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Structural, Mechanical, Electronic, and Magnetic Properties of LiO in Cesium Chloride, Rocksalt and Zinc-blende Structures

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ABSTRACT: The structural, mechanical, electronic, lattice dynamic and magnetic properties of LiO in the Cesium Chloride (CsCl), Rocksalt (Rs) and Zinc-blende (ZB) structures is presented. The first-principles calculations was implemented using the spin-polarized (DFT) approach. It was observed that LiO compound exhibits ferromagnetic (FM) character at the equilibrium lattice constants in the three phases. Applying the stability conditions for cubic phases, the calculations reveal that the compound is mechanically unstable. The study also confirmed that except for the ZB structure which exhibits the brittle property, the others portray ductile nature and they are of good plasticity. We find also that the LiO structures can be synthetized, and their half-metallic property can be preserved over a broad ambit of the lattice contraction which offers the possibility to epitaxially grow such compound on a wide range of semiconductors.

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Half-metallic ferromagnetism (HMF) has been the center of attraction in the recent past. The dual character which the (HMF) exhibits, either as a metal in one spin channel or as a semiconductor (or insulator) in the other spin channel within the Fermi level make them very useful in spintronics device applications. de Groot *at al*., (1983) first predicted HMF in Heusler alloys in a calculation using the augmented-spherical-wave method. Since then, there have been several HMF theoretical predictions and confirmed experimentally, such as $Zn_{1-x}Cr_xSe$ (Xin-feng and Yuan-min, 2009), XY (X = Cr, V, Mn; Y=P, N, Sb, As, S, Te, Se) (Galanakis and Mavropoulos, 2003), $Cd_{1-x}Cr_xTe$ Noor *et al.*, (2011), and $Al_{1-x}Cr_xAs$ (Zhao *et al.*, 2009). Recently, in the zinc-blende (ZB) structure, the electronic, structural and magnetic properties of $Cd_{1-x}V_xSe$ were investigated usig the First Principles Calculations (Ahmadian and Makaremi, 2012). The results confirmed that it has half-metallic property and has a total magnetic moment of $3\mu B$. Also, in Gao *et al.,* (2007), the ZB structure, the electronic and magnetic properties of $BC(B = Mg, Ca, Sr, Ba)$ compounds were calculated, the (HMF) character was confirmed, with a large half-metallic band gaps up to $0.8ev$ and their half-metallic properties were preserved for lattice constants compression $14\%, 13\%,$ and 9% for CaC, SrC and BaC respectively. In the works of Zhang *et al*., (2003), HMF was also predicted in ZB –type $CrBi$ with a magnetic moment of $3\mu B$ per formula and its half-metallicity was preserved over a wide range of the lattice constant (between -8 and 8%). And based on First –Principles calculation, Akinaga *et al*., (2000), predicted a (HMF) in ZB-type $CrAs$ and also fabricated film on substrate of $GaAs$ compound. Recently, Lei *et al.,* (2016) reported the presence of HMF in Rs $XO(X = Li, K, Rb, Cs)$. They studied the structural, electronic and magnetic properties of these compound only in the Rs structure. In the present paper, we extended the earlier report on Rs LiO compound to other structures such as Cesium Chloride (CsCl), Rocksalt (Rs) and Zinc-blende (ZB) structures.

MATERIALS AND METHODS

We performed the First-Principles total energy calculations with a basis set of a Plane-Augmented-Wave Pseudopotential (PAW PP) method using the QE code as carried out in Giannozzi *et al.* (2009). The generalized gradient approximation (GGA) was equally implemented as in Perdew *et al.,* (1996). To achieve convergence, a PAW basis set with kinetic energy cut-off of 65*Ry*, charge density cut-off 260*Ry*,

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convergence threshold of 1.0×10^{-6} and lattice parameters of 2.533Å, 4.121Å and 4.474Å in CsCl, Rs and ZB structures were applied respectively. To obtain the ground state properties of the LiO compound in these structures, structurally the lattice parameter was optimized through energy minimization as shown in Fig. 1. Fitting the data generated from energy-lattice parameters to the Birch-Murnaghan equation of state, the equilibrium lattice constant and bulk modulus were obtained.

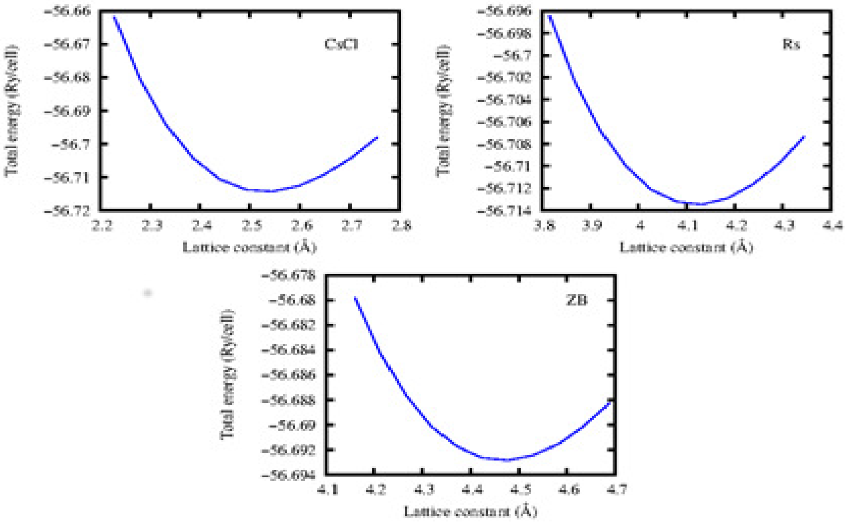


Fig 1. The total energies per unit cell as a function of lattice constants for the CsCl, Rs and ZB structures of LiO.

RESULTS AND DISCUSSIONS

Structural and Mechanical Properties: In the CsCl, Rs and ZB structures, the total energy as a function of the lattice constant of the LiO compound was investigated by carrying out a spin polarized and unpolarized calculations. There was a fair agreement between the present results and the other available theoretical results as summarized in Table 1. Both the spin-polarized ferromagnetic phase (FM) and the spin-unpolarized non-ferromagnetic phase (NM) where studied. It was observed that the ferromagnetic magnetic states are more stable than the non-ferromagnetic states in the three structures investigated. These results confirm that the LiO compound exhibits ferromagnetic character as reported in Fig. 2. The formation energy ΔH of the LiO in the three structures were investigated to verify whether they can be synthetized experimentally. The calculation was done by using equation 1:

$$\Delta H = E_{total}^{comp} - \left(E_{bulk}^{Li} + E_{bulk}^{O}\right) (1)$$

Where E_{bulk}^{Li} and E_{bulk}^{O} = the total energy of Li and O respectively, and E_{total}^{comp} = the total energy of the LiO compound.

The calculated values of the formation energy for the three structures are presented in Table 1. From the results, it is obvious that this compound can be synthetized because of the negative formation energy that were obtained. To measure the strength of the binding force of the atoms in the compound, we investigated the cohesion energy ΔC using equation 2:

$$\Delta C = E_{cohesion}^{comp} = E_{atom}^{Li} + E_{atom}^{O} - E_{total}^{comp} (2)$$

Where E_{atom}^{Li} and E_{atom}^{O} = the total energy of Li and O atoms respectively, and E_{total}^{comp} = the total energy of the LiO compound.

The positive values obtained from the calculation indicate that it is stable in the three structures investigated. From the results of the ΔH and ΔC one can infer the possibility of its existence in real life. The mechanical properties of LiO in the CsCl, Rs and ZB structures have been computed and presented in Table 2. It is essential to note that the results of the elastic constants is a function of the stability and stiffness of the materials (Wu *et al.,* 2007). Therefore, applying these conditions for cubic phases as presented in Sin'ko and Smirnow (2002), we found that LiO is not mechanically stable in the structures studied since some of the conditions were not satisfied.

Table 1. The Structural properties: the lattice constant a (Å) , bulk modulus B (GPa) , formation energy Δ*H* (eV), cohesion energy Δ*C* (eV) , half-metallic gap E_{HM} (eV) , energy band gap E_g (eV) and other theoretical results (T.R.) for the various structures.

Structure	**a**	**B**	Δ*H*	Δ*C*	E_{HM}	E_g
CsCl	2.533	79.22	-3.72	4.91	0.63	8.05
Rs	4.121	65.25	-3.71	4.90	0.94	8.28
Other T.R.	4.11[a]	--	-4.21[a]	5.49[a]	--	--
ZB	4.474	47.17	-3.43	4.62	0.78	5.89

a = Ref. (Lei *et al.,* 2016)

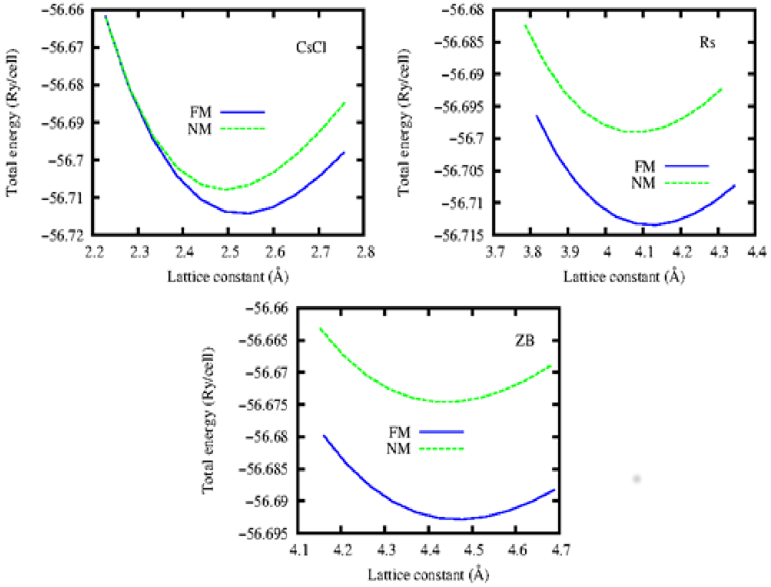
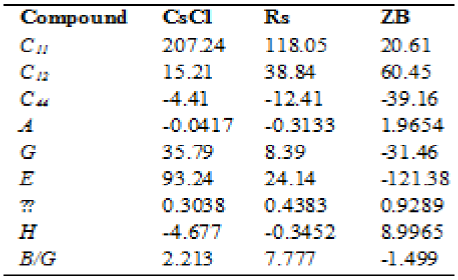


Fig 2. The total energies per unit cell as a function of lattice constants for the ferromagnetic (FM) and non-magnetic (NM) states of LiO in CsCl, Rs and ZB structures.

The bulk (B), Young (E), and shear (G) moduli are also parameters used to quantify the mechanical properties of solids. They show the extent of resistance of the alloys or compounds to volume and shear deformation respectively.

Table 2. The mechanical properties: the elastic constants C_{11} , C_{12} and C_{44} (GPa), Zener anisotropy *A*, shear modulus *G* (GPa), Young modulus *E* (GPa), Poisson's ratio *v*, hardness *H* (GPa), and the *B/G* ratio for the various structures of LiO.



Compound	**CsCl**	**Rs**	**ZB**
C_{11}	207.24	118.05	20.61
C_{12}	15.21	38.84	60.45
C_{44}	-4.41	-12.41	-39.16
A	-0.0417	-0.3133	1.9654
G	35.79	8.39	-31.46
E	93.24	24.14	-121.38
??	0.3038	0.4383	0.9289
H	-4.677	-0.3452	8.9965
B/G	2.213	7.777	-1.499

The higher their values, the stronger the deformation resistance offered by the solid. From Tables 1 and 2, it is obvious that the deformation resistance offered by the compound decreases in trend in three structures investigated from CsCl → Rs →ZB.

An empirical relation to determine the plastic properties of materials is given by the ratio of the bulk to the shear moduli (B/G). The critical threshold value of the ratio for delineating ductile from brittle materials is about 1.75 (Pugh, 1954). From the present result in Table 2, it shows that except for the ZB structure which portrays a brittle character, the other structures studied exhibit ductile nature since the values exceed the critical threshold value of the B/G ratio. The anisotropy factor A of the LiO was also investigated. The Zener anisotropy factor = 1 for isotropic materials, otherwise it is anisotropic. The present result shows that the structures are isotropic. The Poisson's ratio reveals the nature of the bonding forces in solids and it is also used to predict the stability of the material against shear stress. The value range is the order $0 < \upsilon < 0.5$ (Boucetta, 2014). The value of Poisson's ratio indicates a large volume compression of the material. The higher the Poisson's ratios, the better the plasticity. From present results in Table 2, LiO compounds are of good plasticity. Microhardness H, a mechanical property that measures the resistance to a localized plastic deformation of a material was studied, and it is given by the relation, Cheng, 2013; Yousef,El-Adawy and El-KheshKhany, (2006)

$$H = \frac{(1-2\upsilon)}{6(1+\upsilon)} (3)$$

Comparing the present results for H in Table 2 with the Mohs scale, ranging from 1 on the soft end for talc to 10 for diamond (Callister, 2006), it was observed that the Rs CsCl structures are extremely soft material. While the ZB appears harder.

Electronic Properties: We present the calculated spin-polarized band structures of LiO compound in the CsCl, Rs and ZB structures in Figs. 3 - 5. As predicted, the minority-spin channel is metallic whereas in the majority-spin channel it portrays a semiconductor property since it has an energy band gap situated around the Fermi level. In Fig. 6, we present the spin-resolved (PDOS) of LiO at its equilibrium lattice constants in the three structures. From the three structures, the plots revealed that the major contribution that lead to the half-metallic character came from the O – 2p orbital at the Fermi level. In the valence bands, it was found that the O atoms played dominant role while in the conduction bands, the Li atoms widely dominated the band especially the Li – 2s orbital as observed in the three structures.

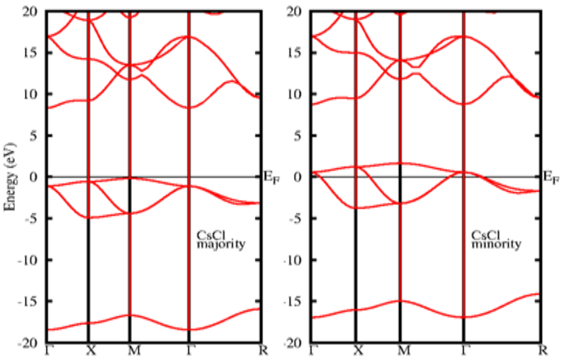


Fig 3. Electronic band structures of LiO in CsCl structure.

It was also observed from the band structures that they are direct band gap HM ferromagnets and semiconductors. The values of the HM band gaps and the energy band gaps are presented in Table 1. From the PDOS graphs, it can be seen that similar hybridizations between the Li and O orbitals occurred in the three structures. At the lower end of the valence bands, there exist a weak hybridization between the Li – 2p and O – 1s orbitals. At the Fermi level, the hybridization between the Li – 1s, Li – 2s and O – 2p is equally very weak. And at the conduction bands we observed stronger hybridization between Li – 2p and O – 1s orbitals. This features indicate that the covalent bond between these two atoms is weak, and could be responsible for the mechanical instability observed in the calculation.

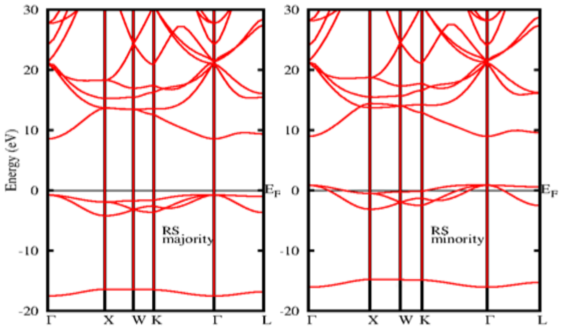


Fig 4. Electronic band structures of LiO in Rs structure.

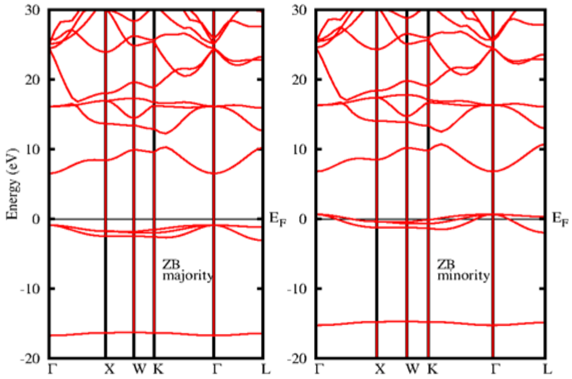


Fig 5. Electronic band structures of LiO in ZB structure.

Magnetic Properties: The magnetism in these three structures was investigated and presented in Table 3 and Fig. 7.

Table 3. The magnetic properties: the total magnetic moment M_{tot} (μB), atomic magnetic moments of Li and O; M_{Li} (μB) and M_O (μB) , and magnetic ground states Mg for the various sructures

Structure	M_{tot}	M_{Li}	M_O	Mg
CsCl	1.00	-0.0227	1.0577	FM
Rs	1.00	-0.0208	1.0333	FM
Other T.R.	1.00[a]	--	--	FM
ZB	1.00	-0.0222	1.0321	FM

a = Ref. (Lei *et al.,* 2016)

The local magnetic moments are approximately similar. Also, it was observed that the value of the magnetic moment is preserved until a critical value of the strained lattice constants of 2.32Å, 3.38Å and 2.36Å for CsCl, Rs and ZB respectively. From Fig. 6, it is clear that the total magnetic moment of LiO mainly originate from O – 2p orbitals of the O atom and with little contribution from the Li – 2s orbital of the Li atom.

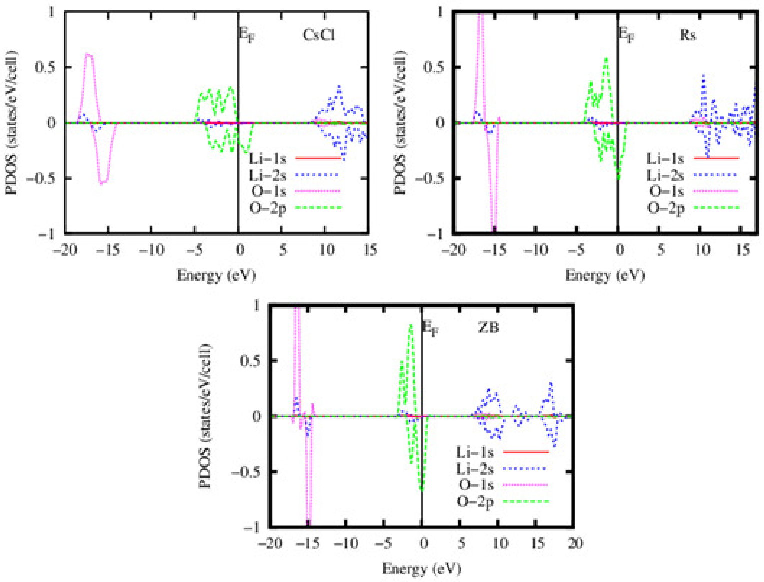


Fig 6. The spin-dependent partial density of states of LiO in the three structures, with positive and negative DOS corresponding to the majority and minority states.

The other property studied in this work is phonon dispersion curves. Among the three structures, only the CsCl is found to be dynamically stable as presented in Fig. 8

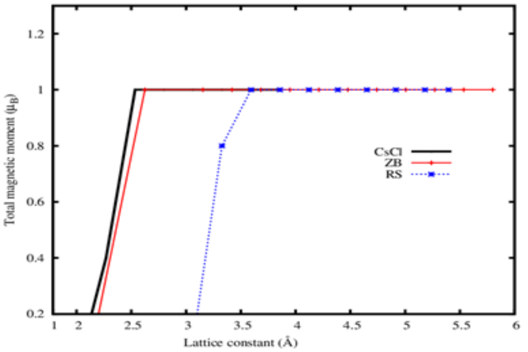


Fig 7. Total magnetic moment per formular unit as a function of lattice constants for LiO in the three structures.

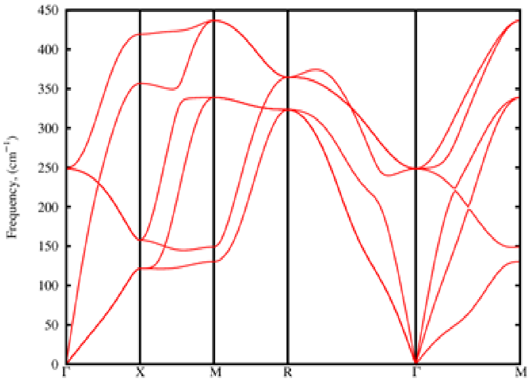


Fig 8. Phonon dispersion curves along symmetry directions of the LiO in the CsCl structure.

Conclusions: From the investigation of the spin-polarized (FM) and spin-unpolarized (NM) phases, it was found that (FM) states are more stable than (NM) states, hence the LiO compound exhibits (FM) character. In the calculation of the resistance to volume and shear deformation, it was found that CsCl structure offered highest deformation resistance compared to others. Furthermore, it was observed that their half-metallic property can be preserved up to contraction of the lattice constant of 8%, 18%, and 47% for CsCl, Rs and ZB respectively, which provides the chances of epitaxially grow LiO on a broad ambit of semiconductors.

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