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First Principle Study of Lithium Halides Lix (X=H, I)

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Abstract: ***We have investigated the electronic properties and band structure of lithium halides by using the first principle calculation in NaCl structure. Li compounds crystallize in NaCl structure in ambient conditions. These properties are found to be in good agreement with experimental and theoretical data.***

Keywords: Electronic properties; density functional theory; alkalihalides

1. Introduction

Over few decades, numerous studies have been reported on alkalihalide materials to understand the various physical and chemical properties to know the practical applications of these materials. These studies are related to variation of physical properties of materials such as crystal structure, electronic and dynamic band structure, density of states of electron and phonon, elastic, optic and dynamic properties with pressure [1, 2]. Due to the investigation of band-overlap metallization, new crystal structures, soft- mode transition and technological applications, the behavior of materials under pressure has become quite interesting. Lithium halides exhibit in NaCl Structure and are typically ionic crystals. Verma et al [3] devoted the theoretical investigation of the lattice vibrations in LiH, LiF and LiCl. Narayan et al. [4] studied the new theory of compressible ions –structure of the alkali halides. Asaumi [5] investigated that there is no structural change in LiH up to 48 GPa. Singh et al. [6] devoted the pressure induced phase transformations in alkali metal hydrides (LiH, NaHand KH). Florez et al [7] reported the B1-B2 phase stability in the alkali-halides by using the localized Hartree-Fock model. Verma et al. [8] investigated the comparative study of pressure dependence of Lithium halides. Erdinc et al. [9] performed the ab-initio calculations to understand physical properties of alkali chlorides XCl (X=K, Rb and Li) under pressure. Pandey et al.[10] studied the equation of state of lithium halides under pressure. Banger et al. [11] reported the structural and elastic properties of alkali halides by using first principle approach. Kapoor et al. [12] devoted the mechanical properties of lithium halides under high pressure at room temperature.

In the present study we have used density functional theory with the generalized gradient approximation. We have used plane wave pseudo potential density functional theory as implemented in the quantum espresso code [13]. The ground state properties of B1 structure of lithium halides have been studied using this approach. We further report the electronic band structure (BS) and density of states (DOS) for present compounds.

First Principle Calculations and Electronic Properties

The Kohn-Sham single- particle functions were expanded on a basis of plane-wave set with a kinetic energy cut-offof 32 Ry. Brillouin zone was sampled with 12 × 12 × 12 k-point mesh in order to get well converged ground state energy. The Lithium halides considered in the present work crystallize in NaCl-type (Fm3m, 2 2 5) structure at ambient conditions. The lithium atom is positioned at (0, 0, 0) and X (H, I) at (1/2, 1/2, 1/2). These halides do not transforms to CsCl-type (Pm3m, 221) structure even at 120GPa.The exchange and correlation effects have been treated within the GGA. The lattice parameter, bulk modulus and pressure derivative of the bulk modulus were determined by the standard procedure of computing the total energy for different volumes and fitted to Murnaghan's equation of state [14].

To study the ground state properties of LiCl, LiBr, LiH and LiI the total energies are calculated as a function of lattice constant in NaCl-type structure using the first principles pseudo-potential (PWSCF) method. The equilibrium lattice constants were obtained by minimizing the total energy and they are used in the non self-consistent calculations for band structure.

For Quantum Espresso these energy values have been fitted to the Murnaghan's equation of state[24] to obtain the equilibrium lattice constant (a), bulk modulus (B_T) and its pressure derivative (B_T') at minimum equilibrium volume V_0.

$$P(V)=\frac{B_T}{B_T'}\left[\left(\frac{V_0}{V}\right)^{B_T'}-1\right] \qquad (1)$$

Where the fit parameter are the equilibrium volume V_0, the bulk modulus B:

$$B_T=-V\frac{\partial P}{\partial V}=V\frac{\partial^2 E}{\partial V^2} \qquad (2)$$

And its derivative with respect to the pressure, $B_T' = dB_T/dP$.

2. Results and Discussion

The calculated electronic band structure (BS) along with the principle symmetry direction LiH and LiI are presented in fig.1 and 2. It is obvious from this figure that LiX shows the insulator behaviour. Below the Fermi level halogen atoms play a significant role in forming energy levels for all of these structures. Even though above the Fermi level both halogen and corresponding lithium in each compound of LiX play roles in energy levels. The density of energy states around the Fermi level in the valence band for Hand I atoms is higher than that of Liatom. It is due to higher electro-negativity in halogen atoms and more electrons belonged to halogens which are engaged in bond. As it was seen, these compounds are known as members of the insulator group of materials because of their wide band gap. To present a better view, we focus on their band structure here. So, we have computed the ground state properties of Li halides by using two approaches (GGA and PWSCF) and are listed in table 1.

The gap values are identified as 6.785 and 4.606eV for LiH and LiI respectively. In order to understand the elementary contribution of all the atoms to the electronic structure of present compounds we have studied total density of states (TDOS) at ambient pressure and presented in fig. 3 and 4. It is clear from total density of states (TDOS) that the energy gap at around 0eV have been observed, which is taken as Fermi energy level.

3. Conclusion

Finally, we can conclude that the band structure diagrams of LiX compounds indicate that they belong to insulator group and it is observed that LiH is better insulator.

Table 1: Computed ground state properties of LiX compounds

Solids	a (Å)			BT(GPa)			BT’		Bandgap(eV)
	PWSCF	Exp	Other	PWSCF	Exp	Other	PWSCF	Other	PWSCF
LiH	4.25	4.06[a]	4.08[c]	31.55	35.7[d]	40.9[c]	5.09	5.38[c]	6.78
LiI	5.96	6.00[b]	-	16.95	18.7[e]	17.1[f]	5.98	6.24[f]	4.60

a. Ref[15], b. Ref [16], c. Ref [17], d. Ref [11], e. Ref [2], f. Ref[8]

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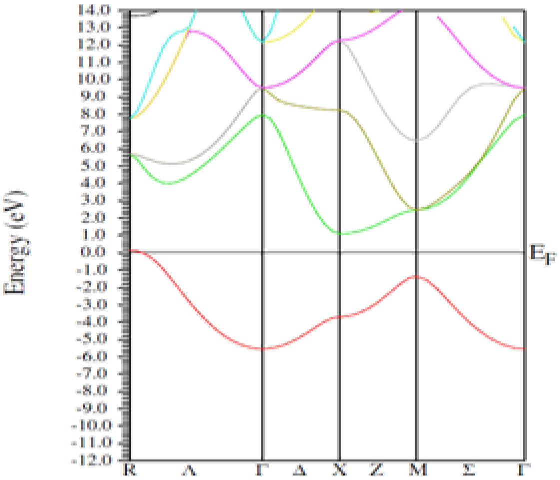

Figure 1: Band structure of LiH

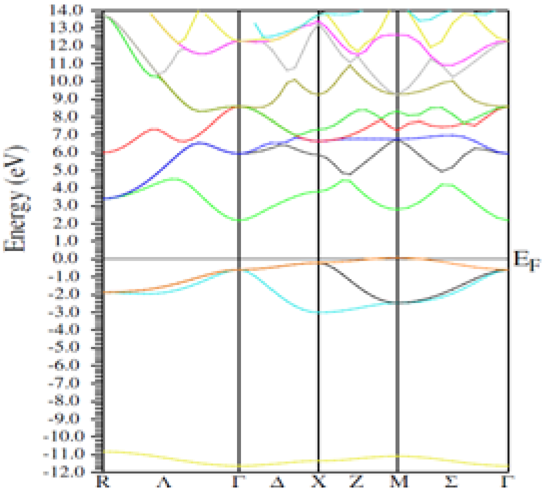

Figure 2: Band structure of LiI

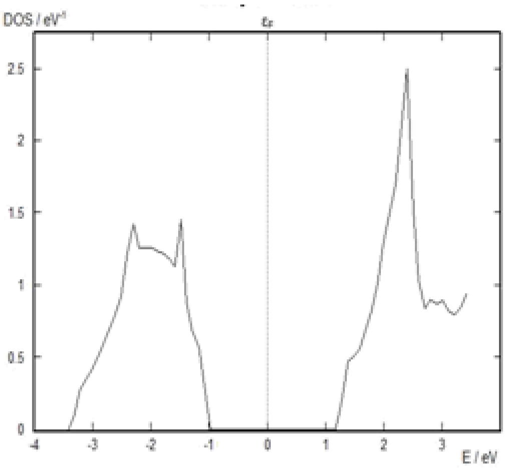

Figure 3: TDOS of LiH

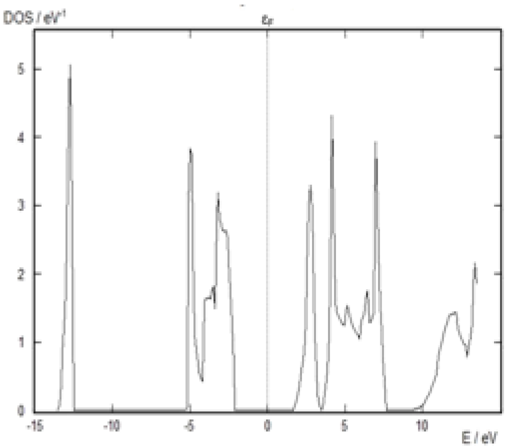

Figure 4: TDOS of LiI