Study of Electronic Properties and Chemical Bonding of Perovskite LaFeO\textsubscript{3}

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Abstract:
LaFeO\textsubscript{3} is one of the prominent perovskite used as catalyst for methane combustion, thin film gas sensors and cathode materials for solid oxide fuel cells (SOFCs) and many electronic devices used for photo voltaic applications. Electronic properties of perovskite lanthanum ferrite (LaFeO\textsubscript{3}) have been studied using Tight Binding Linear Muffin-Tin Orbitals Atomic Sphere Approximation (TB-LMTO-ASA) and LDA+U approximation. In this strongly correlated system, it is important to treat large on-site Coulomb interactions and their screening effects. The localization of wave functions of La 4f and 3d orbitals of Fe is crucial. The band gap of LaFeO\textsubscript{3} is found to be 1.74 eV using LDA+U approximation which agreed well with experimental value 2.1 eV. From density of state (DOS) calculations, the magnetic moment of Fe atom on LaFeO\textsubscript{3} is found to be 4.23 $\mu_B$ using LDA+U method which also agreed well with experimental value 4.6$\mu_B$ within 8% discrepancy. From DOS as well as charge density analysis, it is found that bonding between Fe and O is mainly covalent in nature whereas La-O bonding is found to be ionic.

Keywords:
Perovskite, TBLMTO-ASA, L(S)DA+U, Electronic and Magnetic Properties, Chemical Bonding

1. Introduction

In recent years there has been a lot of attention focused on the perovskite-type oxides (general, formula ABO\textsubscript{3}, A and B are the metallic ions) due to their potential commercial applications as catalysts for various reactions and their interesting physical effects: colossal magneto resistance (CMR) \cite{1,2}, giant magneto-caloric effect (GMCE), and high thermoelectric performance (TEP) at high temperature. LaFeO\textsubscript{3} is studied as a thermoelectric material with high Seebeck coefficient and high power factor and it can be used as catalyst for methane combustion, the thin film gas sensors \cite{3,4}. The LaFeO\textsubscript{3} thin film can be used as sensitive O\textsubscript{2} gas sensors and nano-sized LaFeO\textsubscript{3} powder can be used as catalyst for the auto reforming of sulfur-containing fuels or for partial oxidation of methane (POM) to (H\textsubscript{2} /CO) \cite{5}. The
interest on such materials is also due to searching of potential candidates for the use in photo voltaic, photo catalytic and other photo active applications [6,7,8].

The local density approximation (LDA) or the generalized gradient approximation (GGA) to density functional theory (DFT) has been widely used to study electronic structures, density of state and charge density. However, these values are not predicted consistently with experimental values due to large on-site Coulomb interaction and the remaining of the self-interaction. On the other hand, LSDA+U method with the on-site Coulomb interaction U of the Hubbard-type Hamiltonian can remove the self-interaction and makes wave functions localize [9]. On-site Coulomb interaction of d-d electrons is screened by other non-3d electrons and affected by the hybridization between Fe(3d)-O(2p) and Fe(4s)-O(2p) electrons in LaFeO₃ and the lattice relaxation effects in crystal. All those factors may reduce the value of the interaction constants U and J, where J is the exchange parameter [10].

Spin polarized DFT calculation of LaFeO₃ were performed by Lee et al. [11] using VASP within GGA+U approximation. The band gap and magnetic moment (Fe) for LaFeO₃ are 2 eV and 4.1 μB respectively using U=7 eV and J=1 eV (U_eff=6 eV)[11]. The band structures of the LaFeO₃ compound is calculated by the abinitio pseudopotential method with the VASP program package [12]. According to Shein et al. [12], the band gap and the magnetic moment (Fe) for the LaFeO₃ compound are 2.78 eV and 4.23 μB respectively using U =6.0 eV and J=0.6 eV (U_eff =5.4 eV) [12]. The experimental values of the band gap and the magnetic moment (Fe) for the LaFeO₃ are approximately equal to 2.1 eV and 4.6 ± 0.2 μB [13].

In this paper, we investigated the electronic and magnetic properties of LaFeO₃ using atomic sphere approximation in density functional theory within LDA and LDA+U using TB-LMTO-ASA code [14]. The main motivation towards the TBLMTO-ASA is due to successful study of our previous work [15,16,17,18] and now want to apply on LaFeO₃ to go more insight on it. The organization of present paper is as follows: The computational detail and theoretical background for the calculation is described in section II. The results of the present work has been described in section III which are also discussed and analyzed in the same section and finally Section IV consists of concluding remarks of the present work.

2. Materials and Methods

The first Principle calculation of the perovskite LaFeO₃ is performed using atomic sphere approximation implemented in TB-LMTO code [14]. The exchange correlation potential is calculated within LDA and LDA+U approximation. In TB-LMTO-ASA method, the Wigner-Seitz cell is replaced by an atomic sphere having the same volume. Atomic sphere approximation which takes the potential has muffin-tin form, i.e. spherically symmetric inside Wigner-Seitz (WS) spheres whose overlap is neglected and flat in the interstitial region due to tail cancellation [14,19]. Mathematically the muffin-tin potential in the LMTO is defined as

\[
V_{\text{MT}}(r) = \begin{cases} 
V(r) - V_{\text{MTZ}} & \text{for } r \leq a \\
0 & \text{for } r > a 
\end{cases}
\]

(1)

In which \(V(r)\) is spherically symmetric and \(V_{\text{MTZ}}\) has constant value and is negative in sign. In perovskite LaFeO₃, the sphere radii (a) used for iron, lanthanum and oxygen are 2.26 a. u. (1.19 Å), 3.94 a.u. (2.08 Å) and 2.02 a. u. (1.07 Å) respectively. The wave function in the region \(r > a\) is expanded in term of the phase shifted wave in
contrast to the plane wave expansion in APW method. To make a computationally more efficient eigenvalue problem, Anderson replaced the energy variable $E$ in $R_1(E, r)$ by a fixed but arbitrary energy $E_0$ and constructed energy independent muffin-tin orbitals composed of the partial radial wave function $R_i(E, r)$ and their first energy derivatives $R_i'(E, r)$ [19] APW method.

The self-consistent band structure has been calculated by using the atomic-sphere approximation linear muffin-tin orbitals (ASA-LMTO) method, in which the on-site Coulomb interaction $U$ correlation has been taken into account. Based on the original LSDA+U method first proposed by Anisimov [20, 21, 22], the orbital-dependent one-electron potential used in our calculation has been written in the form [23]:

$$V_{m_1,m_2}^\sigma = \sum U_{m_1,m_2,m_1',m_2'} (n_{m_1,m_2}^\sigma - \bar{n}_{m_1',m_2'}) + \sum (J_{m_1,m_2,m_1',m_2'} - J_{m_1,m_2,m_1',m_2''}) (n_{m_1,m_2}^\sigma - \bar{n}_{m_1',m_2'})$$

(2)

Where $m$ ($m_1$, $m_2$) and $\sigma$ represent the orbital and spin respectively. $n_{m_1,m_2}^\sigma$ is the density matrix [14]. $\bar{n}_{m_1',m_2'}$ is the $m_1' m_2'$-dependent average density i. e. $\bar{n}_{m_1',m_2'} = \langle \hat{n}_{m_1',m_2'} \rangle$. The matrix elements $U_{m_1 m_2 m_1' m_2'}$ and $J_{m_1 m_2 m_1' m_2'}$ can be expressed in terms of complex spherical harmonics and effective Slatter integrals $F_k$. For d-electron $U=F^0$ and $J = (F^2 + F^4)/14$ ($F^4 / F^2 \approx 0.625$ for 3d-electrons). If the averaging parameters $U$ and $J$ are known, the $F^0$, $F^2$ and $F^4$ can be obtained from above equation & hence two matrices $U$ and $J$.

In spherical LDA+U method, the matrix of the one electron potential is given by equation as,

$$V_{m_1,m_2}^\sigma = V_{LDA} + (U-J) \left( \frac{1}{\xi} \delta_{m_1 m_2} - n_{m_1,m_2}^\sigma \right)$$

(3)

and the corresponding total energy is expressed as,

$$E = E_{LDA} + \frac{(U-J)}{2} \left( \sum n_{m_1,m_2}^\sigma - \sum n_{m_1,m_2}^\sigma \right)$$

(4)

In Eq.(4) the interaction between electrons with opposite spins $U_{m_1 m_1}$ is not included; it has been canceled by the same term appearing in the corresponding double counting energy, which represents the interaction energy between localized electrons considered in the standard LSDA. Thus, only the Coulomb interaction between the localized electrons with the same spin is considered in this scheme [10].

In the LDA+U method, the electrons are divided into two classes: delocalized $s, p$ electrons which are well described by LDA and localized $d$ or $f$ electrons on which orbital-dependent potential is used. It is known that the on-site Coulomb interaction $U$ in a strong-correlated system can shift the LDA occupied orbitals about -$U/2$ and unoccupied ones by $U/2$, which lead to opening of a gap by $U$ for a single-d band system [10].

3. Results and Discussion

The stable structure, band structure and density of states with some discussions are explained within this section. Moreover, it also contains bonding effects and charge density distribution plots for element and compound has been discussed within this section.
3.1. Stability and Electronic Calculations

The perovskite LaFeO₃ compound has cubic structure with space group Pm-3m (221) [14, 24]. The atomic position in the elementary cell are Fe, 1a (0, 0, 0); La, 1b (1/2, 1/2, 1/2) and O, 3d (0, 0, 1/2). The experimental value of lattice parameter is 3.93 Å (7.42 a.u.) [13]. In structure shown in Fig.1, the Fe cation is 6-fold coordinated and the La cation is 12-fold coordinated with the oxygen anions. The La atom occupies the center of the cube, while the Fe atoms at the corners bond with the adjacent oxygen atoms to form the FeO₆ octahedra. The inter-atomic distances and the unit cell parameter (a) are related as follows: Fe–O = a/2, O–O = La–O = a/√2 and Fe–La = a√3/2. Using 3.93Å (7.42 a. u) as lattice parameter, we have calculated band structure of lanthanum ferrite.

![Figure 1. Crystal structure of lanthanum ferrite showing FeO₆ octahedra [24].](image1)

![Figure 2. Comparison of band structure and density of state of LaFeO₃ using LDA+U.](image2)

Band structure of LaFeO₃ in the high symmetry directions in the Brillouin zone is shown in Figure 2. Zero of energy represents the position of Fermi level. There are 31 bands in total. 9 valance bands are due to O 2p-orbitals. These 9 valence bands at Γ point are three fold degenerate levels (¹Γ₁₅ , ²Γ₂₅ , ²Γ₁₅ ) with energy separation 0.82 eV (¹Γ₁₅ − ²Γ₂₅ ) and 2.61 eV (Γ₂₅ − ²Γ₁₅ ) due to electrostatic interaction between O 2p-orbitals and by crystal field.

![Figure 3. Partial density of states for LaFeO₃. Zero of energy scale represents the position of Fermi level.](image3)

The bottom of the conduction band mainly consist of mixture of Fe 3d and La 5d-orbitals. Major contribution of Fe 3d and La 5d-orbitals are around 0.5 - 4 eV and 1 - 6 eV respectively. The 4f-orbitals of La are 7 eV above from Fermi level with
bandwidth 2 eV as shown in Figure 3. From partial density of states in Fig. 3, there exist strong p-d hybridization between O 2p and Fe 3d-orbitals in valance band around -5eV.

From LDA calculation, it is found that LaFeO$_3$ is metallic which agree with other LDA calculation [12,13]. But strongly correlated system LaFeO$_3$ is Mott insulator and has band gap. LDA fails to explain strongly correlated system because of orbital dependent potential and localized d and f-electrons. This paper used LDA+U method to open band gap. Direct band gap appears between the top of the valence band and bottom of the conduction band at $\Gamma$ point. The calculated band gap is 1.74 eV which is smaller than experimental value of 2.1 eV [15] band gap. This discrepancy is due to suppression of Jahn-Teller distortion and use of local density approximation which underestimates the band gap even for insulator. Comparison of band gap and magnetic moments are shown in Table I.

**Table I.** Comparison of the calculated and experimentally observed bandgap, magnetic moment of atoms for cubic FM-LaFeO$_3$.

<table>
<thead>
<tr>
<th>System</th>
<th>This work</th>
<th>Shein et al.[14]</th>
<th>Lee et al. [13]</th>
<th>Expt. [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeO$_3$ (Band gap) (U = 7.5 eV, J = 0.5 eV for La and U = 8.30 eV, J = 0.87 eV for Fe)</td>
<td>1.74 eV</td>
<td>2.00 eV</td>
<td>4.1</td>
<td>4.6 ± 0.2</td>
</tr>
<tr>
<td>Fe magnetic moment ($\mu_B$)</td>
<td>4.23</td>
<td>4.32</td>
<td>4.1</td>
<td>4.6 ± 0.2</td>
</tr>
<tr>
<td>O magnetic moment ($\mu_B$)</td>
<td>0.26</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total magnetic moment ($\mu_B$)</td>
<td>4.49</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**3.2. Chemical Bonding**

Ionic character in the material arises due to charge transfer between anion and cation. There exist a significant hybridization of Fe 3d with O 2p-orbitals in LaFeO$_3$ as shown in above section. This implies that the bonding in the system is not purely ionic but contains covalent character to large extent. To understand the types of chemical bonding among La, Fe and O atoms in LaFeO$_3$, charge density distribution are shown in (100) and (110) planes in Figure 4 and Figure 5 respectively.

**Figure 4.** The valance charge distribution for LaFeO$_3$ in (100) plane(a) in two dimensions and (b) in three dimensions.

There is sharing of charge between Fe and O due to Fe 3d and O 2p hybridization as shown in the Figure 4. Bonding between Fe and O is covalent in nature. Charge distribution around La site in (110) plane shown in Figure 5 indicates no charge...
sharing among the contours of La and O atoms. Bonding between La and FeO$_3$ is ionic.

![Figure 5](image)

**Figure 5.** The valance charge distribution for LaFeO$_3$ in (110) plane (a) in two dimensions and (b) in three dimensions.

4. Conclusions

In this paper, we have investigated the electronic properties and chemical bonding of LaFeO$_3$ in cubic phase using TB-LMTO-ASA method with in LDA+U approximation. Band gap in LaFeO$_3$ is direct band gap at high symmetry Γ point in Brillouin zone. Band gap calculated in present work is 1.74 eV using LDA+U method and is smaller than the experimentally reported value 2.1eV because of suppression of Jahn-Teller distortion and use of local density approximation. From density of state calculation, magnetic moment of Fe atom in LaFeO$_3$ is found to be 4.23 μ$_B$ which agrees well with other theoretical calculations and experimental value 4.6 μ$_B$. Chemical bonding in LaFeO$_3$ is also analyzed. The bonding between Fe and O is mainly covalent bonding because of hybridization of Fe 3d with O 2p in LaFeO$_3$.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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References


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