Theoretical investigation of magnetic order in ReOFeAs, Re = Ce, Pr

H. M. Alyahyaei and R. A. Jishi

Department of Physics, California State University, Los Angeles, California 90032

(Dated: November 15, 2008)

Density functional theory (DFT) calculations are carried out on ReOFeAs, Re = Ce, Pr, the parent compounds of the high-\(T_c\) superconductors ReO\(_{1-x}\)F\(_x\)FeAs, in order to determine the magnetic order of the ground state. It is found that the magnetic moments on the Fe sites adopt a collinear antiferromagnetic order, similar to the case of LaOFeAs. Within the generalized gradient approximation along with Coulomb onsite repulsion (GGA+U), we show that the Re magnetic moments also adopt an antiferromagnetic order for which, within the ReO layer, same spin Re sites lie along a zigzag line perpendicular to the Fe spin stripes. While within GGA the Re 4f band crosses the Fermi level, upon inclusion of onsite Coulomb interaction the 4f band splits and moves away from the Fermi level, making ReOFeAs a Mott insulator.

I. INTRODUCTION

Recently, a new class of layered, iron-based, high temperature superconductors, has been discovered. Kamihara et al.\(^{1}\) reported a superconducting transition temperature \(T_c = 26\) K in fluorine doped LaOFeAs. This is a member of a family of compounds known as quaternary oxypnictides with a general formula LnOMPn, where Ln is a lanthanide (La, Ce, Pr, ...), M is a transition metal (Mn, Fe, Co, ...) and Pn is a pnicogen (P, As, ...). Shortly afterwards, it was shown\(^{2}\) that under pressure the transition temperature increased to 43 K. Hole doping, achieved by replacing trivalent La with divalent Sr gave a compound with \(T_c = 25\) K\(^{3}\). Replacement of La with other rare earth elements gave a series of superconducting compounds ReO\(_{1-x}\)F\(_x\)FeAs with Re = Ce, Pr, Nd, or Sm, with transition temperatures close to or exceeding 50 K\(^{4,5,6,7,8}\). Using high pressure techniques, fluorine-free but oxygen deficient samples were synthesized and found to superconduct at 55 K\(^{9}\).

The parent compound, ReOFeAs, is a layered compound consisting of a stack of alternating ReO and FeAs layers. At high temperatures, the crystal structure is tetragonal with space group P4/nmm and a unit cell, shown in Fig. 1 that contains two molecules. But at low temperatures, the crystal undergoes a structural phase transition to an orthorhombic phase with Cmma space group and a unit cell that contains four molecules. The FeAs layer consists of a square planar sheet of Fe sandwiched between two sheets of As. Upon fluorine doping these compounds become superconductors. It is not understood at this stage what mechanism lies behind superconductivity in these compounds. Understanding the electronic structure of the undoped parent compounds is necessary to understand the doped compounds, especially that in these iron-based compounds, there is an interplay between magnetism and superconductivity, as is the case in the high-\(T_c\) cuprates.

Initial calculations using density functional theory (DFT) concluded that LaOFeAs is metallic and nonmagnetic but with possible antiferromagnetic (AFM) fluctuations.\(^{10,11,12}\) More extensive calculations on states with various possible magnetic orders in LaOFeAs, however, showed that the magnetic moments of the Fe ions are ordered antiferromagnetically in a stripe-like pattern in the Fe plane, resulting in a magnetic unit cell with \(\sqrt{2}a\times\sqrt{2}a\times c\) supercell structure, in contrast to the nuclear axaxc unit cell.\(^{13,14,15}\) Indeed, neutron scattering measurements on LaOFeAs reveal the existence of such a collinear AFM state at temperatures below 137 K\(^{17}\).

In this work we study the electronic structure of the parent compounds ReOFeAs, Re = Ce, Pr, using DFT within the generalized gradient approximation (GGA). We consider various possible magnetic orders of the Fe and Re ions. We show that in the ground state the magnetic moments of the Fe ions adopt a collinear AFM order as in the case of LaOFeAs. Within GGA, the Ce sites are paramagnetic, but when the onsite Coulomb interaction is taken into account (GGA+U), the magnetic moments on the Ce sites, resulting from the 4f electrons, also adopt an AFM order with a zigzag-like pattern. On the other hand, within both GGA and GGA+U, the magnetic moments on the Pr sites adopt an AFM order similar to that on the Ce sites.
II. METHOD

The first-principles calculations presented in this work were performed using the all-electron full potential linear augmented plane wave plus local orbitals (FP-LAPW+lo) method as implemented in WIEN2K code [18]. In this method the core states are treated in a fully relativistic way but the valence states are treated at a scalar relativistic level. The exchange-correlation potential was calculated using the generalized gradient approximation (GGA) as proposed by Pedrew, Burke, and Ernzerhof (PBE) [19].

For calculations in this work, the crystal is taken to be orthorhombic, being the low temperature phase, with space group C\textit{mmm}. The lattice constants are \( a = 5.66263 \) \AA, \( b = 5.63273 \) \AA, \( c = 8.6444 \) \AA, for the case of Ce-OF\textit{e}As\textsuperscript{[20]}, and \( a = 5.6374 \) \AA, \( b = 5.6063 \) \AA, \( c = 8.5966 \) \AA, for the case of Pr\textit{O}Fe\textit{As}\textsuperscript{[21]}. In the low-temperature orthorhombic phase, the unit cell has four Re atoms with crystal coordinates Re1 (0, 0.25, \( z \)), Re2 (0, 0.75, \( -z \)), Re3 (0.5, 0.25, \( -z \)), and Re4 (0.5, 0.75, \( z \)), where \( z = 0.1402 \) or 0.1385 for Re = Ce or Pr, respectively. Re1 and Re4 belong to an Re-plane above the O-plane, while Re2 and Re3 belong to an Re-plane below the O-plane. These two Re-planes, along with the O-plane sandwiched between them, constitute the ReO layer. The radii of the muffin-tin spheres are chosen so that the nearby muffin-tin spheres are almost touching. For all structures considered in this work we set the parameter \( R_{\text{MT}} K_{\text{max}} = 7 \), where \( R_{\text{MT}} \) is the smallest muffin-tin radius and \( K_{\text{max}} \) is a cutoff wave vector. The valence wave functions inside the muffin-tin spheres are expanded in terms of spherical harmonics up to \( l_{\text{max}} = 10 \), while in the interstitial region they are expanded in plane waves with a wave vector cutoff \( K_{\text{max}} \), and the charge density is Fourier expanded up to \( G_{\text{max}} = 13a_0^{-1} \), where \( a_0 \) is the Bohr radius. Convergence of the self consistent field calculations is attained with a strict charge convergence tolerance of 0.00001 e.

III. RESULTS AND DISCUSSION

To begin with, we consider within GGA, various magnetic orders of the Fe magnetic moments in the Fe plane: nonmagnetic, ferromagnetic (FM), antiferromagnetic (AFM), and collinear antiferromagnetic (c-AFM). We find that the c-AFM order of the Fe magnetic moments has the lowest energy. The energy of the c-AFM order of the Fe moments is lower that the AFM order by 0.031 eV per Fe atom, lower than the FM order by 0.156 eV per Fe atom, and lower than the nonmagnetic phase by 0.146 eV per Fe atom. In the AFM order, every spin-up Fe site is surrounded by four nearest neighbor (NN) spin-down Fe sites, whereas in the c-AFM order, among the four NN Fe sites surrounding a spin-up Fe site, two along the b-axis are spin-up and the other two along the a-axis are spin-down, but the four next nearest neighbor (NNN) Fe sites are all spin-down. The AFM and the c-AFM orders within the Fe plane were described elsewhere in connection with LaOFeAS. That the ground state has a c-AFM order of the Fe magnetic moments, in CeOFeAs and PrOFeAs, is consistent with what has already been found in LaOFeAS, and with neutron diffraction measurement on these crystals.\textsuperscript{[20]}

In the remaining calculations we fix the spin order within the Fe-plane to be c-AFM, with the Fe spin stripes taken to be along the b-direction in the magnetic unit cell. A spin-up stripe in the \( a - b \) plane is a line of Fe ions, parallel to the \( b \)-axis, with up-spins; this is surrounded in the \( a - b \) plane by two spin-down stripes, also parallel to the \( b \)-axis. Fixing the spin order in the Fe-plane, we now focus our attention on the spin order of the Re ions. Considering only the Re sites in ReOFeAs, we note that every Re site (for example, Ce1) has four NN Re sites (2 Ce2 sites at a distance of 3.72 Å and 2 Ce3 sites at a distance of 3.73 Å) and 4 NNN Re sites (4 Ce4 sites at a distance of 3.998 Å). Thus for the magnetic order on the Re sites we consider six different cases:

1) The nonmagnetic (NM) phase, where the magnetic moment on every Re site is constrained to be zero.
2) The paramagnetic (PM) phase, where the magnetic moment on each Re site is non zero, but the spins on different Re sites are not correlated.
3) The ferromagnetic (FM) order, where the magnetic moments on all Re sites are aligned in the same direction.
4) The antiferromagnetic order (AFM), where the four Re ions in the unit cell, Re1-Re2-Re3-Re4, whose crystal coordinates were given earlier, have the spin arrangement uudd, where u stands for up and d stands for down. In this phase, considering an ReO layer (one O-plane surrounded by two Re-planes) the Re spins in one plane are all up, while the Re spins in the other plane are all down. That is, in each Re-plane the order is ferromagnetic (FM), but the magnetization in one Re-plane is opposite to that in the nearby Re-plane lying across from the O-plane.
5) The zigzag-along-a antiferromagnetic (z-a-AFM) order where a spin-up Re site has two NN spin-up Re sites, two NN spin-down Re sites, and four NNN spin-down Re sites. The four Re ions in the unit cell, Re1-Re2-Re3-Re4, have the spin arrangement udud. Here, if we connect the same-spin NN Re ions in a given ReO layer, we obtain a zigzag chain running parallel to the a-axis direction, as shown in Fig. 2. In this phase, if we consider a single Re-plane (for example, the one containing Re1 and Re4), then it is clear that the Re magnetic moments in this plane adopt a simple AFM order where each spin-up Re ion (for example Re1) is surrounded by 4 spin-down Re ions (4 Re4 ions). So in each of the two Re-planes surrounding the O-plane in the ReO layer, the magnetic order is AFM in such a way as to produce same-spin zigzag chains running along the a-direction.
6) The zigzag-along-b antiferromagnetic (z-b-AFM) order for which the four Re ions in the unit magnetic cell, Re1-Re2-Re3-Re4, have the spin arrangement uudd.

\textsuperscript{[21]}
This is similar to case 5 except that the same-spin Re ions lie on zigzag chains running along the b-direction. In an isolated ReO layer, and assuming that Re1-Re2 separation is the same as Re1-Re3 separation, this phase will have the same energy as the previous z-a-AFM phase. But because in the orthorhombic structure Re1-Re2 separation is slightly less than Re1-Re3 separation, and the Fe-plane has spin stripes along the b-axis, it follows that these two phases will not be degenerate, particularly if the Fe and Re spins interact.

We make the following two remarks about how the calculations are performed:

i) It is not really possible to calculate directly the total energy of the paramagnetic (PM) phase, because in this phase the magnetic moments on the Re sites are randomly oriented; it follows that a unit cell in the (PM) phase will contain a very large number of Re atoms. On the other hand, the average magnetic moment per Re site is zero in the PM phase. Therefore, one way to calculate the total energy of the PM phase is to constrain the magnetic moment on every Re site to be zero; this will make the total energy of the PM phase coincide with that of the nonmagnetic (NM) phase, which is not the case in reality. To get around this problem, we note that in the high temperature $\gamma-$phase of elemental Cerium crystal, the NN distance between Ce atoms is 3.65 Å and that in this phase, while the 6s and 5d valence electrons are itinerant, the 4f electron is localized on the Ce site, giving rise to a localized magnetic moment. In CeOFeAs, the distance between the NN Ce sites is 3.72 Å, slightly larger than in $\gamma-$phase Ce; hence we expect that here the 4f electrons are strongly localized on the Ce sites, giving rise to magnetic moments localized on these sites. We calculate the total energy of an isolated Ce atom for both cases when the atom is nonmagnetic (half the 4f electron is spin-up, the other half is spin-down) and when it is magnetic. We find that the energy difference is

$$E_{\text{magnetic}}(\text{Ce}) - E_{\text{nonmagnetic}}(\text{Ce}) = -0.168 \text{ eV}.$$
cases where \( U-J \) is taken to be 3 eV or 5 eV for both Ce and Pr.

A summary of the total energy calculations is given in Table I, where we report the differences in the total energy among the six cases listed earlier. We take the energy of the NM phase, in which the Fe moments adopt c-AFM order and the Ce ions are nonmagnetic, as our zero energy. The results in Table I show that within GGA, in the absence of the onsite Coulomb interaction, the ground state of CeOFeAs is one where the Fe magnetic moments adopt c-AFM order while the Ce sites are paramagnetic. In the presence of onsite Coulomb interaction, on the other hand, the Fe magnetic moments adopt the c-AFM order and the Ce magnetic moments the z-\( a \)-AFM order. For the case of PrOFeAs, our results indicate that the Pr magnetic moments also adopt the z-\( a \)-AFM order both within GGA and GGA+U. The spin order in this phase is shown in Fig. 2. Indeed, the AFM ordering of the magnetic moments on the Ce sites has been inferred from low temperature specific heat measurements.\(^{25}\) Furthermore, neutron diffraction measurements also revealed an AFM order, at low temperatures, of the Re magnetic moments in ReOFeAs for Re = Ce, Pr, and Nd.\(^{20,21,28}\)

The electronic density of states (DOS) in ReOFeAs in the phase \{Fe: c-AFM; Re: z-\( a \)-AFM\} is shown in Figs. 3 and 4 as calculated within GGA and GGA+U, for Re=Ce, Pr. Note that the GGA calculation produces a wide Re 5d-band and a narrow Re 4f band both crossing the Fermi level; the DOS at the Fermi energy is dominated by 4f states, making ReOFeAs a metal. With onsite Coulomb interaction taken into account, ReOFeAs becomes a Mott insulator. By examining the DOS plots, it is noted that within GGA+U, the Re 4f band splits and moves away from the Fermi level. Photoemission experiments should reveal the positions of these bands,
providing a check on the validity of the results obtained in these calculations.

IV. CONCLUSIONS

In conclusion, the DFT calculations indicate that the Fe magnetic moments in ReOFeAs, Re = Ce, Pr, adopt a collinear antiferromagnetic order, similar to that in LaOFeAs. Whereas the La ion in LaOFeAs is nonmagnetic, the Re ion in ReOFeAs carries a magnetic moment due to its localized 4f electrons. Within GGA+U, we show that the Re magnetic moments also adopt an antiferromagnetic order similar to that adopted by the Fe ions. However, while the Fe ions in the FeAs layer all lie in one plane, giving rise to a collinear AFM order, with stripe-like pattern, the Re ions in the ReO layer lie in two different planes surrounding the oxygen ions plane. In each Re plane, an Re ion is surrounded by four Re ions that have spins opposite to the spin of the central ion. Viewed in this light, we can say that in the ground state, within each Re plane, the spin order is simply antiferromagnetic, where each spin-up site is surrounded by 4 spin-down sites in the same plane. However, for a given spin-up Re ion in a given Re plane, its four NN Re ions all lie in the other Re plane of the ReO layer; of those four NN Re ions, two will be spin-up and two will be spin-down. If we connect each spin-up Re site to its NN spin-up sites within a given ReO layer, we will end up with a zigzag chain running perpendicular to the Fe spin stripes in the Fe-plane. A similar zigzag chain is obtained if we connect NN spin-down Re sites within any one ReO layer.

1 Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
2 H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, and H. Hosono, Nature 453, 376 (2008).
3 H. H. Wen, G. Mu, L. Fang, H. Yang, and X. Y. Zhu, Europhys. Lett. 82, 17009 (2008).
4 D. A. Zocco, J. J. Hamlin, R. E. Baumbach, M. B Maple, M. A. McGuire, A. S. Sefat, B. C. Sales, R. Jin, D. Mandrus, J. R. Jeffries, S. T. Weir, and Y. K. Vohra, Physica C: Superconductivity 468, 21, 2229 (2008).
5 Z. A. Ren et al., Mater. Res. Innov. 12, 105 (2008).
6 X. H. Chen et al., Nature 453, 761 (2008).
7 G. F. Chen et al., Phys. Rev. Lett. 100, 247002 (2008).
8 Z. A. Ren et al., Europhys. Lett. 82, 57002 (2008).
9 Z. A. Ren et al., Europhys. Lett. 83, 17002 (2008).
10 H. Eschrig, arXiv:Cond-mat. 0804.0186 (2008).
11 G. Xu. et al., Europhys. Lett. 82, 67002 (2008).
12 K. Haule. et al., Phys. Rev. Lett. 100, 226402 (2008).
13 S. Ishibashi, K. Terakura, and H. Hosono, J. Phys. Soc. Jap. 77, 053709 (2008).
14 T. Yildirim, Phys. Rev. Lett. 101, 057010 (2008).
15 J. Dong. et al., Europhys. Lett. 83, 27006 (2008).
16 F. Ma. et al., Phys. Rev. B 78, 033111 (2008).
17 C. de la Cruz. et al., Nature 453, 899 (2008).
18 P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2K, an augmented plane wave + local orbitals program for calculating crystal properties (Techn. Universität, Wien, Austria, 2001), ISBN 3-9501031-1-2.
19 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
20 J. Zhao. et al., arXiv:Cond-mat. 0806.2528 (2008).
21 J. Zhao. et al., Phys. Rev. B 78, 132504 (2008).
22 D. C. Koskinen and K. A. Gschneidner, Jr., Handbook on the physics and chemistry of rare earths: Metal. edited by K. A. Gschneidner, Jr. and L. Eyring, (North Holland physics publishing, Amsterdam, 1981, vol 1, chap.4).
23 V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991).
24 M. Cococcioni, and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005).
25 D. A. Anderson, S. I. Simak, B. Johansson, I. A. Abrikosov, and N. V. Skorodumova, Phys. Rev. B 75, 035109 (2007).
26 C. Loschen, J. Carrasco, K. M. Neyman, and F. Illas, Phys. Rev. B 75, 035115 (2007).
27 F. Tran. et al., Phys. Rev. B 77, 085123 (2008).
28 Y. Qiu. et al., arXiv:Cond-mat. 0806.2195 (2008).