Antiferromagnetic superexchange interactions in LaOFeAs

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From first-principles calculations, we have studied the electronic and magnetic structures of the ground state of LaOFeAs. The Fe spins are found to be collinear antiferromagnetic ordered, resulting from the interplay between the strong nearest and next-nearest neighbor superexchange and antiferromagnetic interactions. The structure transition observed by neutron scattering is shown to be magnetically driven. Our study suggests that the antiferromagnetic fluctuation plays an important role in the Fe-based superconductors. This sheds light on the understanding of the pairing mechanism in these materials.

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Recently an iron-based material LaOFeAs was reported to show superconductivity with a transition temperature \( T_c \sim 26\text{K} \) by partial substitution of O with F atoms\textsuperscript{[1]}. Soon after, other families of Fe-As oxyselenides with La replaced by Sm\textsuperscript{[2]}, Ce\textsuperscript{[3]}, Pr\textsuperscript{[4]} and other rare earth elements were found superconducting with \( T_c \) more than 50K. Like cuprates, these iron arsenides have a layered structure. The superconducting pairing is believed to happen in the iron-based FeAs layers. The high transition temperature and the preliminary band structure calculation suggests that the superconductivity in these Fe-arsenide superconductors is not mediated by electron-phonon interaction. It is commonly believed that the understanding of electronic structures of the parent compound LaOFeAs is the key to determine the underlying mechanism to make it superconducting upon doping.

The early band structure calculations suggested that the pure LaOFeAs compound is a nonmagnetic metal but with strong ferromagnetic or antiferromagnetic (AFM) instability \textsuperscript{[5,6,7,8,9,10,11,12]}. Later, it was found that the antiferromagnetically ordered state\textsuperscript{[8,9]} has a lower energy than the nonmagnetic one, probably due to the Fermi surface nesting\textsuperscript{[8]}. Dong et al.\textsuperscript{[10]} predicted that the AFM state should form a collinear-striped structure by breaking the rotational symmetry. This collinear ordered AFM state has been experimentally determined\textsuperscript{[11,12]}.

In this paper, we report the theoretical result on the electronic and magnetic structures of the ground state of LaOFeAs obtained from first-principles band structure calculations. We find that there are strong nearest and next-nearest neighbor superexchange interactions in this material (similar conclusion was obtained by Yildirim\textsuperscript{[13]}). The nearest and next nearest neighbor superexchange interactions have almost the same amplitude within error of calculation. Their competition affects strongly the electronic structure of the ground state. This drives a small monoclinic lattice distortion and a collinear ordering of Fe spins, as observed by neutron scattering.

In our calculations the plane wave basis method was used\textsuperscript{[14]}. We adopted the local (spin) density approximation and the generalized gradient approximation of Perdew-Burke-Ernzerhof\textsuperscript{[15]} for the exchange-correlation potentials. The ultrasoft pseudopotentials\textsuperscript{[16]} were used to model the electron-ion interactions. After the full convergence test, the kinetic energy cut-off and the charge density cut-off of the plane wave basis were chosen to be 600eV and 4800eV, respectively. The Gaussian broadening technique was used and a mesh of \( 16 \times 16 \times 8 \) k-points were sampled for the Brillouin-zone integration. LaOFeAs has a tetragonal layered structure with \( P4/nmm \) symmetry. A crystal unit cell consists of eight atoms with alternating FeAs and LaO layers along the c axis. In the calculation, the internal atomic coordinates within the cell were determined by the energy minimization.

The previous band structure calculations\textsuperscript{[5,6,7,8,9] used an \( a \times a \times c \) crystal unit cell as the working cell, in which two Fe, As, La, and O atoms were included. To explore the magnetic structure, in particular the collinear AFM state of LaOFeAs, here we use a \( \sqrt{2}a \times \sqrt{2}a \times c \) unit cell (Fig. 1). In order to determine the values of the nearest and next-nearest neighbor coupling constants of spin-spin interaction, \( J_1 \) and \( J_2 \) (see Fig. 1), we have evaluated the minimal energies of four different magnetic states of Fe ions with constraints imposed if not stable. These four states have nonmagnetic, ferromagnetic, square AFM, and collinear AFM orders, re-
FIG. 1: (Color online) Schematic top view of the FeAs layer in LaOFeAs. The small dashed square is an $a \times a$ unit cell while the large dashed square is a $\sqrt{2}a \times \sqrt{2}a$ unit cell. The collinear ordered Fe spins in the ground state are shown by red arrows.

respectively. If the energy of the nonmagnetic state of LaOFeAs is set to zero, we find that the energies of the ferromagnetic, square AFM, and collinear AFM states are $(0.0905, -0.010875, -0.21475)$ eV/Fe, respectively. Thus the ground state is a collinear-ordered AFM state, in agreement with the experimental observation\cite{11, 12}. The magnetic moment around each Fe atom is found to be about $2.2 \sim 2.6 \mu_B$, varying weakly in the above three magnetically ordered states. This suggests that the spin of Fe ions is between 1 and 3/2. The magnetic moment obtained from the neutron scattering model is about 6 times smaller than this result. This is probably because the correlated effect, especially the strong competition between different AFM states, has not been fully included in the density functional theory calculation.

To quantify the AFM interactions in this material, we assume that these energy differences are predominantly contributed from the interactions between the Fe spins which can be modeled by the following frustrated Heisenberg model with the nearest and next-nearest neighbor couplings $J_1$ and $J_2$

$$H = J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \vec{S}_i \cdot \vec{S}_j,$$

whereas $\langle ij \rangle$ and $\langle\langle ij \rangle\rangle$ denote the summation over the nearest and next-nearest neighbors, respectively. From the calculated energy data, we find that $J_1 \sim 0.0498$ eV/$S^2$ and $J_2 \sim 0.0510$ eV/$S^2$ (the detail how these parameters are determined is given in the Appendix). If the spin of each Fe ion $S = 1$, then $J_1 \sim 0.0498$ eV and $J_2 \sim 0.0510$ eV.

The above result indicates that there are competing AFM interactions between Fe spins. In particular, the AFM coupling between two next-nearest neighboring Fe spins is very strong. This will frustrate the spin Néel structure and give rise to a collinear ordered AFM ground state.

To explore the origin of these AFM interactions, we have calculated the charge distribution around Fe and As ions. The result (see Fig. 2a and 2b) shows that there is almost no charge distribution between two diagonal Fe atoms, but there is a strong bonding between Fe and As ions. This indicates that the AFM coupling $J_2$ is induced by the superexchange bridged by As ions. This superexchange is AFM because the intermediated state associated with the virtual hopping bridged by As ions is a spin singlet.

The charge distribution between two nearest Fe ions is finite. Thus there is a direct exchange interaction between two neighboring Fe spins. Since there is a strong Hund’s coupling between the spins of 3d electrons within each Fe ion, the direct exchange interaction is found to be ferromagnetic when the distance of two Fe atoms is between 2.4Å and 2.85Å. However, the overall magnetic coupling $J_1$ between the two nearest Fe spins in LaOFeAs is antiferromagnetic. Thus $J_1$ is also dominated by the superexchange interaction bridged by As 4p orbitals.

In the collinear AFM phase, we find that a small structural relaxation, for which the lattice is slightly expanded along the antiferromagnetic ordering direction ($\gamma$-axis in Fig. 1) and shrunk along the ferromagnetic ordering direction ($x$-axis in Fig. 1), can further lower the ground state energy. This changes the angle between two principal axes in ab-plane, $\gamma$, from 90° to 90.47°. The corresponding energy gain is 7meV. However, we find that this

FIG. 2: (Color online) Charge density distribution of LaOFeAs in the (001) plane crossing Fe-Fe atoms (a) and in the (110) plane crossing Fe-As-Fe atoms (b).

FIG. 3: (Color online) Total and orbital-resolved partial density of states (spin-up part) of LaOFeAs in the stripe-ordered antiferromagnetic state. The Fermi energy is set to zero.
small lattice distortion affects weakly the band structure and the Fe moments.

Fig. 3 shows the total and projected density of states of LaOFeAs at the collinear AFM phase. In comparison with the nonmagnetic phase, we find that most of the states around the Fermi level are gapped by the collinear AFM order. This suppresses the total carrier density by more than two orders of magnitude. The strong suppression is consistent with the Hall coefficient measurement which shows that the absolute value of the Hall coefficient is enhanced by more than 150 times in the AFM phase at 4K versus the nonmagnetic phase above 150K. Furthermore, we find that the density of states at the Fermi level is also suppressed compared with the nonmagnetic state\[8\]. However, it is not suppressed as strongly as for the total carrier density. The corresponding electronic specific heats are evaluated as 0.65mJ/(K^2mol) (stripe-ordered AFM) and 4.28mJ/(K^2mol) (nonmagnetic), respectively. This is also consistent with the specific heat measurement.

We have also calculated the band structure of LaOFeAs with 5% F- or 5% Sr-doping by taking the virtual crystal approximation in the collinear AFM phase. We find that the overall band structure is hardly changed by 5% electron or hole doping. The Fe moment is also unchanged. Only the Fermi energy moves up or down with electron or hole doping. However, as shown in Fig. 4, the Fermi surface changes dramatically.

By projecting the density of states onto the five 3d orbitals of Fe (Fig. 4), we find that the five up-spin orbitals are almost completely filled and the five down-spin orbitals are only partially filled. However, the down-spin electrons are nearly uniformly distributed in these five 3d orbitals. This indicates that the crystal field splitting imposed by As atoms is relatively small and the Fe 3d-orbitals hybridize strongly with each other. As the Hund rule coupling is strong, this would lead to a large magnetic moment formed around each Fe atom, as found in our calculations. The frustration between the \( J_1 \) and \( J_2 \) terms will suppress strongly the AFM ordering at the two Fe-sublattices, each connected only by the \( J_2 \) terms. This, together with the quantum fluctuation, will reduce strongly the average magnetic moment around each Fe measured by experiments.

Fig. 5 shows the band structure and the Fermi surfaces of electrons in the collinear AFM state. Unlike in the nonmagnetic state, there are now only three Fermi surface sheets in undoped case, one small hole cylinder along \( \Gamma Z \) and two electron-type pockets between \( \Gamma \) and \( X \). \( \Gamma X \) corresponds to the parallel-aligned moment line and \( \Gamma \bar{X} \) corresponds to the antiparallel-aligned moment line. (d) The Fermi surface of the 5% F-doped compound. (e) The Fermi surface of the 5% Sr-doped compound.

FIG. 3: The total and projected density of states at the five Fe-3d orbitals around one Fe atom. The Fermi energy is set to zero.

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est and next nearest neighbor superexchange interactions in LaOFeAs. The interplay between these AFM interactions can affect strongly the magnetic structure of the ground state. Upon doping, the AFM ordering will be suppressed. However, we believe that the remanent AFM fluctuation will survive, similar as in cuprate superconductors. Thus the effective low energy model for describing these Fe-based superconductors, no matter whether it is a single- or multi-band Hamiltonian, should include the frustrated Heisenberg terms defined by Eq. (1).

In the Fe-based superconductors, the magnetic fluctuation, induced by either the AFM superexchange interactions or the on-site Hund’s rule coupling, can be responsible for the superconducting pairing. The former interaction favors a spin singlet pairing, while the latter favors a spin triplet pairing. However, the superconductivity induced by the Hund’s rule coupling would generally involve the interband pairing, which is limited by the available phase space if the total momentum of Cooper pair is zero. This would suggest that the spin triplet pairing is not energetically favorable in a system with strong AFM fluctuations. Moreover, from the study of high-Tc cuprate superconductivity, we know that the strong next-nearest neighbor AFM interaction favors an extended s or d_{xy}-wave pairing. Therefore, we believe that the leading pairing instability will be in spin singlet channel, if the superconductivity is driven by the AFM fluctuation. However, the competing nearest neighbor AFM interaction may introduce a small new component with different symmetry, for example a d_{x^2-y^2}-wave gap, to the pairing function. Thus the resulting gap parameter will generally be a superposition of two components with different symmetries, for example an extended s plus d_{x^2-y^2} pairing state.

In conclusion, we have presented first-principles calculations of the electronic structure of LaOFeAs. We find that there are strong antiferromagnetic nearest and next-nearest neighbor superexchange interactions, bridged by As 4p orbitals. The next nearest neighbor antiferromagnetic coupling is comparable to the nearest neighbor one. This gives rise to the collinear AFM ordering of Fe spins in the ground state as observed by neutron scattering. The existence of strong antiferromagnetic fluctuations in the Fe-based superconductors bears a strong analogy to the high-Tc cuprates. This suggests that the superconductivity in these two different kinds of high-Tc materials may have a common origin.

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Note added in revision: In a 2 x 2 Fe-Fe lattice of the J_{1}-J_{2} model with periodic boundary conditions, the J_{1} and J_{2} terms are overcounted by a factor of 2 and 4, respectively. This overcounting has not been considered in our previous estimation of J_{1} and J_{2}, which leads to an overestimation of the values of these parameters as well as the ratio J_{2}/J_{1}. This error has been corrected in this revised version.

APPENDIX: DETERMINATION OF J_{1} AND J_{2}

To determine the value of J_{1}, one need to first evaluate the energy of a pair of nearest Fe-Fe moments in parallel (E_{F,1}) and anti-parallel (E_{A,1}) alignments with respect to a non-magnetic reference state, respectively. Then from their difference, one can determine the value of J_{1} by the following formula

$$J_{1} = (E_{F,1} - E_{A,1})/(2S^2), \quad (2)$$

where S is the spin of each Fe ion. It should be emphasized that E_{F,1} is not necessary to be equal to -E_{A,1} since the energy of the reference state may not be located exactly at the middle of the energy between the ferromagnetic and antiferromagnetic states. This energy lineup between the nonmagnetic and any other magnetic state needs self-consistent total energy calculations to determine, that is what we have done. Thus E_{F,1} and E_{A,1} should be determined independent. Similarly, J_{2} can be determined from the difference between the energy of a pair of next-nearest Fe-Fe moments in the parallel (E_{F,2}) and anti-parallel (E_{A,2}) alignments:

$$J_{2} = (E_{F,2} - E_{A,2})/(2S^2). \quad (3)$$

To determine the values of E_{F,1} - E_{A,1}, E_{F,2} - E_{A,2}, we have calculated the total energies of the ferromagnetic (E_{FM}), square antiferromagnetic (E_{AF}), and collinear antiferromagnetic (E_{Col}) states, respectively. The spin configurations of these three states are shown in Fig. 6. The corresponding energy differences with respect to
FIG. 7: Variations of $J_1$ and $J_2$ with $E_{FM} - E_{NM}$. The dashed line denotes our calculated value.

the nonmagnetic state ($E_{NM}$) are (0.0905, -0.10875, -0.21475) eV/Fe. If these energy differences result mainly from the exchange interactions between the nearest or next-nearest Fe moments, then we obtain the following equations

\[
E_{FM} - E_{NM} = 2E_{F,1} + 2E_{F,2} = 0.0905eV, \\
E_{AF} - E_{NM} = 2E_{A,1} + 2E_{F,2} = -0.10875eV, \\
E_{Col} - E_{NM} = E_{F,1} + E_{A,1} + 2E_{A,2} = -0.21475eV.
\]

From them, we further find that

\[
E_{F,1} - E_{A,1} = 0.0996eV, \\
E_{F,2} - E_{A,2} = 0.1028eV.
\]

Thus the values of $J_1$ and $J_2$ are

\[
J_1 = 0.0498eV/S^2, \quad (4) \\
J_2 = 0.0501eV/S^2. \quad (5)
\]

The energy of the current ferromagnetic state is less accurately determined since this state is not a stable state. The error in $E_{FM} - E_{NM}$ will give rise to the error in $J_1$ and $J_2$. Fig. 7 shows how $J_1$ and $J_2$ change with $E_{FM} - E_{NM}$. As we see, we find that $J_2 > J_1/2$ even we assume the deviation of $E_{FM} - E_{NM}$ from our calculated value is as big as 0.1 eV. Thus we believe that the collinear antiferromagnetic order observed in LaOFaEs is indeed due to the competition of superexchange interactions.

The above estimation indicates that $J_1 \sim J_2$ within the error of calculation for LaOFaEs. In this parameter range, as shown by Yao and Carlson\textsuperscript{[17]} with the spin wave approximation, the $J_1$ superexchange interaction term will compete strongly with the $J_2$-term. This results in a strong reduction of the magnetic moment of Fe, which would naturally explain why the observed magnetic moment ($\sim 0.36 \mu_B$) is significantly smaller than that obtained from the density functional calculations for LaOFaEs.

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