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Band structure, metallization and superconducting transition of *CsBr* under high pressure

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Abstract : The results of a full potential linear muffin-tin orbital (FP-LMTO) study on the electronic properties of ionic insulator cesium bromide (*CsBr*) under pressure is presented. The equilibrium lattice constant, bulk modulus, pressure derivative of bulk modulus and the phase transition pressure at which the compounds undergo structural phase transition from *CsCl* to *HCP* structure is predicted from the total energy calculations. The ground state properties and band gap values are compared with the experimental results. At normal pressure *CsBr* is a direct bandgap semiconductor. 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 direct closing of band gap in *CsBr* (metallization). On further increase of pressure, *CsBr* becomes superconductor, and this material comes under the class of electron-phonon-mediated high pressure superconductor. The superconducting transition temperatures (*Tc*) of *CsBr* is obtained as a function of pressure for *HCP* structure. It is also confirmed that the metallization, structural phase transition and onset of superconductivity do not occur simultaneously in ionic compounds.
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INTRODUCTION

The physical properties of materials undergo a variety of changes when they are subjected to high pressure[1]. 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[2] 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[1]. In this list new compounds are now being included. One such compound is the simple ionic salt CsI[3]. 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[3-6]. Experimentally it is found that, the ionic insulator CsI is a metal under high pressure and as the pressure is increased, superconductivity sets in[3]. These results lead us to expect superconductivity in other alkali halides under high pressure, especially those alkali iodides which have already become metals.

The alkali halides are of great physical interest; since they find application in manufacture of optoelectronic devices and serve as a typical model for other ionic compounds[7]. The electronic band structure calculations on alkali halides suggest that the insulator-metal transitions are due to the reordering of the energy bands[8] with the empty d-like band dropping in energy below the top of the filled p-like bands. There are many investigations both theoretical and experimental on the band structure and metallization of CsBr[9-13].

In 1973 Metallization of alkali halide crystals under super high pressure was reported by Zhdanovet al[9]. The equation of states were obtained for both phases in a wide range of pressures , from 0 to 2000 Kbar. In 1984 Pressure- induced structural transition of CsI and CsBr was reported by Huang et al[10]. In this study a pressure- induced phase transition of CsBr was found by using energy dispersive X- ray diffraction with a synchrotron X-ray source. The cubic phase CsBr was found to undergo transformation to hexagonal crystal structure under high pressure similar to that recently reported for CsI. In 1995 High pressure low- symmetry phases of cesium halides was reported by Stefano Baroni et al[11]. In this report the results for CsI ,CsBr ,CsCl upto pressures of approximately 100 Gpa were presented. In 1998 Studies on CsBr with synchrotron radiation under ultra high pressure upto 115 GPa was reported by Wang Li- Jun et al[12]. In this study the maximum pressure is 115 GPa. CsBr is changed from simple cubic phase to tetragonal phase at about 53 GPa. No pressure induced metallization transition has at high pressure upto 115 GPa. In 1998 Conduction bands and invariant energy gaps in alkali bromides was reported by De Boer et al[13]. In this study electronic structure calculations of the alkali bromides LiBr , NaBr , KBr , RbBr and CsBr were reported. It was felt that many disagreements exist between theory and experiment[9] in the prediction of equilibrium lattice constants, band gaps, structural phase transitions and metallization and this necessitated further theoretical studies in this system. It is also suggested that it would be interesting and useful if one investigates the pressure dependence of *Tc* which has been observed experimentally for CsI[3]. Hence, to gain a fundamental understanding of the structural phase transition, metallization and superconductivity of CsBr, the electronic band structure studies of this material is essential and this motivated the present investigation. In Section 2, we give the details of the calculational procedure, electronic band structure and density of states corresponding to various pressures. The ground-state properties, structural phase transition, metallization and superconducting transition temperature *T*c and its variation under pressure are discussed in Section 3. Concluding remarks are given in Section 4.

BAND STRUCTURE AND DENSITY OF STATES

Calculational procedure

Alkali bromide CsBr crystallizes in CsCl structure under ambient conditions and undergo structural phase transition from CsCl to HCP structure under pressure[14]. We have obtained (i) normal pressure band structure and density of states of CsBr (with CsCl structure) and (ii) high pressure band structure and density of states of CsBr (with HCP structure). Also, we have analyzed the structural phase transition from CsCl → HCP structure, metallization and superconducting transition. The electronic band structure calculations were performed for *CsBr* corresponding to different reduced volumes in *CsCl* and *HCP* structures, by the first-principle FP-LMTO method with in generalized gradient approximation

(GGA)[14]. We have used the exchange-correlation potential of Ceperley and Alder as parametrized by Perdew and Zunger[15]. similar to our earlier studies on ZnSe and CdSe the details of the FP-LMTO method are well described in the literature[13] and we give here only the calculational details.

The electronic configurations of Cs (Z=55) and Br (Z=35) are [Xe]$6s^1$ and [Ar] $3d^{10}$ $4s^2$ $4p^5$ respectively. The valence electronic configurations of Cs and Br are $5p^6$ $6s^1$ and $4s^2$ $4p^5$ respectively. There are 14 electrons contribute to the valence band. The final energy convergence is within 10^{-5} Ry. The calculated total energies were fitted to Murnaghan's equation of state (EOS)[16], to determine the phase-transition pressure and other ground-state properties. The band structure results are used to compute the superconducting transition temperature (*Tc*) and its pressure variation.

Band structure and density of states of CsBr under pressure

The band structure and density of states of *CsBr* was computed for various reduced volumes ranging from V/V_o=1.0 to 0.3 in steps of 0.05. Even though we have obtained the band structure for V/V_o values from 1.0 to 0.3, we have presented here the band structures of *CsBr* along the symmetry directions *Γ-H-N-Γ-P-N* and the corresponding density of states of *CsBr* (Figures1 to 4). The volume compressions corresponding to V/V_o=1.0 and V/V_o=0.377 for CsBr, The normal pressure band structure and density of states of CsBr is given in Figures 1 and 2 respectively. The overall topology of the band structure and density of states of CsBr at normal pressure is similar to previous calculations[11,12]. It is seen that the band structure exhibits characteristic features similar to CsI. In Figure 1, the single band, which is positioned at the bottom of valence band, arises from Br-4s electrons and the triplet bands nearer to the single band are due to 5p electrons of Cs. The three bands appearing just below the Fermi energy E_F are from Cs-6s and Br-4p electrons of CsBr. The empty conduction bands above the Fermi level are due to 6p, 5d states of Cs and 5s, 5d states of bromine (Figure 1). At normal pressure, the direct band gap E_g is found to be 7.3 ev for CsBr. The levels arising from Cs- 5p electrons give the longest spike (Figure 2). The spike near the origin is due to Br-4s electrons and the short spikes near E_F are due to Cs-6s , Br-4p electrons. The short spikes above the Fermi energy E_F are due to the 6p 5d states of Cs and 5s 4d states of Br. As the pressure is increased, there is a charge transfer from s, p to d state ; this causes the increase in the width of the valence band and also the empty conduction bands get widened. These changes lead to the narrowing of the band gap[14,15].

At normal pressure, the band gap of CsBr is direct with valence band maximum at *Γ* point and conduction band minimum at *Γ* point with band gap value 7.3 eV. The calculated energy gap is in agreement with the experimental value of 7.36eV (TABLE 1). As pressure increases the width of the valence band and the empty conduction band get widened[16]. These changes leads to the narrowing of the band gap under pressure (Figures 3 and 4). The general features of the band structure and density of states (Figures 1-4) are similar to that of the alkali halide CsI[17]. This trend is changed under high pressure. 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 also increase in the width of the valence band and empty conduction bands. When pressure increases the value of E_F increases whereas no density of states is avail-

TABLE 1 : Equilibrium lattice constant (a_o), bulk modulus (B_o) and its pressure derivative (B_o^1) of *CsBr* in *CsCl* structure

Ground State Properties	*CsBr*		
	Present work	Experi mental works[4,12]	Previous theoretical works[9,10]
a_o a.u.	8.1197	8.2	7.89
B_o Mbar	0.1301	0.1358	0.152
B_o^1	5.5	5.7	5.276
E_g eV	7.3	7.36	6.65

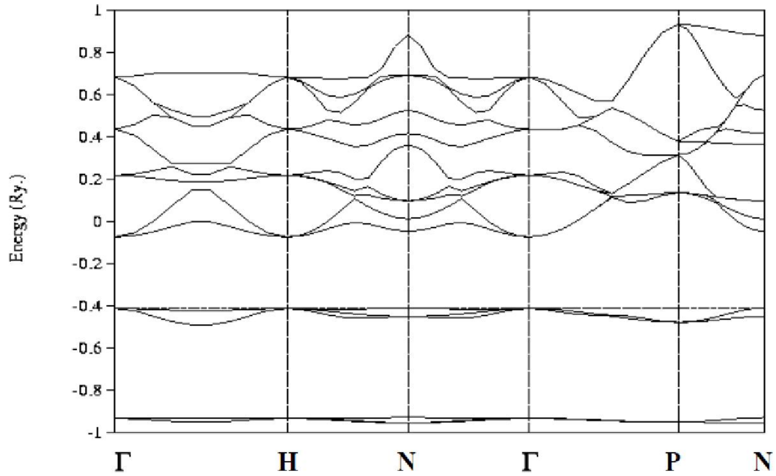

Figure 1 : Band structure of *CsBr* at V/Vo=1 in CsCl structure (normal pressure)

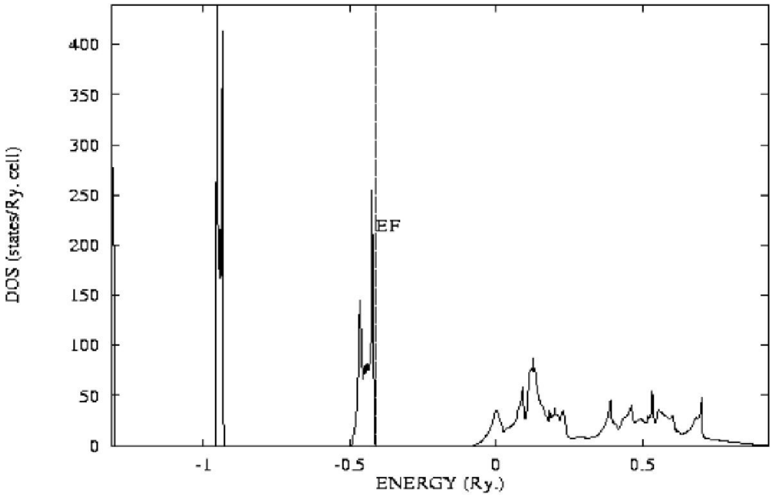

Figure 2 : Density of states of *CsBr* V/Vo=1 in CsBr structure (normal pressure)

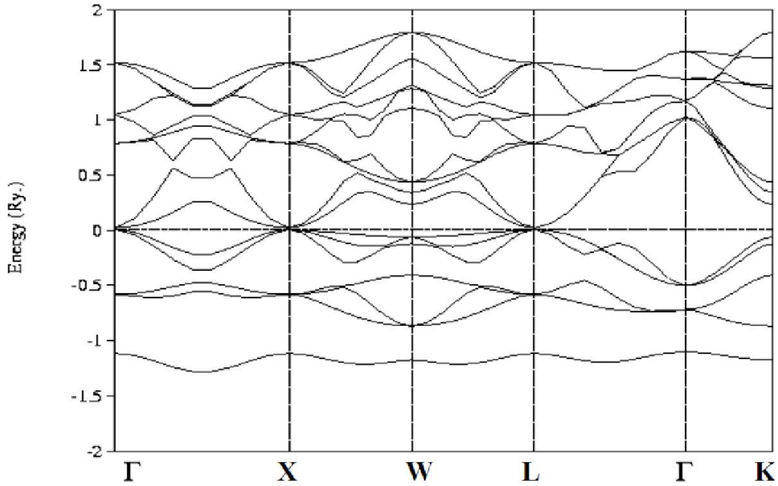

Figure 3 : Band structure of *CsBr* at V/Vo=0.377 in HCP structure

able at the Fermi level up to metallization pressure. In Figure 4, there is appreciable value for $N(E_F)$ at V/V_o =0.377, for *CsBr* in *HCP* structure, which indicates metallization in *CsBr*. Further increase in pressure leads to enhanced density of states at the Fermi level which induces superconductivity[13].

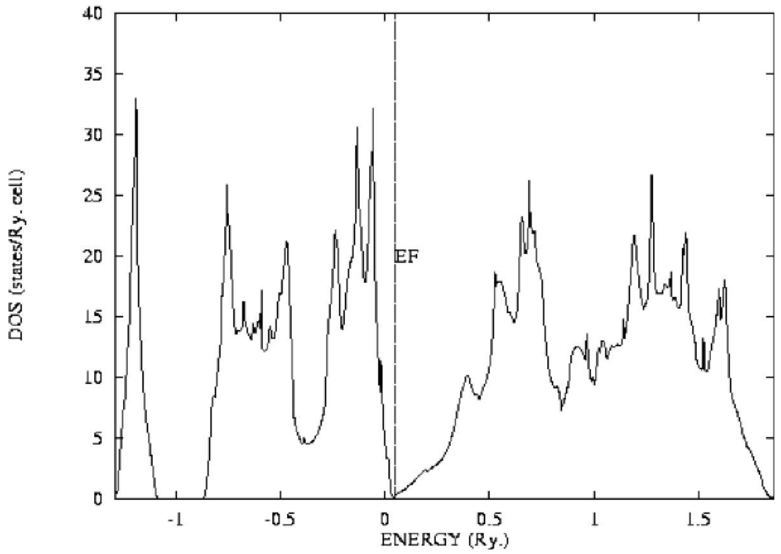

Figure 4 : Density of states of *CsBr* at V/Vo=0.377 in HCP structure

RESULTS AND DISCUSSION

Ground state properties

The ground state properties and structural phase transitions of *CsBr* is studied from its total energy obtained from our calculation. The total energy is calculated as a function of reduced volume (V/V_o) for *CsCl* and *HCP* phases of *CsBr*. Here, V_o is the experimental equilibrium volume corresponding to the experimental equilibrium lattice constant. The calculated total energies were fitted to Murnaghan's equation of state[16]

$$P = 1.5B_o [(V_o/V)^{7/3} – (V_o/V)^{5/3}]$$
$$[1 + 0.75 (B_o^1 - 4) \{(V_o/V)^{2/3}-1\}] \qquad (1)$$

to obtain the equilibrium lattice constant and other ground state properties.

The variation in the total energy as a function of reduced volume for *CsBr* is calculated. Up to V/V_o= 0.5856, *CsCl* structure has the lowest energy and on further reduction of volume *HCP* structure becomes more stable in energy than the *CsCl* structure. In TABLE 1, the equilibrium lattice constant (a_o), band gap (E_g), bulk modulus (B_o) and its pressure derivative (B_o^1) values are compared with experimental and previous theoretical works[9-13].

Structural phase transition

In our calculation we have chosen the *CsCl* structure for CsBr at ambient pressure. The phase stability of the Cs*Cl* and HCP structure of *CsBr* is analysed using the enthalpy calculation[13]. The enthalpy *H(P)* is defined by

$$H(P) = E_{tot}(P) + PV(P) \qquad (2)$$

and the transition pressure corresponding to the phase transition from *B3* to *B1* is obtained from the relation

$$H_{CsCl}(P) = H_{HCP}(P) \qquad (3)$$

where H_{CsCl} and H_{HCP} are the enthalpies of the *CsCl* and *HCP* phases respectively. The phase transition pressure (P_T) and the corresponding reduced volume $(V/V_o)_T$ estimated in our calculation are given in TABLE 2. For *CsBr*, our calculated phase transition pressure is in good agreement with the experimental and previous theoretical results. The mechanism for the phase transition is a geometric effect involving a change in the coordination number from 8 in the *CsCl* phase to 12 in the *HCP* phase[17].

Metallization

At normal pressure *CsBr is* wide gap insulator. With the increase of the pressure, the band gap decreases and at a particular pressure, there is a closing of the band gap. The band structure and density of states corresponding to metallization of *CsBr* are shown in Figures 3 and 4 respectively. In *CsBr,* the metallization occurs through direct closing of the band gap between valence band maximum at Γ point and conduction band minimum at Γ point. The metallization volume of *CsBr* is V/V_o=0.377 (*HCP* structure), which corresponds to the pressure $P_M = 1.738$ Mbar.

At the metallization pressures, the values for density of states at Fermi energy $N(E_F)$ are very small (pseudo gap), which indicate that metallization has just set in CsBr (Figure 4). Thereafter $N(E_F)$ increases slowly with pressure and becomes fairly large at a particular value of V/V_o. The values of E_F and $N(E_F)$ corresponding to different V/V_o are used in studying the pressure variation of superconducting transition temperature[13]. However, there are no experimental or theoretical study available for comparison at these pressures.

Superconductivity in CsBr under pressure

The promotion of *s* electron to *d* shell in solids is one of the factors which will induce superconductivity. Under very high pressure, alkali halides are not only metals but also superconductors. The theory of Gaspari and Gyorffy[18] in conjunction with McMillan's formula is used to calculate *Tc*.

The electron –phonon mass enhancement factor , λ is[19]

$$\lambda = \frac{N(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle} \qquad (4)$$

where *M* is the atomic mass, $\langle\omega^2\rangle$ is an average of the phonon frequency square and $\langle I^2\rangle$ is an average (over the Fermi energy) of the electron – phonon matrix element square[19].

$\langle I^2\rangle$ (in Rydbergs) can be written as

$$\langle I^2\rangle = 2\sum_l \frac{(l+1)}{(2l+1)(2l+3)} M^2_{l,l+1} \frac{N_l(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)} \qquad (5)$$

where $M_{l,l+1} = -\phi_l\,\phi_{l+1}[(D_l(E_F)-1)(D_{l+1}(E_F)+l+2) + (E_F-V(S))S^2]$ and in this,

ϕ_l is the radial wave function at the muffin-tin sphere radius corresponding to the Fermi energy.

D_l is the logarithmic derivative of the radial wave function at the sphere boundary.

$V(S)$ is the muffin-tin potential at the sphere boundary.

S is the radius of the muffin-tin sphere.

The above quantities are taken from the band structure results[20].

The average of the phonon frequency square is

$$\langle\omega^2\rangle = \frac{1}{2}\theta_D^2 \qquad (6)$$

The variation of Debye temperature with pressure $\theta_D(P)$ is given by[13]

$$\theta_D(P) = \frac{\sqrt{E_F}}{\sqrt{E_F^o}}\frac{a_o}{a}\theta_D^o \qquad (7)$$

where θ_D^o, a_o and E_F^o are normal pressure quantities.

The McMillan's formula[20] used for *Tc* calculation,

$$Tc = \frac{\theta_D}{1.45}\exp\left[\frac{-1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] \qquad (8)$$

gives the good estimate of the *Tc* value. Here μ^* is the electron-electron interaction parameter which is estimated using the relation[21],

$$\mu^* = \frac{0.26N(E_F)}{1+N(E_F)} \qquad (9)$$

where $N(E_F)$ is the density of levels per atom per eV at E_F.

With the results obtained from the self-consis-

TABLE 2 : Metallization, phase transition and superconducting transition pressures in *CsBr*

Cesium Compound	Metallization		Phase transition *CsCl to HCP*		Onset of superconducting transition	
	P_M Mbar	$(V/V_o)_M$	P_T Mbar	$(V/V_o)_T$	P_S Mbar	$(V/V_o)_S$
CsBr	1.738	0.3770	0.3	0.5856	2.0	0.366

TABLE 3 : Variation of *Tc* as a function of pressure for *CsBr in HCP* structure

Pressure P $_{\text{Mbar}}$	λ	θ_D K	μ^*	Tc K
2.0	0.8306	138.49	0.1251	4.9000
2.1	0.7376	144.13	0.1025	4.6022
2.2	0.6850	148.79	0.0951	4.2276
2.3	0.4500	153.49	0.0917	1.1433
2.4	0.3000	161.37	0.0900	0.4358

tent calculation, we have computed θ_D, λ, μ^* and *Tc* as a function of pressure using Eqs.(4 - 9). The calculated values at high pressure (*HCP*) structure is given in TABLE. 3. As pressure increases our computed value of *Tc de*creases and reaches a minimum value. The calculated *Tc* values depend more sensitively on changes in λ than μ^*, indicating that this compound is electron-phonon-mediated superconductor.

CONCLUSION

In the present investigation, the pressure dependent band structures and density of states of *CsBr* are computed and the results are used to study the metallization and superconductivity under high pressure for the first time. 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 gap in *CsBr* (metallization). On further increase of pressure, *CsBr* becomes superconductor, and CsBr comes under the class of electron-phonon-mediated high pressure superconductor. It is also confirmed that the metallization, structural phase transition and onset of superconductivity do not occur simultaneously in Cesium compounds.

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