

***Ab-initio* LSDA Study of the Electronic States of Nano Scale Layered LaCoO₃/Mn Compound: Hubbard Parameter Optimization**

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Abstract: Influences of spin polarization on the electronic traits of undoped and Mn-doped LaCoO₃ nano scale layers in the rhombohedral phase have been investigated in this paper. First, we employed the local density approximation (LDA) method with the generalized gradient approximation (GGA) under density functional theory (DFT). The calculated results did not show an appropriate consistency with experimental values. Knowing the presence of 3d orbitals in Co atom, to taking account the strong localization of electrons, we used the local spin density approximation plus a Hubbard-like term (LSDA+U). Calculations were performed using different U values at low temperature and the obtained results showed high consistency with the experimental values and the optimum results were obtained for U=1. The calculated band structures along with the partial densities of states (PDOS) shows the nonmagnetic nature of LaCoO₃ at low temperatures. Also, adding Mn has a significant effect on the electronic properties of LaCoO₃. It was revealed that Mn changes the nonmagnetic characteristic of the compound to the magnetic feature. The bandgap values for spin up (SU) and spin down (SD) states have been calculated 0.9 eV and 1.2 eV, respectively and both states have direct bandgap.

Keywords: Perovskite, DFT, LSDA+U, Electronic Properties, Bandgap.

1. INTRODUCTION

Complex perovskites oxides are very intriguing candidates for superconductivity, ferroelectricity, charge ordering and spin dependent transport [1]. These materials are also very promising choice for clean energy resources [2,3]. Furthermore, owing to high electrical and ionic conductivity, LaCoO₃ possesses a remarkable industrial interest. Having Co ions in low spin state with total spin S=0, it does not show magnetic properties at low temperatures [4]. At T=90K, the semiconductor becomes a paramagnetic compound while above

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500K a transition to metallic behavior happens and the cobalt ions can be found either in high ($S=2$) or intermediate ($S=1$) spin state [5]. To describe the mentioned variations, fundamental study of the band structure of the compound seems necessary [6-10]. The bulk LaCoO_3 has been studied in details by density functional theory (DFT) method [11-13]. To our best knowledge, the layered structure of the material has not been studied by DFT. In the meantime, the strong Coulomb interaction between 3d electrons cannot be explained appropriately by local density approximation (LDA) or GGA [14]. Korotin *et al.* [15] used Hubbard U parameter (LDA+U) to explain the Coulomb repulsion among the 3d electrons. Hsu *et al.* supposed that the U parameter was a function of structure [16]. Lee *et al.* suggested that U value needs to be modified for being consistent with the experimental oxygen binding energy [17]. Pandey *et al.* [18] proposed that plus Hubbard parameter; the spin-orbit coupling has also to be considered to calculate a persuasive valence band structure. Buckeridge *et al.* [19] used a wide range of standard density functional theory approaches to modeling the perovskite LaCoO_3 , focusing on optimizing the Hubbard U parameter in order to determine the most appropriate method to study defect formation and the effect of spin on local structure. They demonstrate that the generalized gradient approximation (PBEsol+U) is most appropriate for studying structure versus spin state, while the local density approximation (LDA+U) is most appropriate for determining accurate energetics for defect properties. Xiao *et al.* [20] investigated the structural, vibrational, phonon dispersion spectrum, and thermodynamic properties of LaCoO_3 using the projector augmented wave (PAW) pseudopotentials within GGA + U and LDA + U to describe the 3d electrons. They calculated the related thermodynamic properties such as heat capacity, entropy, free energy, and the coefficient of thermal expansion at various temperatures from the lattice dynamical data obtained by quasi-harmonic approximation. Reviewing more papers shows that to close the theoretical results to the experimental reports, various modifications have been taken into account in DFT methods. In this project, different proposed ways were tested to obtain reasonable band spectra for the layered LaCoO_3 compound. Amongst them, most prominent within the framework of DFT was the local spin density approximation plus Hubbard parameter (LSDA+U). LSDA+U is specifically advantageous because of less demanding computational procedure that enables it to be used easily for larger systems. Besides, with LSDA+U it is doable to systematically enhance the strength of the on-site repulsion U for getting insight into the influence of Coulomb correlations. The total energy in the LSDA+U route is the summation of the LSDA total energy and a Hubbard-like term.

The LSDA+U method has shown to be successful in reproducing the accurate

band structure of the Mott insulators [21]. Mott materials possess a partially filled d (or f) shell, and a d-d (or f-f) bandgap. This bandgap is created by a large on-site Coulomb repulsion that splits the d (or f) bands in a lower (occupied) and upper (unoccupied) Hubbard band. Hao Liu et al. [22] made comparisons of experimental XAFS data of Sr doped LaCoO₃ samples taken at room temperature and LDA+U (with U = 0, 4eV and 8eV, respectively) model calculations of LaCoO₃. They found that when U takes 4eV or 8eV, the ground state of LaCoO₃ is Mott insulator and the curve shape of calculated XAFS data was even the same as that of the experimental data; when U=0 the HOMO-LUMO band gap vanished and the calculated XAFS data got an extra peak. H.A. Rahnamaye Aliabad et al. [23] studied the spin polarization effects on electronic properties of pure LaCoO₃ and doped compounds (La_{0.5}Y_{0.5}CoO₃, LaCo_{0.5}Mn_{0.5}O₃) in the rhombohedral phase. They employed the full potential linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA+U) under density functional theory. They found that Mn alters insulating behavior of this compound to the half metallic for spin up state. However, their evaluated band structure did not show appropriate consistency with experimental results. In the present study, using LSDA+U, we try to reconstruct the band structure of the Mn-doped LaCoO₃ layered structure.

2. COMPUTATIONAL DETAILS

The crystal structure of LaCoO₃ is rhombohedral with $R\bar{3}c$ crystal symmetry (Fig.1) at room temperature [23]. This structure shows the highest stability up to 1600 K [24].

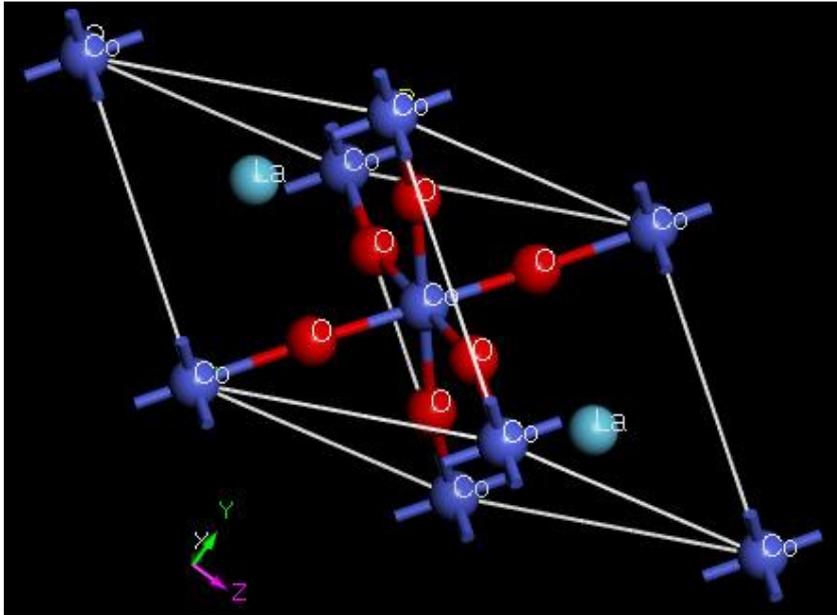


Fig.1. Unit cell of rhombohedral LaCoO_3 .

In the present study we perform DFT calculations using CASTEP package [25]. The electronic properties of pure and Mn doped LaCoO_3 thin films with nanometer scale were studied using a $2 \times 2 \times 1$ supercell with host Co atoms (Fig.2) substituted by one Mn atom.

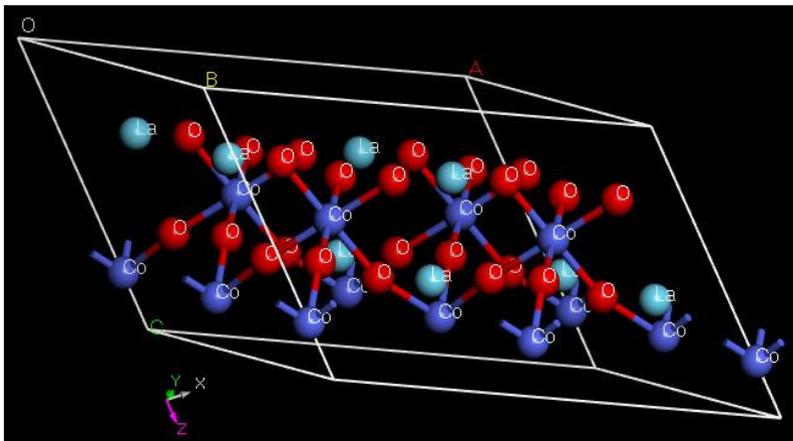


Fig.2. The side view of the optimized structure of $2 \times 2 \times 1$ structure of LaCoO_3 nanostructured layer.

A LaCoO₃ (001) slab surface containing 1 layer of LaCoO₃ atoms and two vacuum of 10 Å upper and bottom of the slab was constructed.

To optimize the structure, the exchange–correlation functional within the local spin density approximation plus a Hubbard-like term (LSDA+U) was employed. Calculations were performed using different values of U. The structures of LaCoO₃ at 4.2-1248 K were taken from Ref. [26].

3. RESULTS AND DISCUSSION

3.1 Electronic Properties of Undoped LaCoO₃ Layer

The study of band structure is crucial for understanding the electronic properties of a material. The calculated band structures of pure LaCoO₃ layers in spin-up (SU) and spin-down (SD) states for different values of Hubbard term are shown in Fig. 3.

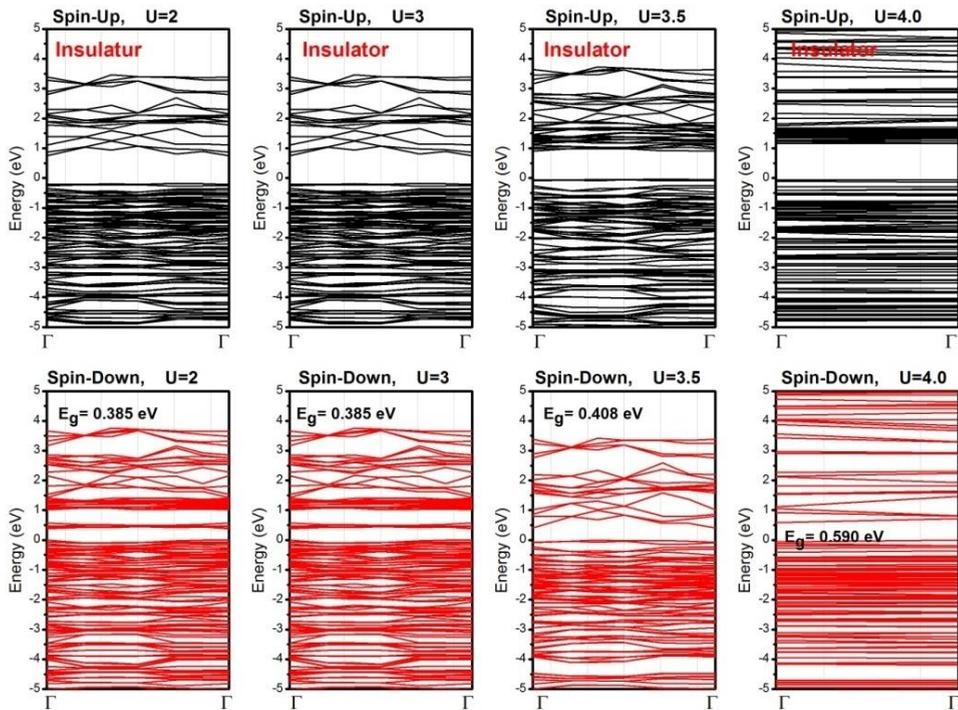


Fig.3. Calculated band structure of spin-up and spin-down states of undoped LaCoO₃ nano scale layer based on LSDA+U approach for different values of U.

From the figures, it is found that the SU states of the compound are insulator while the SD states of the pure LaCoO₃ layers are semiconductor. However, LSDA evaluates a metallic feature for LaCoO₃ at SD opposite to experiment. This may be due to that LSDA usually overestimated the tendency of delocalization. Adding U term heals this drawback. This confirms the accuracy of the LSDA+U method that has been used here. When Hubbard U was introduced (LSDA+U), the occupied states were pushed down, while empty states went upward, as shown in Fig.3. We can see that the width of band gap clearly depended on the value of U. The band structure for different values of U is direct with the values increasing from 0.385 eV (U=2) to 0.590 eV (U=4). The experimental bandgap value of LaCoO₃ was estimated to be 0.3-0.9 eV [27-29]. It is seen the obtained results by LSDA+U are well consistent with the experimental data. The difference between SU and SD band structures imply that the compound is spin polarized.

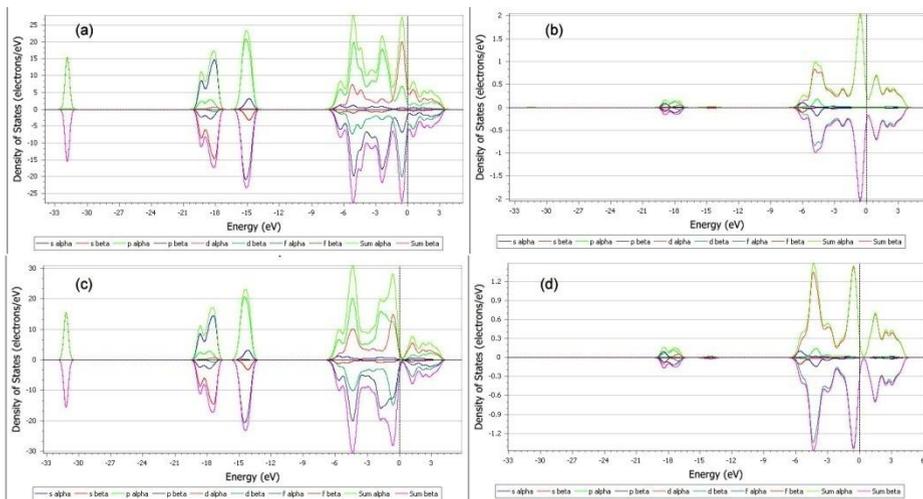


Fig. 4. PDOS of LaCoO₃ nano scale layer based on LSDA+U approach for different values of U: (a) U=2, (b) U=3, (c) U=3.5 and (d) U=4.

The total DOS and partial DOS (PDOS) of LaCoO₃ nano scale layer are shown in Fig. 4 for different values of U. The plots of the DOS for the SU states given in Fig. 4 show that the orbital states in the lowest energy region (below 4.2 eV) are mainly linked to La-p and O-s, and the peaks below the Fermi energy can be assigned to Co-d and O-p states. On the other hand, states in the conduction band are chiefly due to La-f with a little share of La-d and O-p.

PDOS spectra also confirm the magnetic characteristic of the band structure of LaCoO₃ nano scale layer. It has been illustrated that LaCoO₃ is a

nonmagnetic material at low temperature [15]. It has been found that a transition from a nonmagnetic to a magnetic state occurs for LaCoO₃ with temperature increment [27]. When the temperature is very low (lower than 90 K), Co³⁺ locates in the low spin state ($t_{vg}^{\uparrow} e_g^{\downarrow}$, S=0); around 90 K, it undergoes a thermal excitation and a magnetic state emerges that is called the intermediate spin state ($t_{vg}^{\downarrow} e_g^{\uparrow}$, S=1); and when the temperature reaches 1210 K, the high spin state ($t_{vg}^{\uparrow} e_g^{\uparrow}$, S=2) becomes dominated. Results obtained in the present study show high consistency with the experimental data compare to the other DFT calculated results [15, 30].

3.2 Mn-doped LaCoO₃ nano scale layer

The variation of the band structure and PDOS of the SU and SD states for Mn-doped LaCoO₃ nano scale layer are shown in Figs. 5 and 6, respectively. To the best of our knowledge, applying hybrid DFT to examine the spin excited states for Mn-doped LaCoO₃ layers has never been reported. Mn-doped LaCoO₃ would have the characteristics related to both Mn and Co. Different values of U were tested to obtain the electronic properties of Mn-doped LaCoO₃ nano scale layer and the optimum results were obtained for U=1.

It is clear from Fig. 5 and Fig.6 that the valence band for SU state is composed of the electronic orbitals of Co-d, O-p, O-s and Mn-d. The states above the Fermi level are composed of La-f, Mn-d and O-p, while in the SD state of Mn-doped LaCoO₃ the states below the Fermi level are related to O-p, La-p, O-s and Mn-p. The principal contribution to the conduction band is from Co-d and La-f with a little contribution of Mn-d and La-d.

LaCoO₃ has a rhombohedrally distorted perovskite structure. Introducing Mn to the compound causes substitution of some Co sites by Mn atoms. In such a crystal field (D_{3d} symmetry), the five 3d orbitals are grouped into two doublets and one singlet. One of the doublets has orbitals oriented toward oxygen, showing much e_g character, while the other has orbitals pointing away from oxygen. The singlet, pointing away from oxygen, is exactly dz². For SU Co (Mn), the majority-spin electrons occupy all five orbitals, forming a spherically shaped charge distribution that gives a negligible EFG. V_{zz} SU is mainly contributed by the minority-spin electron, occupying the singlet dz² orbital that leads to a large in magnitude EFG. For SD Co (Mn), the three orbitals pointing away from oxygen are doubly occupied.

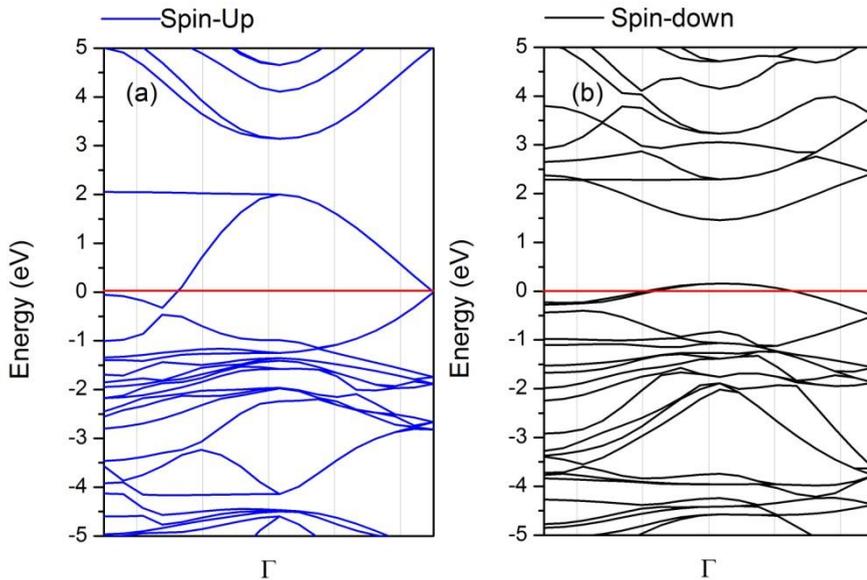


Fig. 5. Calculated band structure of spin-up (a) and spin-down (b) states of Mn-doped LaCoO₃ nano scale layer based on LSDA+U approach for U=1.

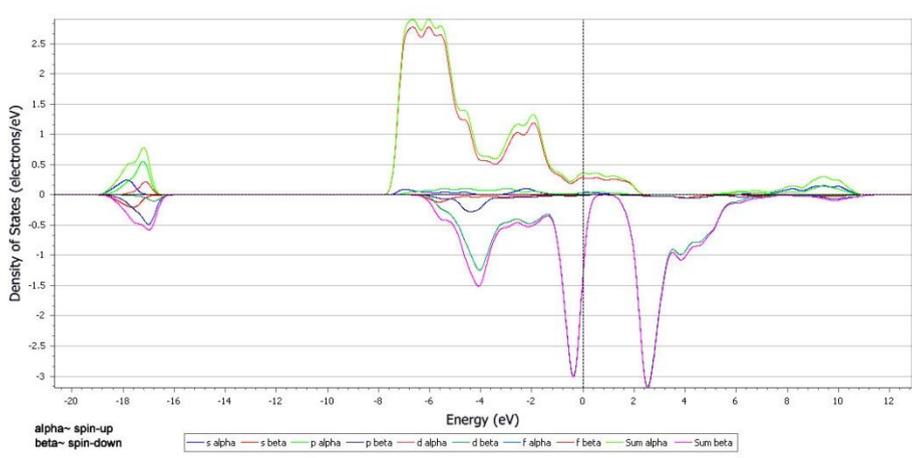


Fig.6. PDOS of Mn-doped LaCoO₃ nano scale layer based on LSDA+U approach for U=1.

From Fig. 5, the bandgap values for SU and SD states are 0.9 eV and 1.2 eV, respectively. As well, both states have direct bandgap. Meanwhile, the substitution of La by Mn changed the bandgap of both SU and SD states. However, the difference between bandgap for SU and SD states is an indication

of spin polarization in the compound.

CONCLUSION

In this study, a systematic DFT calculation based on LSDA+U approach was carried out on different spin states for undoped and Mn-doped LaCoO₃ nano scale layer at room temperature. For undoped LaCoO₃ the calculated band structures for SU states showed an insulator behavior while the bandgap value for SD state increased as the U value changed from 2 to 4. The evaluated results agreed well with experimental measured data. For Mn-doped LaCoO₃ nano scale layer, it was observed that adding Mn caused intense spin polarization. Also, both SU and SD states were semiconductor with higher bandgap values than that of undoped one.

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