

# First Principle Investigation of Structural, Electronic and Magnetic Properties of Perovskite Lanthanum-Iron Oxide (LaFeO<sub>3</sub>) Superconductor

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## Abstract

*Perovskite oxide superlattice of LaFeO<sub>3</sub> has shown varying magnetic, electronic properties through atomic ordering. Recently, LaFeO<sub>3</sub> superlattice has shown an anomalous optical band gap of 1.6 eV, ~1 eV below that of either parent compound, making it suitable for many applications such as solar and superconducting materials. In this work, Density functional theory (DFT) as implemented in Quantum ESPRESSO has been used to investigate the electronic and magnetic ordering of LaFeO<sub>3</sub>. The spin polarization is included throughout the calculation. The results show that the calculated ground state structure for LaFeO<sub>3</sub> was assumed to be orthorhombic and the stable optimized magnetic state was found to be the antiferromagnetic. The electronic band structure, Density of state (DOS) and projected density of state (PDOS) were also obtained, from the results the compound shows an antiferromagnetic behavior with the band gap of about 1.091 eV and average magnetic moments of about 24μB. Finally, from the charge density distributions of LaFeO<sub>3</sub> a strong exchange-correlation dependence of the Compton profiles is found showing a possibility of superconducting nature.*

**Keywords:** Perovskite LaFeO<sub>3</sub>, Density functional theory (DFT), Quantum ESPRESSO magnetic and electronic properties

## 1. Introduction

Recently it has been observed that Perovskite oxides in with the formula of the form ABO<sub>3</sub> (such that A= alkaline-earth metal or La, B= 3d transition metal, O= oxygen) are strong and have a very flexible chemical platforms, which exhibit excellent properties (Howard, & Stokes, 1998). In the ABO<sub>3</sub> system, the A site is occupied for example by Ca, Ba, Sr, or La atoms, while the B site is occupied for example by Mn, Co, Fe, or Cr atoms, resulting in perovskites with desired properties and performance. The diversity of A and B atoms can modify the structural, magnetic, and electronic properties of the perovskites, based on the size and valence electrons of the A and B atoms (Woodward, 1997).

These Perovskite oxides shows a great capability that can be used in many technological applications such as insulator, metal, semiconductor or superconductor because they have delocalized energy bands in some cases, or have localized electrons or some transitions between these two behaviors seen. Moreover, most of the perovskites have different magnetic orders (Itoh, & Hinatsu, 1998) and so, physical and chemical behaviors of them such as the density of states, Fermi surface, dielectric function, and phonon dispersion show special character (Wolfram, & Ellialtioglu, 2006).



Among all prototype of these perovskites, the Rare-earth orthoferrites ( $\text{RFeO}_3$ ; R=rare-earth element) which have orthorhombic structure, proven to have high spin (Mott) insulators (Rozenberg et al, 2005). Experimentally, most of the (physical and chemical the behavior of this type of materials has been examined (Xu, Naaman, Rozenberg, Pasternak, & Taylor, 2001). The experimental results show that orthoferrites undergo magnetic, structural and electronic phase transitions a simultaneously (Xu, Naaman, Rozenberg, Pasternak, & Taylor, 2001). The role of lanthanum orthoferrite ( $\text{LaFeO}_3$ ) in photocatalytic reactions has been showed in recently (Li, et al, 2007). In a catalytic study about this material have revealed a dependence of activity on A-site deficiency (Tijare et al, 2012).

Recently the discovery of 26 K superconductivity in F-doped  $\text{LaFeO}_3$  has been reported (Kamihara, Watanabe, Hirano, & Hosono, 2008)., This finding made the beginning of worldwide efforts to investigate this new family of superconductors (Mazin, Singh, Johannes & Du, 2008; Paglione, & Greene, 2010)., and since then,  $T_C$  has been pushed to over 55 K in related FeAs-based materials (Mazin, Singh, Johannes, & Du, 2008). Like the copper oxides, the iron pnictides have well-defined parent systems, such as  $\text{LaFeO}_3$ .

Although many properties of orthorhombic perovskites  $\text{LaFeO}_3$  have been the subject of many studies within the DFT and experiment, still their electronic structure and conductivity type and the interaction between their ferroelectric, antiferromagnetic and other magnetic subsystems are not yet fully understood

In this study, we have presented a detailed study of magnetic ordering structure, electronic of  $\text{LaFeO}_3$  compound which has orthorhombic crystal structure in Pnma space group within the generalized gradient density functional theory (GGA-DFT) as implemented in Quantum Espresso code.

## 2. Methodology

The structures and total free energies were determined using the density functional theory (DFT) method with plane wave basis and the ultra-soft (Vanderbilt) pseudopotentials within the Quantum-ESPRESSO package (Giannozzi et al, 2009). Ultrasoft pseudo-potentials Perdew-Burke-Ernzerhof exchange-correlation (PBE) functional (Ernzerhof, & Scuseria, 1999), within the Generalized Gradient Approximation (GGA) (Perdew, Burke, & Ernzerhof, 1996) were used, where  $5s$ ,  $5p$ ,  $5d$ ,  $6s$ , and  $6p$  states are considered for La with 11 electrons,  $3s$ ,  $3p$ ,  $3d$ ,  $4s$ , and  $4p$  states for Fe with 16 electrons,  $2s$  and  $2p$  states for O with 6 electrons. The integrations over the Brillouin zone were performed through the point sampling technique of Monkhorst and Pack (Monkhorst and Pack, 1976) with k-points in the relevant irreducible wedge (Perdew et al., 1996). Spin-polarization was considered for all calculations.

The Fermi surface effects were treated by the smearing technique of Fermi-Dirac, using a smearing parameter of 0.003 Ry. An energy threshold defining self-consistency of the electron density was set to  $10^{-6}$  eV and a mixing beta defining mixing factor for self-consistency was also set to 0.2. Using convergence tests, the Kohn-Sham wave functions were expressed with plane wave basis set cut-off energy of 40 Ry and a charge density cut-off of 180 Ry. Also, from convergence tests, a Monkhorst-Pack k-point grid of  $8 \times 8 \times 2$  was used.

## 3. Results and Discussions

### A. Structural Properties

One of the important parameters which can give information about structural stability and synthesizability of a material known as the formation enthalpy ( $\Delta H_f$ ) which can be approximately calculated by using internal energy changes (Shigemi, & Wada, 2004). The formation enthalpy of a solid compound whose chemical formula is  $\text{A}_x\text{B}_y$ , is given by the following formula,

$$\Delta H_f = E_{tot} - (xE_A \text{ bulk} + yE_B \text{ bulk}) \quad (1)$$

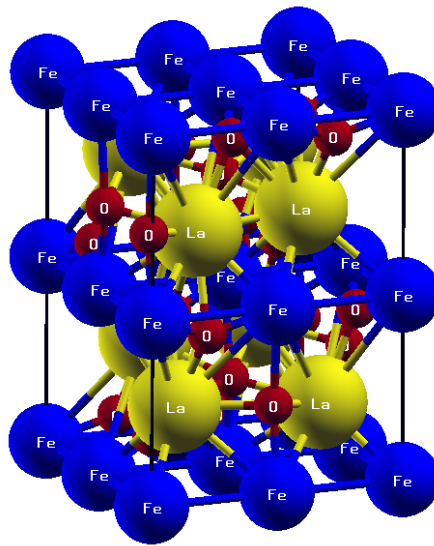
where,  $E_{tot}$  is the total energy of the unit cell.  $E_A \text{ bulk}$  and  $E_B \text{ bulk}$  are the energies of A and B atoms in the ground state crystal structure. Our calculated formation enthalpy value of  $\text{LaFeO}_3$  is found to be -2.963 eV. It can be clearly seen that,  $\text{LaFeO}_3$  is structurally stable and synthesizable material in orthorhombic phase since this material has negative formation enthalpy value. The calculated equilibrium lattice parameters and atomic positions

for orthorhombic phase (Pnma) are tabulated in Table 1. As seen from this table, the calculated lattice parameters for the orthorhombic phase of LaFeO<sub>3</sub> are so close to the available theoretical (Ubic, & Subodh, 2009).

**Table 1.** The calculated equilibrium lattice parameters (*a*, *b*, and *c* in Å), formation enthalpy ( $\Delta H_f$  in B) and atomic positions of atoms for LaFeO<sub>3</sub> compound.

LaFeO <sub>3</sub> (Pnma)	<i>a</i>	<i>b</i>	<i>c</i>	$\Delta H_f$	Atomic Position	$\mu_{tot}$
This work	5.592	5.763	7.941	-2.963	La: 4c (0.439, 0.25, 0.034) Fe: 4b (0.5, 0.0, 0.0) O <sub>1</sub> : 4c (0.709, 0.25, 0.454) O <sub>2</sub> : 8d (0.291, 0.709, 0.545)	20
Experimental	5.556	5.565	7.862			
Theoretical	5.497	5.613	7.799			

Our calculated optimized lattice parameters in orthorhombic phase (Pnma) within DFT-GGA are found to be (*a* = 5.592 Å, *b* = 5.763 Å, and *c* = 7.941 Å), these values are very close to the experimental values and theoretical results reported in (Ubic, & Subodh 2009; Kizaki, & Kusakabe 2012; Ritzmann, Muñoz-García, Pavone, Keith, & Carter 2013). It's clearly seen that the obtained lattice parameters (*a*, *b* and *c*) of this compound within DFT-GGA are only different % 0.65, % 3.5, and % 1.0 from experimental results and % 1.7, % 2.7, and % 1.8 from previous theoretical results, respectively, as seen in Table 1, the optimized structure with these values is given in Figure 4.3



**Figure 1.** The optimized orthorhombic LaFeO<sub>3</sub> structure, with each Fe surrounded by six O atoms to form the FeO<sub>6</sub> octahedral.

Figure 2. shows the optimization of the two magnetic structures, ferromagnetic (FM) and Antiferromagnetic (AFM), from the graph one can see that the AFM state is the most stable for the orthorhombic system. This observation is confirmed by previous theoretical (Zhang, & Yunoki, 2012) and experimental (Gaikwad, Uikey, & Acharya, 2015). Investigations. But experimentally achieving AFM phase in this material required an additional impurity

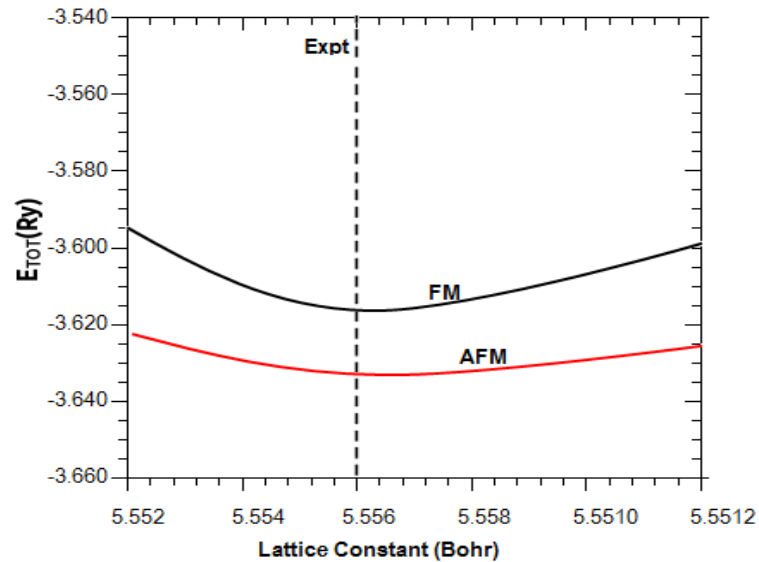


Figure 2. Total energy vs. lattice constant for Two magnetic states (AFM and FM) of orthorhombic LaFeO<sub>3</sub>.

### B. Electronic and Magnetic properties

Figure 3. shows the calculated spin-polarized electronic band structure within DFT-GGA along the high symmetry directions in the first Brillouin zone of this orthorhombic.

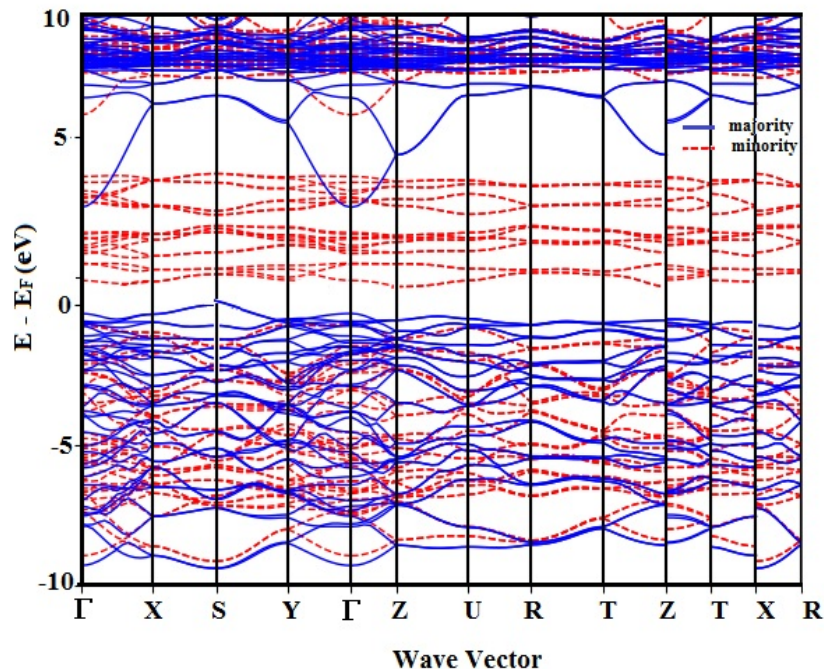
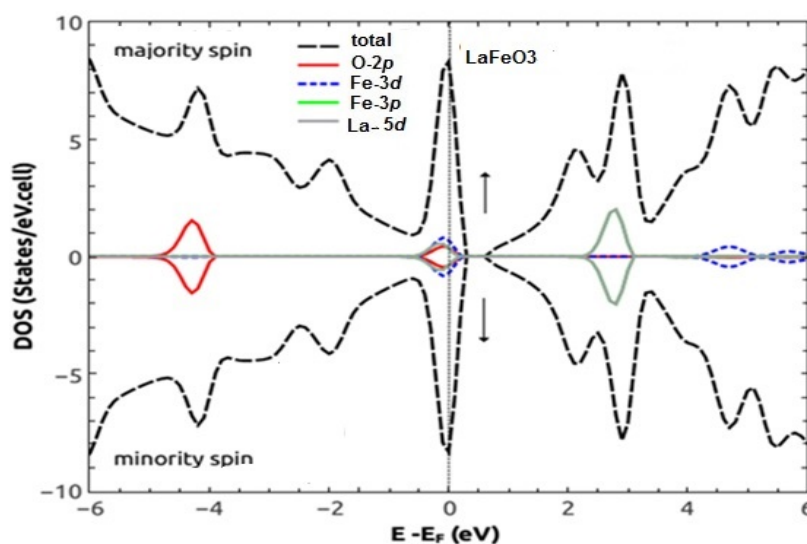


Figure 3. The calculated energy band structure and the total density of electronic state (DOS) which is given between the electronic band structure graphics, within GGA for LaFeO<sub>3</sub> compound. The zero of band energy is shifted to Fermi level ( $E_F$ ).

From the structure one can clearly see that the distribution of majority and minority spin channel of this compound are different and this situation indicates that, this compound has antiferromagnetic behavior with the band gap of about 1.091 eV, in the minority spin part of the compound. This compound clearly shows the behaves as half-metallic in nature with a semiconducting band structure for one spin state (minority spin channel), while the other spin state shows a metallic conduction (majority spin channel). Based on the property of half-metals, the total magnetic moment of this compound is found to be about  $24\mu_B$  because the electronic states about  $E_F$  are only occupied by majority spins.

Figure 4. shows the electronic structures DOS and PDOS of the Fe 3d, O 2p, and La 5d orbitals of the relaxed orthorhombic structure. The analysis of individual orbitals for La, Fe, and O, near the  $E_F$ , shows the important electronic characteristics of the compound. From the graph one can see that the valence region can be considered between -0.5 to -4 eV, and comparing the valence peaks of the O 2p and Fe 3d orbitals, indicate a high degree of hybridization between these orbitals. The VB between -0.5 to -4 eV has approximately the same amount of Fe 3d and O 2p states, indicating a high degree of covalent bonding. The hybridization of Fe 3d and O 2p orbitals are expected in the  $FeO_6$  octahedral and this is demonstrated in the states just below  $E_F$ . 12, 13, 29, the PDOS region between -2 to -3 eV is dominated by O 2p orbitals, and from -0.5 to -2 eV is dominated by Fe 3d orbitals.



**Figure 4.** The total and partial density of electronic states of atoms within DFT-GGA  $LaFeO_3$  compound.

The states above the  $E_F$  can also be categorize into three regions, first from 0.1 to 6 eV (CB), second from 1.0 to 2 eV, and third from 1.5 to 8 eV, respectively. In the first and second region, between 0.1 to 6 eV, the orbitals are dominated by unoccupied Fe 3d states, which are confirmed by experimental observations. (Wadati, et al, 2005). The split between the first and second regions (0.1 to 6 eV) is due to the  $eg-t_{2g}$  crystal-field splitting. (Wadati, et al, 2005). In the third region, between 1.5 to 8 eV, the states are dominated by unoccupied La 5d states, which are confirmed by experimental observations (Wadati, et al, 2005). The presence of unoccupied La 5d states suggests the lack of covalent bonding between La-O and the bonding is more ionic in nature.

### C. Charge Density Analysis

The two-dimensional electron density distributions in the (100) miller planes for Fe and the first neighboring O atoms are shown in figures 5. (a), for  $x=0, 0.5$  and  $1.0$ . Similarly, figures 4.7 (b), show the two-dimensional electron density distributions in the (200) miller planes for La and neighboring O atoms, for  $x=0, 0.5$  and  $1.0$  respectively. From the 2D electron density plot, it is obvious that, the contour lines are extended from Fe to O atom and also from La to O atom, which is an indication of the decrease in the ionic behavior of the systems.



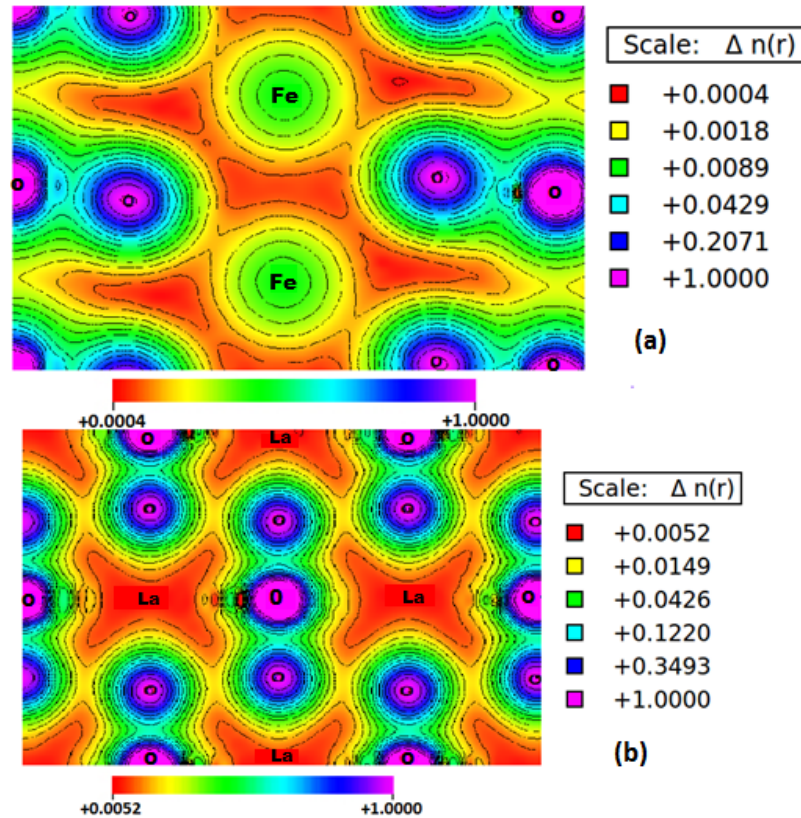


Figure 5 (a) Two-dimensional electron density distribution in the unit cell showing Fe–O1 bond in the (1 0 0) plane (b) showing La–O1 bond in the (2 0 0) plane

The value of the charge density at  $x=0$ , shows that the bonding between Fe and First neighboring O atoms and La and O atoms show an electron density with the values as  $0.3562 \text{ e}/\text{\AA}^3$  (at Fe–O bond) and  $0.1132 \text{ e}/\text{\AA}^3$  (at La–O bond). At  $x=0.4$ , the value of the charge density along the Fe–O bond and also along the La–O bond, further increases showing higher values as  $0.5348 \text{ e}/\text{\AA}^3$  (at Fe–O bond) and  $0.2293 \text{ e}/\text{\AA}^3$  (at La–O bond) which leads to decrease of the ionic behavior of the system and it results in antiferromagnetic behavior.

Similarly, in each case one can observe that the layer thickness of the charge distributions decreases, the contour distribution order is gradually improved with the increasing energy gain and strengthened Fermi surface gapping, while the superconductivity nature expected to be weakened due to the increasingly reduced Fermi level density of states in the high contour distribution state. These results well explain the observed opposite thickness dependencies of contour distribution and superconducting transition temperatures and uncover the nature of competitive interaction between the two collective orders in  $\text{LaFeO}_3$ .

#### 4. CONCLUSION

In conclusion, the theoretical investigation on the structural, electronic, and magnetic properties of the magnetic transition metal oxides  $\text{LaFeO}_3$  in orthorhombic structure within the DFT-GGA as implemented in Quantum ESPRESSO have been presented in systematical way. Ultrasoft pseudo-potentials were used, where  $5s$ ,  $5p$ ,  $5d$ ,  $6s$ , and  $6p$  states are considered for La with 11 electrons,  $3s$ ,  $3p$ ,  $3d$ ,  $4s$ , and  $4p$  states for Fe with 16 electrons,  $2s$  and  $2p$  states for O with 6 electrons. The compounds show a stable antiferromagnetic phase in ground states. The integrations over the Brillouin zone was performed through the point sampling technique of Monkhorst and Pack with  $k$ -points in the relevant irreducible wedge. Spin-polarization was considered for all calculations.

$\text{LaFeO}_3$  shows a stable orthorhombic antiferromagnetic phase with a band gap of about 1.09eV. Similarly, both from the DOS and the electronic band Structure the majority spin channel resulting in a half-metallic character



has been observed. As a typical property of half-metallic compounds, a total magnetic moment is found to be about  $24\mu_B$ . Finally, from the charge distribution contour the material indicated clearly a possibility of been superconductor in nature.

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