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Chemical Bonding and Electronic and Magnetic Structure in LaOFeAs

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The recent work by Kamihara et al.[1] reporting a superconducting transition at 26 K in the Fe-based La[$O_{1-x}F_x$]FeAs ($x = 0.12$, electron doping), which increases up to 43 K under 4 GPa pressure,[2] has renewed the interest in high critical temperature (T_c, HTC) superconductivity. Almost immediately after this discovery, Wen et al.[3] reported superconductivity at 25 K in the [$La_{1-x}Sr_x$]OFeAs material ($x = 0.13$, hole doping). The reported phase diagrams show similarities to the cuprate materials and potentially provide an interesting link between HTC in both classes of materials. Higher and higher T_c values are rapidly emerging[4,5] reaching $T_c = 52$ K in $PrO_{1-x}F_xFeAs$.[6] The discovery of HTC superconductivity in doped LaOFeAs opens new opportunities to approach old questions related to the microscopic mechanism of superconductivity in cuprates. In this Communication we provide strong theoretical evidence showing that, in contrast to previously reported LDA and GGA calculations, LaOFeAs is a complex antiferromagnetic insulator with a physical nature intermediate between Mott−Hubbard and charge-transfer (CT) limiting situations, with important Fe−As covalent interactions and exhibiting a strong spin frustration in its ground state.

LaOFeAs and La[$O_{1-x}F_x$]FeAs show normal conducting states at room temperature with a molar magnetic susceptibility of the order of 10^{-3} emu; at least 1 order of magnitude larger than that of the cuprates.[1] The conductivity of LaOFeAs samples can be described as typical for thermally activated semiconductors or at most "bad-metals". Undoped LaOFeAs shows a complex magnetic behavior with an evident change in both χ versus T curve and conductivity, and undergoes a structural distortion from tetragonal to monoclinic symmetry at 155 K.[7] The material develops also a long-range spin density wave (SDW)-type of antiferromagnetic order below $T_N = 137$ K with a strongly reduced ordered magnetic moment of 0.36 μ_B per iron atom, much smaller than the expected value for a formal $S = 2$ spin particle such as Fe^{2+} in a quasi-tetrahedral environment. This diminishing of magnetic moment is suggested to be due to the existence of magnetic frustrations in the magnetic ground state.[7,8]

To investigate the nature of chemical bonding and the electronic properties of undoped LaOFeAs material we carried out periodic spin polarized density functional theory (DFT) calculations using the experimental structure parameters reported by Kamihara et al.[1] The calculations were done using a range of exchange-correlation ($E_{xc}[\rho]$) functionals treating strongly correlated systems beyond the limitations of local density approximation (LDA) or generalized gradient approximation (GGA) methods. Specifically, we report on results from B3LYP,[9] Fock-35,[10] HSE06.[11] and GGA + U[12] calculations with two kinds of basis sets: plane waves (PW) and atomic orbitals (AO). To compute the relevant magnetic coupling constants as well as to determine the magnetic structure of the electronic ground state, three electronic solutions with different spin distributions have been considered: (i) ferromagnetic (FM) solution, and two antiferromagnetic solutions, (ii) AF1 all nearest neighbors with opposite spin, as in cuprates, and (iii) AF2 ferromagnetically ordered chains along the a' axis with alternating spin along the b' axis of a $\sqrt{2} \times \sqrt{2} \times 1$ supercell (see Supporting Information, SI, for details). The diamagnetic (closed shell) solution is not considered here, as it was found to be much higher in energy.

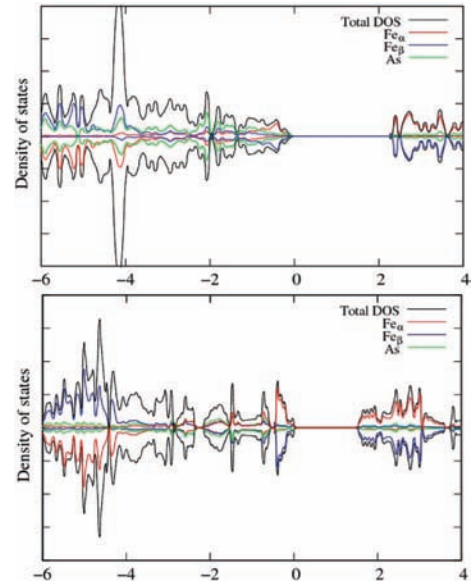

Figure 1. Calculated total and atom projected DOS of the AF2 ground-state of LaOFeAs. The Fe DOS is divided into formally spin α and β iron sites in AF2 solution (spin up and down for each site is drawn as positive and negative DOS values). The calculations were conducted using (top) B3LYP functional and AO (Gaussian) basis sets and (bottom) HSE06 functional and PW wave basis set. The energies are given relative to Fermi level.

The most stable solution predicted by all of the considered functionals corresponds to the AF2 spin distribution, in agreement with the magnetic structure suggested by neutron diffraction studies.[7] In contrast to previously reported results calculated using local $E_{xc}[\rho]$ functionals,[13,14] we find the ground-state of undoped LaOFeAs to be a magnetic insulator with a gap of about 2 eV (this solution is later referred to as AF2), as seen in Figure 1. The calculated density of states (DOS) near the Fermi level show a strong Fe(3d) character with a small contribution of As(4p) orbital states, suggesting that this system cannot be described simply either as a Mott−Hubbard or as a charge-transfer insulator. The band gap is strongly reduced in the FM state, so the thermal excitations of the magnetic manifold give rise to the appearance of the conducting states at room temperature. The above results suggest that the real band gap is of the order of 1.0−2.0 eV which is in line with the

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Table 1. Magnetic Exchange Nearest Neighbor (J_1) and Next Nearest Neighbor (J_2) Coupling Constants Calculated by Fitting Ising Hamiltonian to the Calculated Energy Spectrum (Values in meV)

method	J_1	J_2	J_1/J_2
B3LYP	−17.1	−14.6	1.17
Fock-35	−12.6	−10.1	1.25
HSE06	−13.7	−20.2	0.68
GGA + U	−17.7	−21.6	0.82

observation of low conductivity of the material for temperatures above $T_N = 137$ K which decreases as the antiferromagnetic ordering is restored. Note that PW and AO periodic calculations provide the same description for the AF2 ground state.

The qualitative Mulliken population analysis of the different magnetic solutions shows an alternating series of $(LaO)^{+1}$ and $(FeAs)^{-1}$ charged layers. The FeAs layer involves a significant degree of covalent bonding, which is clearly seen in DOS plots, and which can be assigned to covalence between As(4p) and Fe(3d) orbitals, which is reminiscent of the situation found for cuprates where Cu(3d) and O(2p) are significantly mixed.[15,18] Further analysis of the atom projected spin density (number of unpaired electrons at Fe sites) associated to each solution gives 3.45, 3.42, and 3.60 electrons for AF1, AF2, and FM solutions, respectively. Therefore, Fe in FeAs layer is a $3d^6$ ion with four unpaired electrons, and doubly occupied $d_{x^2-y^2}$ (see note to ref 8).

The net charges and spin densities discussed above are almost independent of the magnetic solution considered, which allows one to use a spin only model Hamiltonian to model their low-energy magnetic spectrum and properties.[15] By using an Ising Hamiltonian to describe relative energies (per formula unit) of the FM, AF1, and AF2 magnetic solutions, we estimate the magnitude and sign of the most important magnetic coupling constants in LaOFeAs (See details in SI). For a magnetic system of particles with $S = 2$ total magnetic moment arranged in a square net we calculate the nearest (J_1) and next-nearest (J_2) magnetic coupling constants. The results presented in Table 1 show that the calculated couplings correspond to a strongly frustrated square planar net independently of the functional used. This frustration leads to both decrease of magnetic order and accumulation of entropy at low temperatures, which can lead to superconductivity, as described in ref 8.

The low magnetic moment at magnetic sites observed experimentally in LaOFeAs has so far been explained by the conducting nature of the ground-state solution.[13,14] However, from the theoretical point of view, one must be aware of the failure of the broadly used LDA and GGA implementations of DFT when applied to strongly correlated magnetic systems.[10] Corrections such as LDA + SIC (self-interaction correction), LDA + U (or GGA + U), the many-body GW approximation, and hybrid functionals[9] have been proposed to remedy the failure of LDA and GGA.[16] In particular, hybrid functionals such as B3LYP[9,17] have shown significant improvement over standard DFT methods to describe transition metal magnetic materials.[10,18] All presented descriptions for the ground-state of LaOFeAs suggest an insulating ground state. These results are in clear contrast with standard LDA/GGA calculations presented in the literature predicting LaOFeAs to be a metal. This discrepancy first appeared for superconductor parent cuprates with compeling evidence that LDA/GGA provides a wrong description.[19]

To summarize, hybrid and GGA + U functionals consistently describe LaOFeAs as a complex insulator with a physical nature intermediate between Mott−Hubbard and CT limiting situations. The electronic structure involves Fe^{2+} cations, in a slightly distorted tetrahedral environment, which can be considered as particles with effective $S = 2$ spin moments localized at Fe^{2+} sites with a local $3d^6$ electronic configuration in a quasi-tetragonal $FeAs_4$ structural unit. The electronic ground-state involves an intricate antiferromagnetic structure with two competing magnetic coupling constants leading to a complex strongly frustrated system in agreement with previous experimental[7] and theoretical results.[8]

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Supporting Information Available: Details on the calculations and complementary results. This material is available free of charge via the Internet at http://pubs.acs.org.

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