. We may now consider the mixing of all the states shown in figure 2.

The qualitative results obtained so far remain unchanged. Qualitatively, the ground state will be a mixture of five states, in four of which the magnitude of the magnetic moment is zero. Therefore, we expect a further reduction in the expectation value of the Fe magnetic moment. In fact we do not need to restrict ourselves to these states; we may also consider mixing with states where one electron resides on the $d_{x^2-y^2}$ orbital. All this leads to the conclusion that strong hybridization between the Fe 3d and As 4p orbitals causes a reduction in the measured value of the Fe magnetic moment, in agreement with neutron scattering measurements \cite{8}–\cite{11}.

We now consider what happens as some oxygen atoms are replaced by fluorine atoms. Fluorine doping causes further negative charge transfer from the ReO/Flayer to the As atoms, since it involves replacing $O^{2-}$ with $F^-$. This strengthens the ionic bond and shortens the distance between the Re and As ions. Indeed, neutron scattering measurements \cite{8} indicate that the La–As separation decreases by 0.03 Å upon F-doping, with a concomitant reduction in the
c-lattice constant. But the extra charge, donated by the Re ions, is not uniformly spread among the As ions; more of this charge resides on As ions close to the F atoms, rather than on those further away, and some local distortion of the As ion positions is expected. With such distortion, and with an uneven charge distribution on the As ions, the crystal field at a given Fe site now has a symmetry lower than $S_4$. Considering a single Fe atom, the Hamiltonian is written as $H_0 + V$, where $H_0$ contains the part of the crystal field with $S_4$ symmetry, while $V$ is the additional part which lowers that symmetry. The orbitals Fe $3d_{xz}$ and $3d_{yz}$ are eigenstates of $H_0$ but not $H$; the perturbation $V$ mixes these two states. Let $\langle 3d_{xz}|V|3d_{xz}\rangle = V_{11}$, $\langle 3d_{yz}|V|3d_{yz}\rangle = V_{22}$ and $\langle 3d_{xz}|V|3d_{yz}\rangle = V_{12}$; these matrix elements are proportional to the F-dopant concentration.

Then the energy splitting $2\Delta$ of the two states is given by

$$2\Delta = \sqrt{(V_{11} - V_{22})^2 + 4V_{12}^2} \quad (22)$$

and the two new split states $|a\rangle$ and $|b\rangle$ are linear combinations of $|3d_{xz}\rangle$ and $|3d_{yz}\rangle$. As the F dopant concentration increases, the energy splitting increases, and if $2\Delta$ becomes larger than $J$, the contribution of state $|2\rangle$, shown in figure 2, to the ground state wavefunction becomes dominant, and the Fe magnetic moment becomes very small, causing the magnetic order to be suppressed.

If the fluorine concentration is $x$, then in the ReO/F layer, every position in the O/F plane is occupied by a fluorine atom with probability $x$ and by an oxygen atom with probability $1-x$. The overall symmetry of the crystal structure, as seen in x-ray measurements, is still tetragonal with symmetry group P4/nmm. The instantaneous potential seen by an electron depends on the ionic positions and is given by

$$V = V_s + \sum_k (\partial V/\partial Q_k) Q_k + \cdots, \quad (23)$$

where $V_s$ is the static part of the potential, $Q_k$ is a lattice normal coordinate, and because of the invariance of $V$ under the crystal symmetry group, $\partial V/\partial Q_k$ transforms according to the same irreducible representation as $Q_k$. Since in the presence of F doping, the Fe electronic orbitals $|i\rangle$ are nondegenerate, then $|i\rangle|\partial V/\partial Q_k|i\rangle$ vanishes unless $\partial V/\partial Q_k$ is totally symmetric under the crystal symmetry group operations. It follows that any spontaneous distortion that occurs must be totally symmetric and will not lower the crystal symmetry. Hence, F doping suppresses the tetragonal-to-orthorhombic distortion.

It is worthwhile to note that the ideas presented in this work may also be applicable to the doping of magnetic ions in 122 pnictide family. Very recently, it has been demonstrated that cobalt substitution in SrFe$_2$As$_2$, to yield SrFe$_{2-x}$Co$_x$As$_2$, causes a rapid decrease in the tetragonal-to-orthorhombic transition temperature, followed by the onset of bulk superconductivity [24]. The doping of Co introduces additional electrons into the FeAs layer, and is thus expected to produce an effect similar to fluorine doping in LaFeAsO. Again we may argue that Co doping in the 122 family distorts the crystal field symmetry at the Fe site and lifts the degeneracy of $3d_{xz}$ and $3d_{yz}$ orbitals, causing a suppression of the structural and spin density wave (SDW) transitions.

In conclusion, we have shown that strong hybridization between the Fe 3d orbitals and the As 4p orbitals introduces some interesting effects. In the undoped systems, it causes a larger downward shift in the electronic energy if the crystal undergoes a tetragonal-to-orthorhombic distortion which lifts the degeneracy of the Fe $3d_{xz}$ and $3d_{yz}$ levels. The ground state, in the presence of hybridization, is found to be a mixture of states, most of them with zero Fe magnetic moment.
moment, so that in this ground state the expectation value of the magnitude of the Fe magnetic
moment is small. We have also argued that the symmetry lowering caused by fluorine doping
suppresses both the lattice distortion and the magnetic order of the Fe moments. Finally, we
note that although the mechanism for superconductivity in the iron-based superconductors is
not understood yet, we believe that the spin fluctuations on the Fe sites, caused by hybridization
between the Fe 3d and the As 4p states, may play a role not only in suppressing the magnetic
order but also in the emergence of superconductivity in these compounds.

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