Origin of the \(~150\) K Anomaly in LaOFeAs: Competing Antiferromagnetic Supercexchange Interactions, Frustration, and Structural Phase Transition

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From first principles calculations we find that the nearest and next nearest neighbor superexchange interactions between Fe ions in LaOFeAs are large, antiferromagnetic (AF), and give rise to a frustrated magnetic ground state which consists of two interpenetrating AF square sublattices with \(M(Fe)=0.48\mu_B\). The system lowers its energy further by removing the frustration via a structural distortion. These results successfully explain the magnetic and structural phase transitions in LaOFeAs recently observed by neutron scattering. The presence of competing strong antiferromagnetic exchange interactions and the frustrated ground state suggest that magnetism and superconductivity in doped LaOFeAs may be strongly coupled, much like in the high-\(T_c\) cuprates.

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The recent discovery of superconductivity at \(T_c\)’s up to 50 K in layered rare-earth (R) transition metal (Tm) pnictide(Pn)-oxide quaternary compounds \(\text{ROTmPn}(\text{R}=\text{La, Ce, Sm, Tm}=\text{Mn, Fe, Co, Ni, Pn= P, As})\)\(^{1,2,3,4}\) has sparked enormous interest in this class of materials. These are the first non-copper based materials that exhibit superconductivity at relatively high temperatures upon electron (\(O_{1-x}F_x\))\(^{1,2,3,4}\) and hole doping (\(\text{La}_{1-x}\text{Sr}_x\))\(^5\) of their nonsuperconducting parent compounds, just like high-\(T_c\) cuprates. Clearly, the understanding of electronic, magnetic, and structural properties of the parent compound LaOFeAs is the key to determining the underlying mechanism that makes these materials superconduct upon electron/hole doping.

Recent theoretical studies suggest conflicting results varying from LaOFeAs being a nonmagnetic metal near a ferromagnetic or antiferromagnetic instability\(^6,7,8\) to a simple antiferromagnetic semimetal\(^9,11\). From optical measurements and density functional calculations, it was also suggested that LaOFeAs has an antiferromagnetic spin-density-wave (SDW) instability due to Fermi-surface nesting\(^9\). Experimental studies including resistivity and magnetic susceptibility show a small but very clear anomaly near 150 K in LaOFeAs\(^1,3\). The origin of this anomaly has been very recently determined by neutron scattering studies\(^12,13\). It has been found that LaOFeAs exhibits an antiferromagnetic long-range ordering with a small \(0.35\mu_B\) per Fe moment followed by a small structural distortion\(^12\). However there is no proposed microscopic theory that explains the origin of the observed stripe-like AF spin decoration and the structural distortion. It is also not clear if the magnetic and structural phase transitions are related to each other. Finally, given the fact that both the cuprates and LaOFeAs exhibit antiferromagnetic ordering, one wonders how strong and what kind of magnetic spin-fluctuations are present in the 2D Fe-square lattice of LaOFeAs.

In this letter, from accurate all-electron density functional calculations we try to answer some of these questions. We find that both nearest neighbor (nn) and next nearest neighbor (nnn) superexchange interactions between Fe ions in the square lattice are very large, comparable to each other and more importantly they are antiferromagnetic. This forces the Fe spins along the square-diagonal to order antiparallel, resulting two interpenetrating square AF sublattices. Since in this configuration we have one parallel and one antiparallel alignment of the spins along the square axes, the nearest neighbor superexchange interaction is totally frustrated. The system lowers its energy by removing this frustration via a structural distortion that makes the two sides of the square-lattice inequivalent. These results including the magnetic moment of the Fe ions and the degree of structural distor-

### FIG. 1: (color online) (a) The crystal structure of LaOFeAs in space group P4/nmm with origin choice 1. (b) Top view of the FeAs-plane and the relations between primitive and \(\sqrt{2} \times \sqrt{2}\) supercell used in our calculations. The dark and light shaded areas indicate the As atoms below and above the Fe-square lattice, respectively.
tion, are in excellent agreement with the recent neutron data\cite{12}. Therefore, we have a nice working microscopic theory that explains the details of both the magnetic and structural properties of the undoped parent compound LaOF\textsubscript{e}As. Our theory also brings our attention to the presence of the strong competing antiferromagnetic interactions in this class of materials. Even though electron doping seems to destroy the long-range magnetic order, the short range spin fluctuations will be always present and probably play an important role in the superconducting phase, much like the high $T_c$ cuprates. In fact, a theory has been already proposed for the superconductivity mediated by antiferromagnetic spin fluctuations in LaOF\textsubscript{e}As\cite{14}.

The calculations were done using the full-potential linearized augmented planewave (FP-LAPW) method, one of the most accurate methods available in electronic structure calculations\cite{15, 16}. We also used the ultra-soft pseudo potential plane-wave (PW) method\cite{17} for cross checking of our results and for phonon calculations. We considered $\sqrt{2} \times \sqrt{2}$ supercell of the primitive cell of LaOF\textsubscript{e}As which is shown in Fig. 1. In order to determine the true ground state, we have considered four different cases. These are non-magnetic (NM, i.e., no spin polarization), ferromagnetic (F) and the two different antiferromagnetic spin configurations shown in Fig. 2. The first one of the antiferromagnetic configurations is AF1 where the nearest neighbor spins are antiparallel to each other. The second antiferromagnetic configuration is AF2, is shown in Fig. 2b. In AF2 the Fe spins along the square diagonal are aligned antiferromagnetically. The AF2 spin configuration can be considered as two inter-penetrating simple square AF sublattices (red and blue sublattices in Fig.2b). We note that since each Fe ion is at the middle of a square AF lattice, the mean field at each spin site is zero. Hence one sublattice can be rotated freely with respect to the other sublattice without costing any energy. For this reason the AF2 spin-configuration is fully frustrated. This can be also seen by the fact that for a given square, we have always one parallel ($J_1S^2$) and one antiparallel ($-J_1S^2$) aligned spin pair, cancelling each others contribution to the total energy. In frustrated magnetic systems, it is known that the frustration is almost always removed by either a structural distortion or by thermal and quantum fluctuations\cite{18, 19}. From the classical energies of AF1 and AF2, one sees that the AF2 spin configuration is stabilized when $J_2 > J_1/2$.

In order to determine which spin configurations among NM, F, AF1, and AF2, is the ground state, we have carried out FP-LAPW total energy calculations for each case. Since in spin-polarized calculations it is very easy to get a local minimum, we followed a different strategy. In our calculations we fixed the magnetic moment per Fe ion and then scan the total energy as a function of Fe-magnetic moment. Our results are summarized in Fig. 3. The zero of energy is taken as the M=0 case (i.e. NM calculation). From Fig. 3, it is clear that LaOF\textsubscript{e}As has only one magnetic ground state which is AF2. The Ferro spin-configuration always results the highest energy regardless the Fe-magnetic moment. Similarly AF1 ordering always yields energies higher than the NM case. For the AF2 ordering, we see that the energy minimum occurs near the fixed moment calculation with M=1. Repeating calculations where magnetization is not fixed, we obtained the optimum magnetic moment as M=0.87 $\mu_B$ per Fe. As we discuss below in detail, the Fe magnetic moment is further reduced almost by a half when the structure is allowed to distort to remove the magnetic frustration. We note that the magnetic moment obtained from FP-LAPW method is significantly smaller than those obtained from pseudo-potential PW based calculations which give moments around 2.5 $\mu_B$. We also note that there is no indication of any ferromagnetic interactions present in LaOF\textsubscript{e}As which is clear from Fig. 3. In fact, the system prefers to reduce its magnetization to zero if spins are forced to be aligned ferromagnetically. Therefore, we conclude that the main superexchange interactions in LaOF\textsubscript{e}As system is anti-
ferromagnetic. The fact that AF2 has lower energy than AF1 indicates that the next nearest neighbor interaction is also antiferromagnetic and satisfies the phase boundary \( J_2 > J_1/2 \).

In order to gain a better insight into the nature of the superexchange interactions present in Fe-square lattice of the LaOFeAs system, we map the calculated total energies of the F, AF1 and AF2 configurations shown in Fig.3a to a simple Heisenberg like model \( H = \sum_{i,j} J_{ij} S_i S_j \) for a given fixed Fe moment \( S \). For fully localized spin-systems this is a perfect thing to do but for the case of LaOFeAs this is only an approximation. Nevertheless, the calculated J\( s \) is a good indication of the superexchange energies present in the system. The Fig. 3b shows the \( J_1 \) and \( J_2 \) obtained from the energies of the F, AF1 and AF2 at given magnetic moment. It is clear that both \( J_1 \) and \( J_2 \) are quite large and positive (i.e. antiferromagnetic). \( J_2 \) is always larger than \( J_1/2J \) and therefore AF2 structure is the only ground state for any given moment of the Fe ion. By looking at the superexchange paths for \( J_1 \) and \( J_2 \) (shown in insets to Fig.3), we notice that the Fe-As-Fe angle is around 75\(^\circ\) and 120\(^\circ\) for nn and nnn Fe-pairs, respectively. Hence it makes sense that the 2nd nn exchange is as strong as the nn exchange because the angle is closer to the optimum value of 180\(^\circ\)\( . \) It is quite surprising and also very interesting that there are strong and competing antiferromagnetic superexchange interactions in LaOFeAs system that result in a totally frustrated AF2 spin configuration. This is very similar to the magnetic ground state of the cuprates where the AF ordered 2D square lattice of the adjacent planes are frustrated [18].

We now briefly discuss the effect of the structural distortion on the electronic structure and the zone center

\[ \text{FIG. 4: (color online) The total energy per cell versus the angle } \gamma \text{ for non-magnetic (NM), Ferromagnetic (F) and two antiferromagnetic (AF1 and AF2) spin-configurations. Note that only the AF2 spin configuration yields structural distortion. The inset shows that as } \gamma \text{ increases, the ferromagnetic aligned Fe ions (i.e., Fe\(_1\)-Fe\(_2\)) get closer while the antiferromagnetically aligned ions (i.e., Fe\(_1\)-Fe\(_3\)) move apart, breaking the four-fold symmetry and thus the degeneracy of the } d_{xz} \text{ and } d_{yz} \text{ orbitals.} \]
phonons. The details will be published elsewhere. Fig. 5 shows the electronic density of states before and after the structural distortion with the AF2 ordering in $\sqrt{2} \times \sqrt{2}$ structure. The N(E$_F$) in both phases are quite small compared to previous calculations in which incorrect AF ordering was considered. It is apparent that the distortion has significant effect both on the N(E$_F$) and the Fe magnetization. Interestingly, the N(E$_F$) is doubled while the magnetization is reduced by half due to structural distortion. The increase in the N(E$_F$) is consistent with the resistivity measurement which shows that LaOFeAs exhibits metallic behavior after the transition. Finally, we note the existing several sharp Van Hove like kinks in the DOS. In particular the distortion brings one of these kinks just next to the Fermi energy. Hence, with a small electron doping, it is quite possible to increase the N(E$_F$) significantly. The effect of such electron doping is under study and will be reported elsewhere.

Finally we explain why Dong et al. did not see any evidence of the structural phase transition in their optical IR measurements[9]. From the the symmetry decomposition of the optical phonons in both P4/nmm and P2/c phases (see Table 1), we note that the distortion does not introduce any new IR active modes but rather just splits the doubly-degenerate modes into non-degenerate ones. However the splitting is quite small; the largest is around 0.2 meV. This explains why no new modes appear in the optical measurements after the transition. We also note that the agreement for the energies of the zone center phonons with IR data is not as good as one expects. In particular, the E$_u$ mode observed at 42 meV is calculated to be 35 meV, a significantly lower value. Interestingly, this particular mode has a strong temperature dependence[9]. We checked that the disagreement is not due to anharmonic phonons. The calculated phonons are harmonic unlike those observed in the MgB$_2$ superconductor[21]. We hope that our observation will motivate others to look at the zone-center phonons carefully to understand the discrepancy.

In conclusion, we have presented a first-principles study of the superexchange interactions between Fe ions and their effect on the magnetic and structural properties of the parent compound LaOFeO of the newly discovered high temperature superconductor LaO$_{1-x}$Fe$_x$As. The competing strong antiferromagnetic exchange interactions and the frustrated ground state suggest that LaOFeAs has many common magnetic properties with the undoped parent compound of the high-T$_c$ cuprates.

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**TABLE I**: The symmetries and energies (in meV) of the optical phonons of LaOFeAs in P4/nmm and P2/c phases. The energies of the IR-active modes are taken from Ref[8]. The * indicates a significant disagreement! The animations of these modes can be found at [http://www.ncnr.nist.gov/staff/taner/laofeas](http://www.ncnr.nist.gov/staff/taner/laofeas).

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FIG. 5: (color online) The total electronic DOS of LaOFeAs for high (P4/nmm) and low (P2/c) symmetry phases.
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