



Electronic band structure, density of states, structural phase transition, metallization and superconductivity in lithium bromide

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Abstract

We have investigated the pressure dependent band structure, density of states, metallization, structural phase transition and superconductivity of cubic rocksalt (NaCl structure) type LiBr using FP-LMTO method. LiBr becomes metal and then superconductors under high pressure, but before that they undergo structural phase transition from NaCl to CsCl structure. The ground state properties and band gap values are compared with the experimental and previous theoretical results. When the pressure is increased there is enhanced overlapping between the wave functions of the neighbouring atoms. As a result the widths of the valence and empty conduction bands increase. These changes lead to the narrowing and closing of band gaps in LiBr (metallization). The mechanism for the phase transition is a geometric effect involving a change in the coordination number from 6 in the NaCl phase to 8 in the CsCl phase. The calculated T_c values depend more sensitively on changes in λ than μ^* , indicating that LiBr is electron-phonon-mediated superconductors. It is also confirmed that structural phase transition, metallization and superconductivity do not occur simultaneously in LiBr.

Keywords: structure, metallization, superconductivity, bromide

1. Introduction

The physical properties of materials undergo a variety of changes when they are subjected to high pressure (Settoug, 2019) ^[1], (Drozdov, 2019) ^[3]. The increase of pressure means the significant decrease in volume, which results in the change of electronic states and crystal structure. The recent development in diamond anvil cell (Weir, 2000) ^[16] enables the experimentalist to perform the investigation at very high value of pressure (5 Mbar). About twenty three new elemental superconductors have already been found at high pressure and this number is increasing (Eremets, 1998) ^[14]. In this list new compounds are now being included. One such compound is the simple ionic salt CsI (Asaumi, 1984). With the development of high pressure experimental techniques, investigations on pressure-induced structural phase transition, insulator-metal transition and superconducting transition are getting the attention of all. In particular, there is a great interest in the pressure induced metallization and superconductivity of simple alkali halides (Yazar, 2003) ^[6], (Knittle *et al*, 1984), (Sathpathy *et al*, 1985) ^[4]. Experimentally it is found that, the ionic insulator CsI is a metal under high pressure and as the pressure is increased, superconductivity sets in (Eremets, 1998) ^[14]. These results lead us to expect superconductivity in other alkali bromides and iodides under high pressure, especially those alkali bromides and iodides which have already become metals (Ramola, 2018, 2019) ^[21].

The lithium halide LiBr is of great physical interest; since they find application in manufacture of opto-electronic devices and serve as a typical model for other ionic compounds (Kootstra, 2000). Because of the large band gap for lithium halides, its crystals are transparent to short wavelength ultraviolet radiation

compared to any other material. LiBr is therefore used in specialized ultraviolet optics, diffracting crystal in X-ray spectrometry (Kowalski, 1986). They are used as radiation detectors to record ionizing radiation exposure from gamma rays, beta particles, and neutrons in thermo luminescent dosimeters (Nicholson, 1985), (Lyday, 2005), (Kano, 2009). They are also used as the neutron reactive backfill material for microstructured semiconductor neutron detectors. These facts lead us to expect superconductivity in these ionic compounds; especially those compounds which have already become metals under high pressure. Prior to metallization these compounds undergo structural phase transition from NaCl structure to CsCl structure. In this study we have got, normal and high pressure band structure and density of states of LiBr (with NaCl structure), and high pressure band structure and density of states of LiBr (with CsCl structure). Also, we have analyzed the structural phase transition from NaCl \rightarrow CsCl structure for LiBr, metallization and superconducting transition of these materials (with normal (NaCl) and high pressure (CsCl) structures). It is hoped that these analyses will enable us to make some general statement regarding the path to high T_c superconductivity in this compound.

2. Details of the calculation

The physical properties of a material are expressed via the interrelation of the equation of state (EOS) between the thermo dynamical variables. Theoretical studies of cohesive, structural and vibrational properties of solids under pressure are performed by means of FP-LMTO calculations (ThusnavisVini, 2015), (Iyakutti, 2004) ^[20]. The accuracy of total energies obtained

within the density functional theory even in its local approximation (LDA) is sufficient to predict which structure at a given pressure has the lowest free energy (Ramola, 2018) [21]. Most calculations still refer to zero temperature, whereas conventional structural optimizations are performed by comparing the free energies of various guessed crystal structures. The electronic configuration of lithium (Li) and bromine (Br) are [He] $2s^1$ ($Z = 3$) and [Ar] $3d^{10} 4s^2 4p^5$ ($Z = 35$) respectively. The valence electronic configurations chosen in our calculation are $2s^1$ for Li and $4s^2 4p^5$ for Br. There are 8 valence electrons contributing to the valence band of LiBr. The band structures of LiBr corresponding to various pressures are obtained using the full potential linear muffin-tin orbital (FP-LMTO) method ((Ramola, 2018) [21]. The calculated total energies were fitted to the Murnaghan's equation of state (EOS) (Murnaghan, 1944) [17], to determine the phase transition pressure and other ground state properties. The final energy convergence is within 10^{-5} Ry.

We have obtained,

1. Normal pressure band structure and density of states of LiBr (with NaCl structure)
2. High pressure band structure and density of states of LiBr (with CsCl structure)

Also, we have analyzed the structural phase transition from NaCl \rightarrow CsCl structure, metallization and superconducting transition (with normal and high pressure structures). The band structure calculations are performed for LiBr corresponding to different reduced volumes in NaCl and CsCl structures, using the first-principle FP-LMTO method (Ramola, 2018) [22].

3. Results and discussion

a. Band structure and density of states at normal and high pressure

The band structures and density of states for LiBr is computed (Figs.1 to 4) for various reduced volumes ranging from $V/V_o=1.0$ to 0.3 in steps of 0.05. But here we have presented the density of states and band structures along the symmetry directions Γ -X-W-L- Γ -K (Fig.1) and Γ -H-N- Γ -P-N (Fig.3) corresponding to volume compressions $V/V_o=1.0$ and $V/V_o=0.5$ for LiBr.

Equilibrium lattice constant (a_o), bulk modulus (B_o) and its pressure derivative (B_o') values of lithium halides *LiBr* and *LiI* ground state structure is given in Table.1 and energy band gap values are given in Table.2 along with experimental (Sirdeshmukh, 2001) and previous theoretical values (Kootstra, 2000). In these tables, our calculated values are in good agreement with experimentally measured values than previous theoretical values. In *LiBr*, at normal pressure, the single band which is positioned at the bottom of the valence band arise from $4s^2$ electrons of Br (Fig. 1). The three bands appearing below the Fermi level are due to the $2s^1$ electrons of Li and $4p^5$ electrons of Br. The empty conduction bands above the Fermi level are due to $2p$, $3d$ states of Li and $5s$, $4d$, states of Br (Fig.1). The characteristic features of *LiBr* (Fig. 1) band structure is similar to the previous studies (Syassen, 1987) [10] and (Zhdanov, 1973). The fundamental energy gap is between the half-filled $2s$ like valence band due to Li, unfilled $4p$ like valence band due to Br

and empty $2p$, $3d$ conduction band of Li, $4d$ like conduction band due to Br (Ramola, 2018) [21].

At normal pressure, the band gap of *LiBr* is direct (7.6 eV) with top of the valence band in Γ point and the bottom of the conduction band at Γ point. (Fig. 1). The band gap value of *LiBr* in NaCl structure is given in Table.2 along with experimental (Sirdeshmukh, 2001) and previous theoretical values (Kootstra, 2000). The calculated band gap is in agreement with the experimental value than the previous theoretical value. These changes lead to the narrowing of the band gap. As the compound is highly compressed, the $3d$, $4d$ electron density gradually increases and there is corresponding decrease in the $2s$, $2p$, $4s$ and $4p$ electron density. This indicates that the bonding between Li and Br atoms becomes less ionic in character under compression. The density of states (DOS) (states/Ry.) calculations for all the reduced volumes has been carried out but here we have given the DOS histograms of *LiBr* corresponding to volume compressions $V/V_o=1.0$ and $V/V_o=0.5$ (Figs.2.and 4 respectively). At normal pressure (Fig. 2) the level arising from $4s^2$ electrons of Br give the long spike near the origin. In Fig.2, the short spikes near the Fermi energy are due to the $4p^5$ electrons of Br and $2s^1$ electrons of Li. The small peaks above the Fermi energy E_F are due to the $2p$, $3d$ states of Li and $5s$, $4d$, states of Br. The above normal pressure trend is changed under high pressure (Ramola, 2018) [22]. The increase of pressure leads to the broadening of bands which results in the decrease of density of states value in most of the energy regions and increase in the width of the valence band and empty conduction band. When pressure increases the value of E_F increases whereas no density of states is available at the Fermi level up to metallization pressure (Table.3).

Table 1: Equilibrium lattice constant (a_o), bulk modulus (B_o) and its pressure derivative (B_o') values of LiBr in NaCl structure

Lithium halide	Present work			Experiment (Sirdeshmukh, 2001)			Previous theory (Kootstra, 2000)		
	a_o a.u	B_o Mbar	B_o'	a_o a.u	B_o Mbar	B_o'	a_o a.u	B_o Mbar	B_o'
LiBr	11.153	0.235	5.230	11.262	0.250	5.250	11.047	0.211	5.150

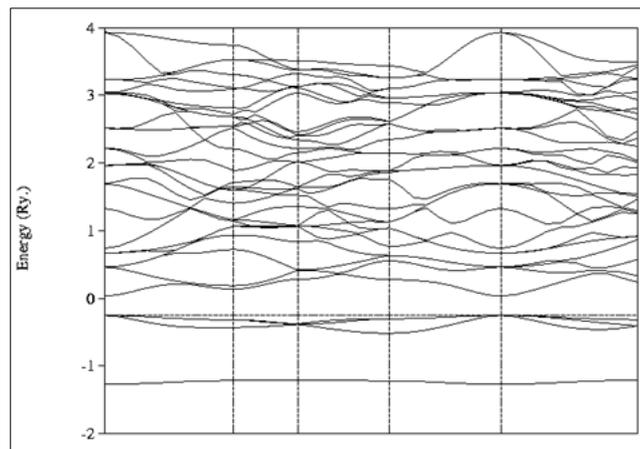


Fig 1: Band structure of *LiBr* at $V/V_o = 1$ (NaCl structure)

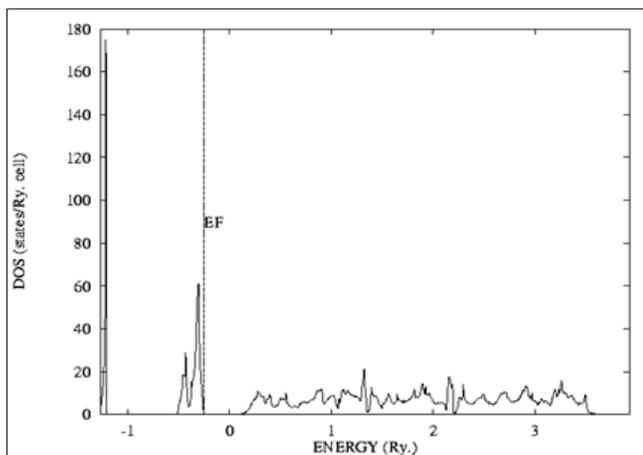
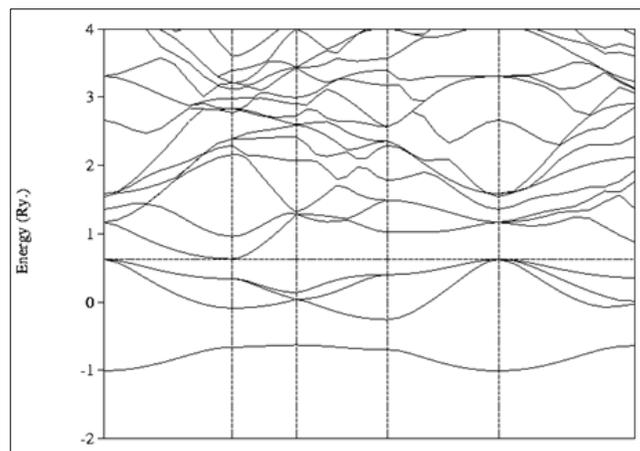

Fig 2: Density of states of *LiBr* at $V/V_0 = 1$ (NaCl structure)

Fig 3: Band structure of *LiBr* at $V/V_0 = 0.5$ (CsCl structure)

Table 2: Band gap values of *LiBr* in NaCl structure

Lithium halide	E_g eV		
	Present work	Experimental work (Sirdeshmukh,2001)	Previous theoretical work (Kootstra, 2000)
<i>LiBr</i>	7.6	8.0	7.2

Table 3: Structural phase transition, metallization, and superconducting transition pressures

Lithium halide	Structural phase transition NaCl to CsCl		Metallization		Onset of superconducting transition		T_c -max K	
	P_T Mbar	$(V/V_0)_T$	P_M Mbar	$(V/V_0)_M$	P_S Mbar	$(V/V_0)_S$	NaCl (normal pressure structure)	CsCl (high pressure structure)
<i>LiBr</i>	0.217	0.7	1.01	0.5	2.4	0.4	3.179	0.653

b. Ground state properties

The ground state properties and structural phase transitions of *LiBr* is studied using the total energies obtained in our calculation. The total energies are calculated as a function of reduced volume (V/V_0) for NaCl and CsCl phases. Here, V_0 is the experimental equilibrium volume corresponding to the experimental equilibrium lattice constant. The calculated total energies are fitted to Murnaghan's equation of state (Murnaghan, 1944) [17] to obtain the equilibrium lattice constant and other ground state properties (Table 1). The variation in the total energy as a function of reduced volume and enthalpy versus pressure curve for *LiBr* is given in Figs.4 and 6 respectively.

From these figures, it is found that in *LiBr* up to $V/V_0 = 0.7$, NaCl structure has the lowest energy and on further reduction of volume CsCl structure becomes more stable in energy than the NaCl structure (Ramola, 2018) [21]. The equilibrium lattice constant (a_0), band gap (E_g), bulk modulus (B_0) and its pressure derivative (B_0^{-1}) values are given along with experimental and previous theoretical results in Table 1.

c. Structural phase transition

As pointed out earlier in our calculation, we have chosen the NaCl structure for *LiBr* at ambient pressure and CsCl structure at high pressure. The phase stability of the B1 (NaCl) and B2 (CsCl) structures is analyzed using the enthalpy calculation (Jesse Pius, 2016). The transition pressure corresponding to the phase transition from B1 to B2 is obtained from the relation

$$H_{B1}(P) = H_{B2}(P)$$

Where H_{B1} and H_{B2} are the enthalpies of the B1 and B2 phases respectively. The enthalpy versus pressure curve for *LiBr* is given in Fig. 6. The phase transition pressure (P_T) and the corresponding reduced volume $(V/V_0)_T$ estimated in our calculation are given in Table 4. For *LiBr*, our calculated phase transition pressure for NaCl to CsCl transition is (0.217Mbar) in good agreement with the experimental (0.20 Mbar (Messaoudi, 2014)) [9] and previous theoretical results (0.152 Mbar (Yazar, 2003)) [6]. The mechanism for the phase transition is a geometric effect involving a change in the coordination number from 6 in the NaCl phase to 8 in the CsCl phase (Ramola, 2018) [22].

Table 4: Structural phase transition pressure for *LiBr*

Lithium halide	Structural phase transition	Present study		Experiment (Messaoudi, 2014)		Previous theory (Yazar, 2003)	
		$(V/V_0)_T$	P_T (Mbar)	$(V/V_0)_T$	P_T (Mbar)	$(V/V_0)_T$	P_T (Mbar)
<i>LiBr</i>	NaCl to CsCl	0.7	0.217	0.75	0.20	0.82	0.152

Table 5: Variation of T_c as a function of pressure for *LiBr* in NaCl and CsCl structure

Pressure P Mbar	NaCl structure				CsCl structure			
	λ	θ_b K	μ^*	T_c K	λ	θ_b K	μ^*	T_c K
2.4	0.264	387.2	0.028	0.911	0.173	262.8	0.028	0.034
3.0	0.284	398.3	0.037	1.065	0.197	295.4	0.036	0.072
4.0	0.395	412.7	0.058	3.179	0.312	328.7	0.066	0.653

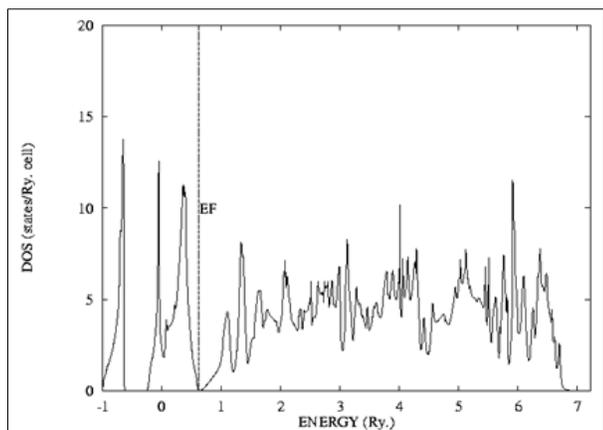


Fig 4: Density of states of *LiBr* at $V/V_0 = 0.5$ (CsCl structure)

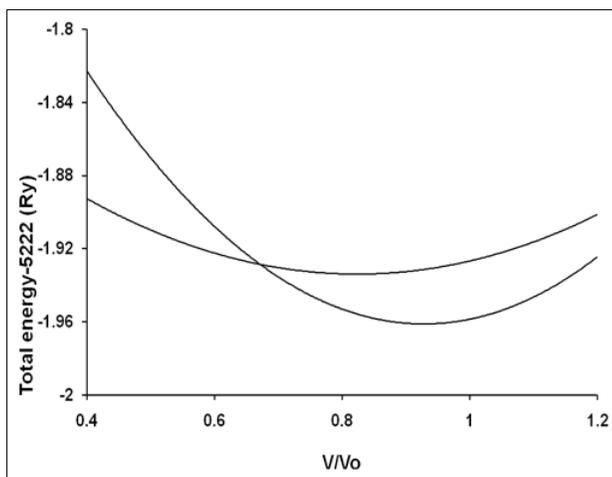


Fig 5: Total energy versus reduced volume curve for *LiBr*

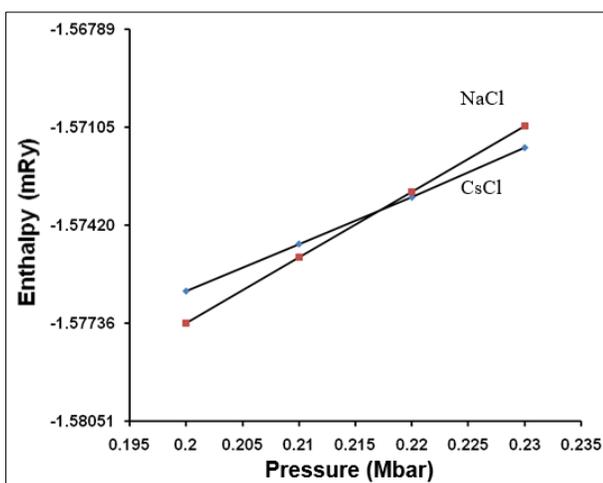


Fig 6: Enthalpy versus pressure curve for *LiBr* in NaCl to CsCl transition

d. Metallization

Most of the metallization is associated with a structural transition from a low coordination non-metallic to a high coordination metallic phase (Weir, 2000) [16]. At normal pressure, *LiBr* is insulator. With increase of the pressure, the band gap decreases and at a particular pressure, there is a closing of the band gap

(Eremets, 1998) [14]. Similar to other alkali halides ((Ramola, 2018). the electronic band structure calculations on *LiBr* suggest that metallization is due to the reordering of the energy bands with the empty *p* - like band (of Br) dropping in energy and touching the top of the filled *s* - like band (of Li). Prior to metallization, *LiBr* undergoes structural phase transition from NaCl to CsCl structure (Ramola, 2019) [23].

The band structures and density of states corresponding to metallization of *LiBr* is shown in Figs. 3 and 4 respectively. In *LiBr*, the metallization occurs through indirect closing of the band gap between valence band maximum at Γ point and conduction band minimum at *H* point (Fig.3). The metallization volume of *LiBr* is $V/V_0=0.5$ (CsCl structure), which corresponds to the pressure $P_M = 1.01$ Mbar (Table.3). Metallization pressure and metallization reduced volume for *LiBr* is given in Table.3. At high pressure of 1.01 Mbar or reduced volume $V/V_0=0.5$ (Fig. 3), the level arising from $4s^2$ electrons of Br give the short spike near the origin. In Fig.3, the short spikes near the Fermi energy are due to the $4p^5$ electrons of Br and $2s^1$ electrons of Li. The small peaks above the Fermi energy E_F are due to the 2*p*, 3*d* states of Li and 5*s*, 4*d*, states of Br. In this figure, we show that upto metallization reduced volume, no density of states available, after that metallization reduced volume density of states increases with reduction of volume. The values of E_F and $N(E_F)$ corresponding to different V/V_0 are used in studying the pressure variation of superconducting transition temperature (Ramola, 2018) [22].

e. Superconductivity

The promotion of *s,p* electron to *d* shell in solids is one of the factors which will induce superconductivity. The theory of Gaspari and Gyorffy in conjunction with McMillan's formula (McMillan, 1968) is used to calculate T_c . With the results obtained from the self-consistent calculation, we have computed θ_D , λ , μ^* and T_c as a function of pressure. The calculated values of T_c at NaCl (retaining the normal structure at high pressure) and CsCl (high pressure) structures of *LiBr* is given in Table 5. When pressure is increased T_c increases and reaches the maximum value in both the normal and high pressure structures. The highest T_c (T_c -max) obtained for the normal pressure structure of *LiBr* is 3.179K (Table. 5) and high pressure structure (CsCl) of *LiBr* is 0.653 K (Table. 5). The calculated T_c values depend more sensitively on changes in λ than μ^* , indicating that *LiBr* is electron-phonon-mediated superconductors. The onset of superconductivity and its continuation depend upon the number of electrons near the Fermi energy or near K_F on the Fermi surface, which will in the superconducting state form cooper pairs. As the pressure is increased the charge transfer from lower *s,p* bands to the *d* bands near the Fermi level increases. This leads to the increase in the DOS at Fermi energy ($N(E_F)$) and hence increase in the electron-phonon and electron-electron interactions. Finally, all these result in the increase of T_c with pressure. The T_c -max values are given in Table.3 for normal and high pressure structures. From Table.5, it is noted that, *LiBr* retained in its normal structure (NaCl) under high pressure gives appreciably high T_c (Ramola, 2018) [22].

4. Conclusion

In summary, we have investigated the pressure dependent band structure, density of states, metallization, structural phase transition and superconductivity of cubic rocksalt (NaCl

structure) type LiBr using FP-LMTO method. LiBr becomes metal and then superconductor under high pressure, but before that it undergoes structural phase transition from NaCl to CsCl structure. The ground state properties and band gap values are compared with the experimental and previous theoretical results. It is also confirmed that structural phase transition, metallization and superconductivity do not occur simultaneously in LiBr.

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6. References

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