

# Ab-Initio Study of Magnetic and Electronic Properties of Co/Ni Substituted Li<sub>2</sub>O

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**Abstract**— Using the ab-initio calculations based on the density functional theory (DFT), we have studied the magnetic and electronic properties of Co/Ni substituted Lithia (Li<sub>2</sub>O). The calculations were performed using Vienna Ab-initio Simulation Package (VASP). We have performed calculations for Li<sub>1.875</sub>Co<sub>0.125</sub>O and Li<sub>1.875</sub>Ni<sub>0.125</sub>O compounds which correspond to the replacement of one Li atom by one Co/Ni atom in the supercell which contains 24 atoms. From the calculated total energies of the ferromagnetic and nonmagnetic phases of these compounds, we have found that the ferromagnetic phase is stable over the nonmagnetic phases. Our calculation shows that a single Co/Ni atom substitution can induce dilute magnetic semiconducting property in Li<sub>2</sub>O. Thus our results suggest that the Co/Ni substituted Li<sub>2</sub>O may be useful materials in semiconductor spintronics.

**Keywords**- half-metallic ferromagnetism, dilute magnetic semiconductors, ab initio study, lithium based compounds

## I. INTRODUCTION

The recent advances in the semiconductor spintronics materials has created substantial interest, due to the fact that they can offer the possibility of materials for information processing and storage functionalities in the same system. In general such materials are required to exhibit magnetism and semiconducting properties simultaneously. The room temperature ferromagnetism in dilute magnetic semiconductors (DMS) is one of the exhaustively studied research areas [1] in the field of spintronics. Half-metallic ferromagnetism plays a major role in this area. From the applications point of view, DMS materials exhibiting half-metallic ferromagnetism around the room temperature is desired for spintronics devices. Half-metallic ferromagnetic materials possess 100% spin polarization and shows metallic character in one spin channel while showing semiconducting nature in other spin channel [2].

Past studies on dilute magnetic semiconductors based on III-V and II-VI semiconductors with transition metals have shown ferromagnetism only at low temperatures [3, 4]. For spintronics applications, the room temperature ferromagnetism in this material is desired. Oxide based dilute magnetic semiconductors are expected to satisfy this condition [5]. Hence a number of transition metal substituted semiconducting oxides like ZnO, SnO<sub>2</sub>, TiO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> compounds have been studied [6]. Room temperature ferromagnetism in these materials has been predicted using first principles calculations which have initiated a number of experimental investigations on these systems [7].

Lithium oxide or Lithia (Li<sub>2</sub>O) is an important material, because of its potential applications. It is a super-ionic insulator and exhibits high ionic conductivity [8]. It is used in energy storage applications such as batteries as well as in heart pacemakers. Lithia has a high melting temperature and it is a light weight compound [9]. It has applications in deuterium-tritium fusion thermal reactors as blanket breeding material [10]. It is combined with Li<sub>3</sub>N for use in hydrogen storage applications [11]. Theoretical and experimental studies on the structural, electronic, mechanical, optical and thermodynamic properties as well as the surface, defect and ion-conduction properties of this compound are studied [12].

Our focus is on the study of the magnetic properties of Co/Ni substituted Li<sub>2</sub>O and in this work, we investigated the electronic and magnetic properties of Co/Ni substituted Li<sub>2</sub>O using the first-principles method. The important issue addressed in this work is the possibility of half-metallic property in Li<sub>2</sub>O with Co/Ni atom substitution. We have considered in our study the concentration of 2.5% Co/Ni atoms and they correspond to the replacement of one Li atom by one Co/Ni atom in the supercell.

The paper is organized as follows. In the next section, we briefly mention the crystal structure of Li<sub>2</sub>O and Co/Ni substituted Li<sub>2</sub>O compounds. The method and techniques used in our calculations are mentioned in section III. The results of our calculation on Li<sub>2</sub>O and Co/Ni doped Li<sub>2</sub>O are summarized and discussed in Section IV. The conclusions are given in Section V.

## II. CRYSTAL STRUCTURE

At ambient pressure  $\text{Li}_2\text{O}$  exhibit the antifluorite type structure, which is related to the ordered  $\text{CaF}_2$  type structure, with  $\text{Li}^+$  substituted for  $\text{F}^-$  and  $\text{O}^{2-}$  for  $\text{Ca}^{2+}$  [13]. In this structure each O atom is at the center of eight Li atoms situated at the corners of a cube. Also each Li atom has a tetrahedron of O atoms around it. The unit cell contains four molecules and the Wyckoff positions of the atoms are  $\text{Li} \pm (0.25, 0.25, 0.25)$  and  $\text{O} (0, 0, 0)$ , with the space group of  $\text{Fm-3m}$  (No. 225). The crystal structure of  $\text{Li}_2\text{O}$  is given in Figure 1a. Our calculations for  $\text{Li}_{1.875}\text{Co}_{0.125}\text{O}$  and  $\text{Li}_{1.875}\text{Ni}_{0.125}\text{O}$  compounds are based on the supercell approach, where one of the Li atoms in a supercell ( $2 \times 1 \times 1$ ) of antifluorite type parent  $\text{Li}_2\text{O}$  is replaced by a Co/Ni atom. Therefore, we construct a ( $2 \times 1 \times 1$ ) supercell using the original unit cell of  $\text{Li}_2\text{O}$  for our calculations. The supercell thus constructed is shown in Figure 1b.

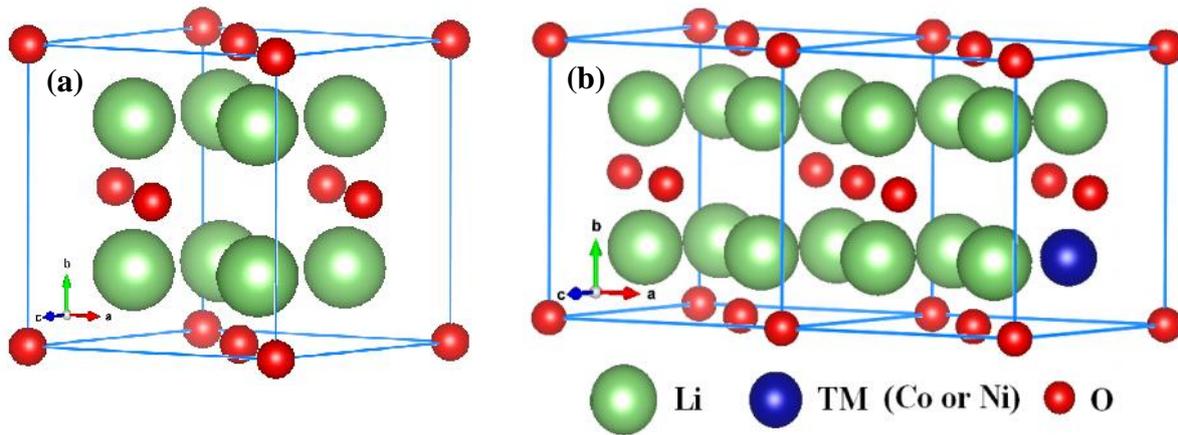


Figure 1. (a) Unit cell of antifluorite-type  $\text{Li}_2\text{O}$  (b)  $2 \times 1 \times 1$  supercell of antifluorite-type  $\text{Li}_2\text{O}$ , with one Li atom replaced by one Co/Ni atom

## III. COMPUTATIONAL METHODOLOGY

Our ab-initio calculations were carried out using the VASP package [14] that implements the Vanderbilt's plane-wave ultrasoft pseudopotential method [15] employing the density functional theory (DFT) [16, 17]. The local density approximation is used for treating the exchange correlation potential [18]. We use the exchange correlation functional of Ceperley and Alder, as parameterized by Perdew and Zunger [19]. The atomic electronic configuration considered is  $\text{Li } 1s^2 2s^1$ ,  $\text{Co } 4s^1 3d^8$ ,  $\text{Ni } 4s^1 3d^9$ ,  $\text{O } 2s^2 2p^4$ . The wave functions were expanded in plane waves up to a cutoff energy of 425 eV. For the calculation of  $\text{Li}_2\text{O}$ ,  $9 \times 9 \times 9$  Monkhorst-Pack mesh [20] grid is adopted, while for the Co/Ni substituted  $\text{Li}_2\text{O}$ ,  $6 \times 12 \times 12$  Monkhorst-Pack mesh grid is adopted. The error associated with both energy cutoffs and k-point sampling is of the order of 0.002 eV. The experimental parameters of  $\text{Li}_2\text{O}$  were first used to construct the initial coordinates of 24-atom ( $2 \times 1 \times 1$ ) super cell. Self consistency was achieved by a highly efficient conjugate gradient (CG) algorithm [21] for convergence acceleration. The geometry optimization for the parent and substituted structures were carried out and the convergence criteria used for the energy and force are respectively  $10^{-8}$  eV and  $0.01 \text{ eV/\AA}$ . The initial magnetic moment required for the self-consistent spin-polarized calculation is taken as  $2.2 \mu_B$ . We used the energy difference between the spin-polarized (ferromagnetic) and non-spin-polarized (nonmagnetic) cases ( $E = E_{FM} - E_{NM}$ ) for obtaining the magnetic stability (a negative  $E$  implies that ferromagnetic phase is favorable) of the system.

## IV. DISCUSSION OF RESULTS

Even though our interest is on the Co/Ni substituted  $\text{Li}_2\text{O}$ , we have first performed calculations for obtaining the optimized structure, equilibrium lattice parameter, bulk modulus, pressure derivative of the bulk modulus, hardness and electronic structure of the parent  $\text{Li}_2\text{O}$  as these results are required for comparing with the results corresponding to the Co/Ni substituted compounds. The calculated values of these parameters are listed in Table 1 along with the corresponding experimental values. The estimated values of the lattice parameter and bulk modulus are found to have good agreement with the experimental values and other theoretical results [22-25].

The total as well as atom decomposed density of states is given in Figure 2. The valence band is dominated by O p electrons and the hybridization of Li-s and p orbital's is significant in this compound. The lowest lying conduction band is mainly originating from the Li-s states and the Li-p states. The density of states of this compound obtained from our calculations is in good agreement with previous results [9, 12, 23, 25]. Our calculations have predicted an indirect band gap [ $\Gamma - X$ ] of 5.095 eV. Our calculated value is compared with the experimental value [8] and the values reported by other theoretical works [9] in Table 1. It may be noted from

the table that the calculated value of the band gap is small compared to the experimental value. The difference mainly arises from the fact the DFT-LDA, in general underestimates the bad gap. The hybridization of the O-p and Li-s orbital are evident from the figure. This bonding characters leads to the insulating nature of this compound.

TABLE 1. CALCULATED PARAMETERS OF PARENT AND SUBSTITUTED SYSTEMS

		Li <sub>2</sub> O	Li <sub>1.875</sub> Co <sub>0.125</sub> O	Li <sub>1.875</sub> Ni <sub>0.125</sub> O
Lattice parameter, a in Å	Present	4.572	4.510	4.503
	Exp.	4.619 <sup>a</sup> , 4.573 <sup>b</sup> , 4.622 <sup>g</sup>		
	Other	4.629 <sup>c</sup> , 4.580 <sup>d</sup> , 4.631 <sup>e</sup>		
Bulk Modules in GPa	Present	92.540	98.744	99.474
	Exp.	81.8 <sup>b</sup> , 75.00 <sup>g</sup>		
	Other	81.7 <sup>c</sup> , 82.2 <sup>e</sup> , 93.6 <sup>f</sup>		
Bulk Modules Derivative	Present	3.761	4.070	3.435
	Exp.	5.2 <sup>g</sup>		
	Other	3.93 <sup>c</sup> , 4.074 <sup>e</sup> , 3.99 <sup>g</sup>		
Bandgap in eV	Present	5.095	-	-
	Exp.	7.99 <sup>c</sup>		
	Other	5.39, 5.02 <sup>d</sup>		
Majority spin bandgap in eV		-	2.684	2.771
E in eV		-	-0.6936	-0.1816
Hardness in GPa		3.668	1.598	1.575
Magnetic moments in μ <sub>B</sub>		-	2.00	1.00

<sup>a</sup> Ref. [13]; <sup>b</sup> Ref. [22]; <sup>c</sup> Ref. [23]; <sup>d</sup> Ref. [9]; <sup>e</sup> Ref. [8]; <sup>f</sup> Ref. [24]; <sup>g</sup> Ref. [25]

We have not taken into account the spin-polarization of Li<sub>2</sub>O because there is no magnetic atom in it. Next we performed the structural relaxation for Co/Ni substituted Li<sub>2</sub>O. We find from our calculations that the lattice parameter of the substituted compound is slightly low when compared to that of the parent compound. In order to investigate the possibility of magnetic order in these compounds, the spin-polarized and non spin polarized calculations are carried out. The total energies at different cell volume for both the magnetic and non-magnetic cases were calculated and are shown in figure 3. From the results one can conclude that the ferromagnetic ordering is energetically favorable in Co/Ni substituted Li<sub>2</sub>O. The spin-polarized band structure of these compounds obtained at the equilibrium lattice parameter is given

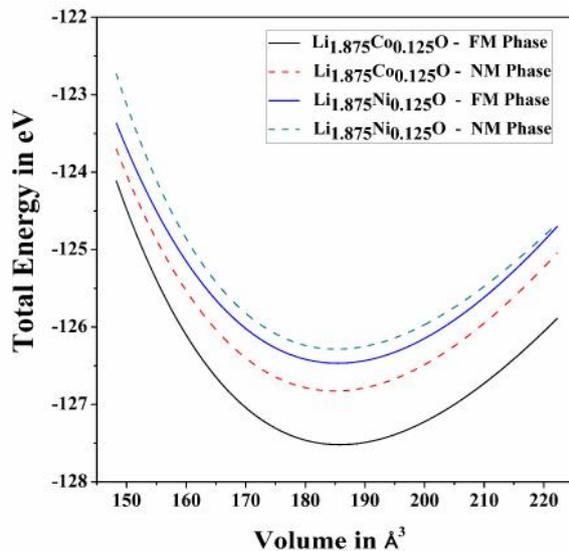


Figure 3. Total energy as a function of the volume for the nonmagnetic and ferromagnetic states of Li<sub>1.875</sub>Co<sub>0.125</sub>O and Li<sub>1.875</sub>Ni<sub>0.125</sub>O compounds

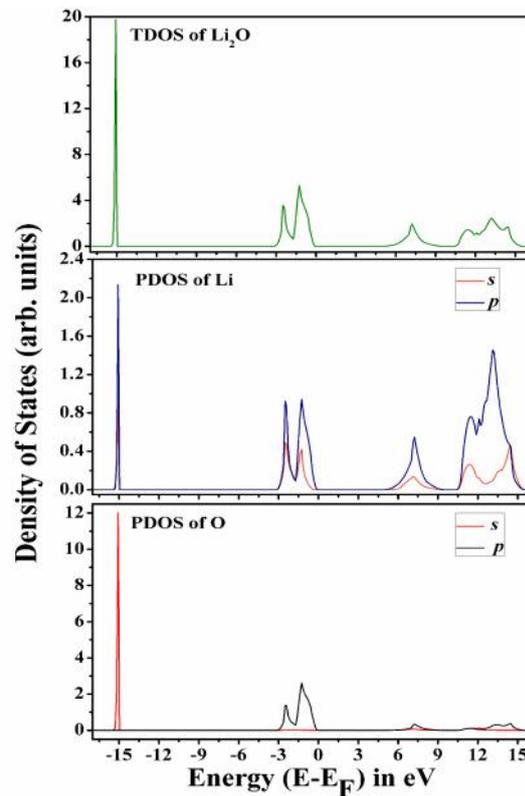


Figure 2. Total and partial DOS of Li<sub>2</sub>O

in Figure 4. It is also evident from the figure that the minority spin bands show metallic character whereas there is an energy gap at the Fermi energy in the bands of the majority spin states. Thus, these two compounds are identified as belonging to the class of half-metallic materials. Further, one can observe from the figure that the energy gap of Li<sub>1.875</sub>Co<sub>0.125</sub>O (2.684 eV) and Li<sub>1.875</sub>Ni<sub>0.125</sub>O (2.771 eV) are very low compared to the value of Li<sub>2</sub>O (5.095 eV) which can be attributed

to the effect of Co or Ni doping. In order to gain further understanding of the half-metallic ferromagnetism of these compounds, we have shown in Figure 5, the spin dependent partial and integrated density of states of the 3d states of the substituted Co/Ni atoms.

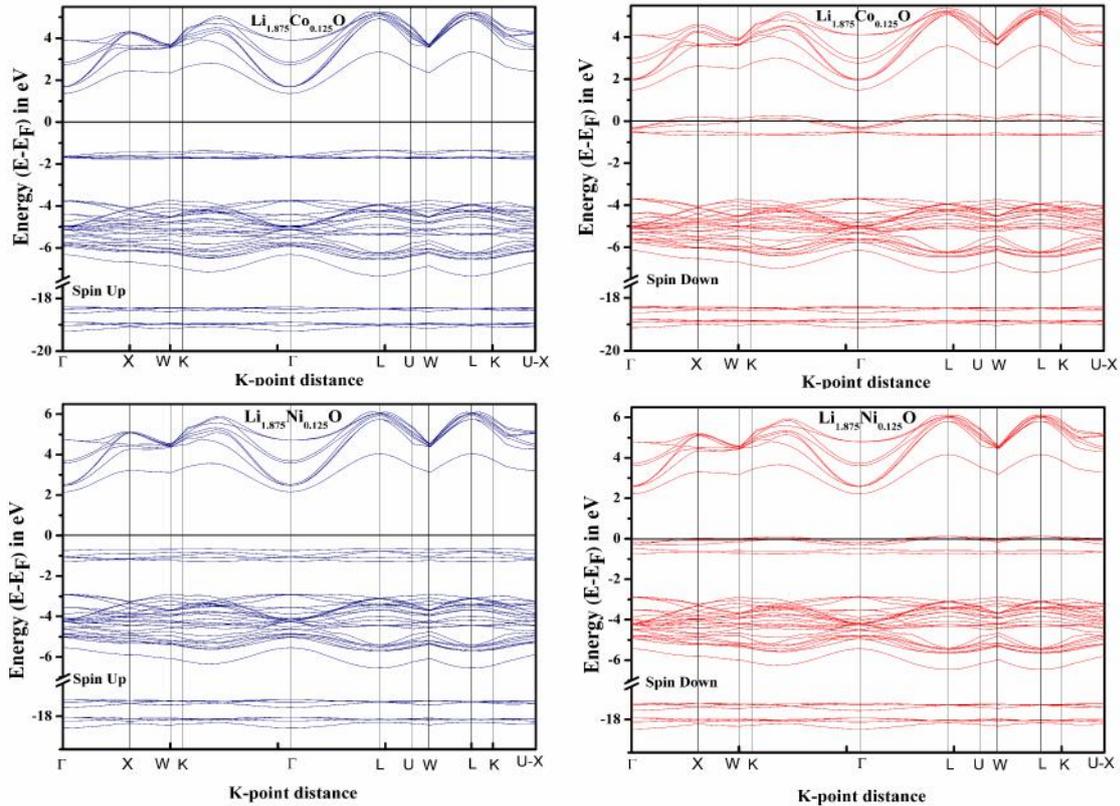


Figure 4. Spin-polarized band structure of antifluorite type  $\text{Li}_{1.875}\text{Co}_{0.125}\text{O}$  and  $\text{Li}_{1.875}\text{Ni}_{0.125}\text{O}$  at their predicted equilibrium lattice constants

It may be observed from the figure 5a that strong exchange splitting is present in the partial density of states of Co/Ni atom and it leads to significant magnetic moment in the system. It may further be observed from this figure that the Co/Ni substitution induces half metallic property in the system. The half metallic property originates from the Co/Ni 3d states in which the spin-up density of states shows a gap whereas the spin-down density of states shows a finite value at the Fermi energy. The integrated density of states of the Co/Ni atom substituted  $\text{Li}_2\text{O}$  obtained from our calculations are shown in Figure 5b. The figure can be used to understand the variation of the spin-dependent band occupations and magnetic moments as the d-electron number is increased. The magnetic moments obtained from our calculations are shown in Table 2. It may be seen from the table that the systems exhibiting half metallic property possess integral values of the magnetic moments.

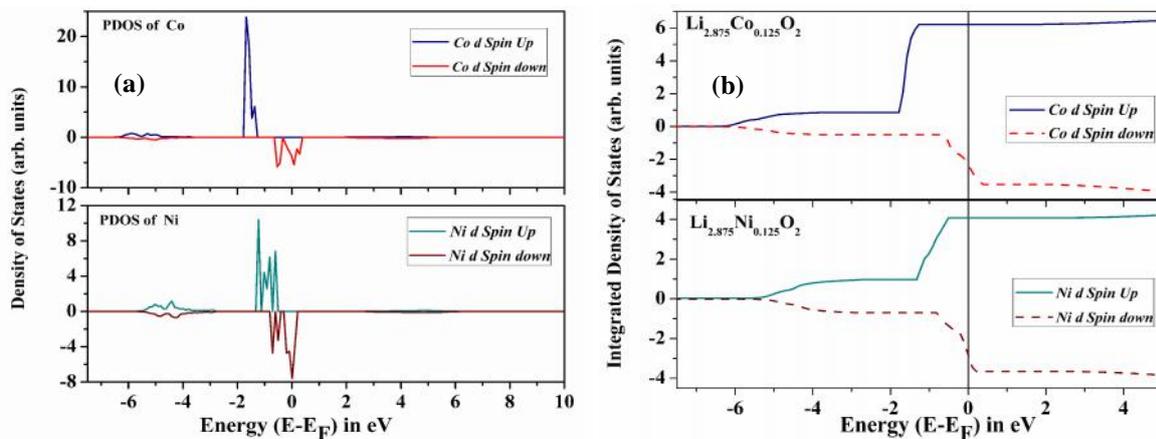


Figure 5. (a) Orbital projected and (b) Integrated density of states of Co and Ni 3d states in antifluorite type  $\text{Li}_{1.875}\text{Co}_{0.125}\text{O}$  and  $\text{Li}_{1.875}\text{Ni}_{0.125}\text{O}$  at their predicted equilibrium lattice constants

## V. CONCLUSIONS

In this paper, we have investigated the half-metallic ferromagnetism and electronic structure of Co/Ni substituted antiferrotype type  $\text{Li}_2\text{O}$  with the ultrasoft pseudopotential method as implemented in the VASP package. We have observed from our study, that the 2.5% of Co/Ni substitution in  $\text{Li}_2\text{O}$  induces magnetic order in this system. The calculated density of states and magnetic moment indicate that the single Co/Ni atom substituted  $\text{Li}_2\text{O}$  are half-metallic materials with a magnetic moment of  $2.00 \mu_B$  and  $1.00 \mu_B$ , respectively. We have observed from our calculations, magnetically stable phases and large values of the magnetic moments in these compounds and it suggests that these compounds may be useful materials for semiconductor spintronics applications.

## ACKNOWLEDGMENT

One of the authors (**G. Jaiganesh**) wishes to thank the Council of Scientific and Industrial Research, New Delhi, India for the award of Research Associateship. The author expresses sincere thanks to Shri. P. Jagadeesan, Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603102 for his timely help.

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