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FULL PAPER

Electronic Band Structure, Density of States, Phase Transitions, Metallization and Superconducting Transition of KBr 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 potassium bromide (KBr) under pressure is presented. The phase transition pressure at which the compound undergoes structural phase transition from NaCl to CsCl 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 KBr is a direct band gap insulator. In KBr, the metallization occurs through indirect closing of the band gap between Γ and H points at the reduced volume V/Vo=0.45 (CsCl structure), the corresponding metallization pressure is 1.274 Mbar. On further increase of pressure, KBr becomes superconductor, and this material comes under the class of electron-phonon-mediated high pressure superconductor. The superconducting transition temperatures (Tc) of KBr is obtained as a function of pressure for both NaCl and CsCl structures. The highest Tc estimated is 5.911 K and the corresponding pressure is 5 Mbar in the NaCl structure and 0.897 K in the CsCl structure. It is also confirmed that the metallization, structural phase transition and onset of superconductivity do not occur simultaneously in ionic compounds.

Keywords: band structure; density of states; phase transition; metallization; superconductivity

1. Introduction

Ionic compounds are ubiquitous materials and are characterized by their highly crystalline nature, high melting points and strong miscibility in polar media. Potassium bromide (KBr) is a large band gap ionic insulator with energy gap = 7.4 eV and its ionic crystalline structure produces its unique high ultraviolet transmissivity. The transition of an insulator to a metal (metallization) at high compression is generally the result of the pressure induced closure of the band gap. Potassium chloride is expected to have a uniquely high metallization pressure among large bandgap solid insulators [1]. Under strong shock compression, the insulating –conducting transition is enhanced by the thermal promotion of electrons across band gap. This is a result of high temperature produced by high pressure (>1 Mbar) shock waves [1]. Recently, ramp compression has been used to compress materials to pressures above 8 Mbar while keeping the temperature low compared to that of shock waves [2]. Band structure calculations reveal that alkali halide compounds are wide-gap insulators that explain their optical transparency [3]. Ionic salts have gained substantial importance recently due to the ability of ionic liquids to dissolve a variety of organic substance including cellulose. Ionic crystals are probably the simplest system to understand, since the interactions among the ions are purely electrostatic in origin. Hence the description of their ground state energies is exact within the limit of calculation [3].

The physical properties of materials undergo a variety of changes when they are subjected to

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high pressure [1]. The increase of pressure means the significant decrease in volume, which results in the change of electronic states and crystal structure [2]. In particular, there is a great interest in the pressure induced insulator – metal transition and superconductivity of simple alkali halides [3]. The alkali iodide KBr which crystallizes in NaCl structure under ambient conditions is of great physical interest; since it find application in manufacture of opto-electronic devices and serve as a typical model for other ionic compounds [4]. Experimentally it is found that, the ionic insulator KCl is a metal under high pressure and as the pressure is increased, superconductivity sets in [1]. These results lead us to expect superconductivity in other alkali halides under high pressure, especially those alkali bromides which have already become metals [3].

The electronic band structure calculations on alkali halides suggest that the insulator-metal transitions are due to the reordering of the energy bands with the empty d-like band dropping in energy below the top of the filled p-like bands [4]. There are many investigations both theoretical and experimental on the band structure, metallization and superconductivity of alkali halides [5-26].

In 1973 Metallization of alkali halide crystals under super high pressure was reported by Zhdanov et al. [21]. The equation of states was obtained for both phases in a wide range of pressures from 0 to 2 Mbar. In 1984, Pressure-induced structural transition of KI and KBr was reported by Huang et al. [22]. In this study a pressure- induced phase transition of KBr was found by using energy dispersive X- ray diffraction with a synchrotron X-ray source. The cubic phase KBr was found to undergo transformation to CsCl crystal structure under high pressure similar to that recently reported for KI. In 1995, High pressure low- symmetry phases of cesium halides were reported by Stefano Baroni et al. [23]. In this report the results for KI, KBr, KCl up to pressures of approximately 1 Mbar were presented. In 1998, studies on KBr with synchrotron radiation under ultra-high pressure up to 1.15 Mbar was reported by Wang Li- Jun et al. [24]. In this study the maximum pressure is 1.15 Mbar. KBr is changed from cubic NaCl phase to CsCl phase at about 0.022 Mbar. No pressure induced metallization transition has at high pressure up to 1.15 Mbar. In 1998, conduction bands and invariant energy gaps in alkali bromides was reported by De Boer et al. [25]. In this study electronic structure calculations of the alkali bromides LiBr, NaBr, KBr, RbBr and KBr were reported. It was felt that many disagreements exist between theory [26] and experiment [22, 24] 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 [13]. Hence, to gain a fundamental understanding of the structural phase transition, metallization and superconductivity of KBr, the electronic band structure studies of this material is essential, and this motivated the present investigation. In Section 3, 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 2. Concluding remarks are given in Section 4.

2. Results and Discussion

2.1. Band structure and density of states

2.1.1. Calculative procedure

Alkali bromide KBr crystallizes in NaCl structure under ambient conditions and undergo structural phase transition from NaCl to CsCl structure under pressure [5]. We have obtained (i) normal pressure band structure and density of states of KBr (with NaCl structure) and (ii) high pressure band structure and density of states of KBr (with CsCl structure). Also, we have analyzed the structural phase transition from NaCl → CsCl structure, metallization and superconducting transition. The electronic band structure calculations were performed for *KBr* corresponding to different reduced volumes in NaCl and CsCl tructures, by the first-principle FP-LMTO method [26-28, 4]. The electronic configurations of K (Z=19) and Br (Z=35) are [Ar]4s1 and [Ar] 3d10 4s2 4p5, respectively. The valence electronic configurations of K and Br are 3p6 4s1 and 4s2 4p5, 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) [29], to determine the phase-transition pressure and other ground-state properties [30, 31]. The band structure results are used to compute the superconducting transition temperature (Tc) and its pressure variation [32, 33].

2.1.2 The Band structure and Density of states of KBr at normal pressure

The normal pressure band structure of KBr (for NaCl structure) is given in Fig. 1. Fermi level is indicated by dotted horizontal line. The overall topology of the band structure at $V/V_o = 1$ is same for previous calculations. The triplet bands which are positioned at the bottom of valence band arise from $3p^6$ electrons of K (Fig. 1). A single band nearer to the triplet bands is due to Br-$4s^2$ electrons (Fig. 1). The three bands appearing just below the Fermi energy E_F are from K-$4s^1$ and Br-$4p^5$ electrons of KBr (Fig. 1). The empty conduction bands above the Fermi level are due to $4p^0$, $3d^0$ states of K and $5s^0$, $4d^0$ states of Br (Fig. 1). At normal condition, the band gap E_g is found to be 0.4672 Ry (6.354 ev) for KBr. The experimental band gap is 7.6 ev for KBr [22]. The general features of band structures are similar to previous calculations [1]. From our calculation, KBr is a direct band gap insulator at normal pressure.

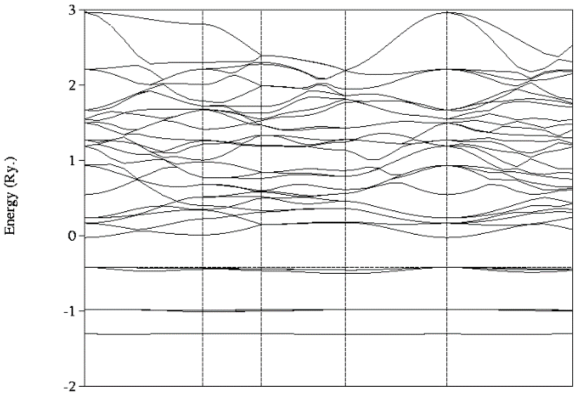

Figure 1. Band structure of KBr at $V/V_o = 1$ (NaCl structure).

The density of states histograms of KBr at normal pressure are given in Fig. 2. From the histogram, it is seen that at normal pressure the levels arising from k- $3p^6$ (Fig.2) electrons give a longest spike with narrow width. The long spike near the origin is due to Br-$4s^2$ electrons and the short spikes near E_F are due to K-$4s^1$, Br-$4p^5$ electrons (Fig. 2). The short spikes above the E_F are due to the $4p^0 3d^0$ and $5s^0 4d^0$ states of KBr (Fig. 2).

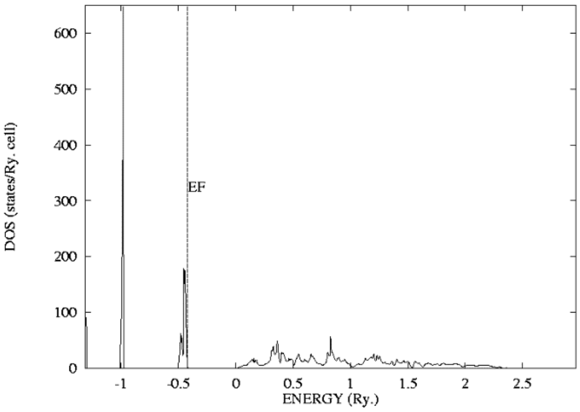

Figure 2. Density of states of KBr at $V/V_o = 1$ (NaCl structure).

3. Material and Methods

3.1 Ground state properties

The ground state properties of KBr is studied from their total energies obtained from our calculation. The total energy is calculated as a function of reduced volume for both B1 and B2 phases of KBr (V/V_o = 1.0 to 0.3 insteps of 0.05). Here V_o is the experimental equilibrium volume corresponding to experimental equilibrium lattice constant a_o = 12.4763 a.u for KBr. The calculated total energies were fitted to Murnaghan's equation of state [29] to obtain the equilibrium lattice constant and

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

other ground state properties. The variations of total energy as a function of reduced volumes for KBr is shown in Fig. 3. Our estimated bulk modulus of KBr is 0.145 Mbar. The compressibility decreases as the size of the cation decreases. In Table 1, the equilibrium lattice constant, bulk modulus and band gap values are compared with experimental [22, 24] and previous theoretical work [25].

Table 1. Equilibrium lattice constant, bulk modulus and band gap.

Compound	Present work			Experiment [22, 24]			Previous theory [25]		
	a_o a.u	B_o Mbar	E_g eV	a_o a.u	B_o Mbar	E_g eV	a_o a.u	B_o Mbar	E_g eV
KBr	12.379	0.145	6.354	12.4763	0.151	7.600	12.056	0.135	6.307

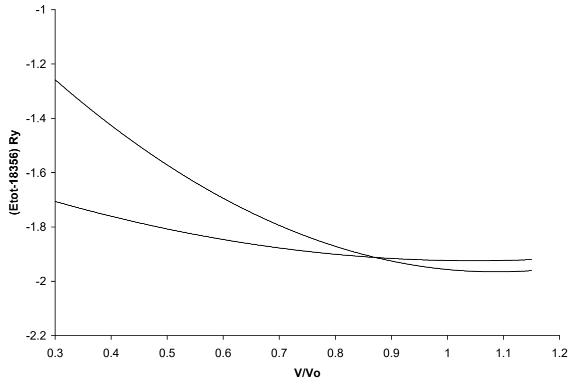

Figure 3. Total energy versus reduced volume curve for KBr (B1 and B2 structures).

3.2 Structural phase transition

Under high pressure KBr undergo a structural phase transition from the NaCl structure (B1) to the CsCl structure (B2). The phase stability of B1 and B2 structures of KBr is analyzed using the enthalpy calculation. The enthalpy is defined by

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

and the transition pressure corresponding to the phase transition from B1 to B2 is obtained from the relation

$$H_{B1}(P) = H_{B2}(P) \qquad (3)$$

where H_{B1} and H_{B2} are the enthalpies of the B1(NaCl) and B2 (CsCl) phases respectively. The enthalpy *versus* pressure plots of KBr is given in Fig. 4. The phase transition pressure (P_T) and the corresponding reduced volume (V_T) estimated in our calculation are 0.0254Mbar and 0.88 respectively. Our calculated phase transition volume and pressure are in good agreement with the experimental value of 0.022 Mbar [24]. The charge transfer causes the phase transition but the mechanism for the phase transition is a geometric effect involving a change in co-ordination number from 6 in the B1 phase to 8 in the B2 phase.

3.3 Metallization

At normal pressure, KBr is a wide gap insulator (figs.1 and 2). As 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. These changes lead to the narrowing of the band gap and at particular pressure, there is a closing of band gap. KBr becomes metals under pressure but before that they undergo structural phase transition from B1 phase to B2 phase. The band structure and density of states corresponding to metallization of KBr is shown in figs. 5 and 6. In KBr, metallization takes place by the indirect closure (Fig.5) of band gap between valence band (at Γ-point) and conduction band (at H-point). The metallization volume of KBr is V/V_o = 0.45, which corresponds to the pressure P_M = 1.274 Mbar (Table 2). These values are in better agreement with the experimental observation of pressure above 1.15 Mbar [22, 24]. The metallization occurs because of the closure of band gap between Br - 4p-like valence band and K - 3d -like conduction band (Fig. 5).

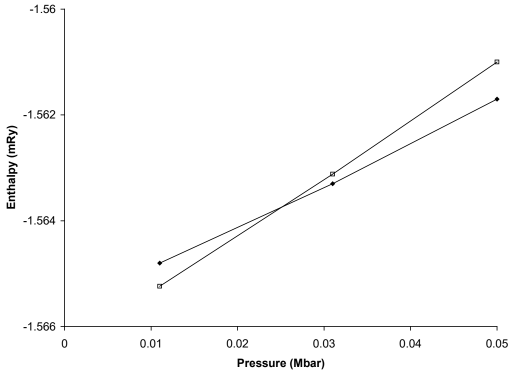

Figure 4. Enthalpy versus pressure curve for KBr.

The increase of pressure causes the broadening of bands which results in the decrease of density of states value in most of the energy regions of DOS histogram. Thus in Fig. 6, the heights of the spikes are considerably reduced. When pressure is increased E_F increases whereas no density of states is available at the Fermi level up to metallization pressure. There are appreciable values for DOS at V/V_o = 0.45 (Fig. 6) indicating metallization in KBr. Further increase in pressure leads to enhanced density of states at the Fermi level which induces superconductivity in KBr.

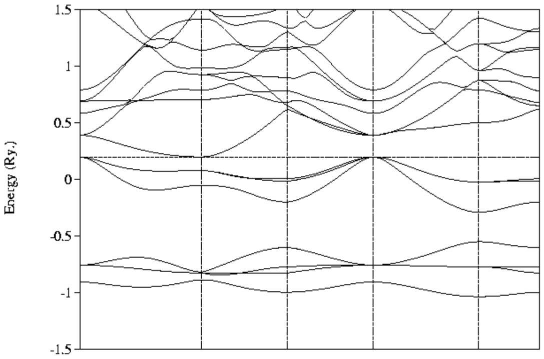

Figure 5. Band structure of KBr at $V/V_o = 0.45$ (CsCl structure).

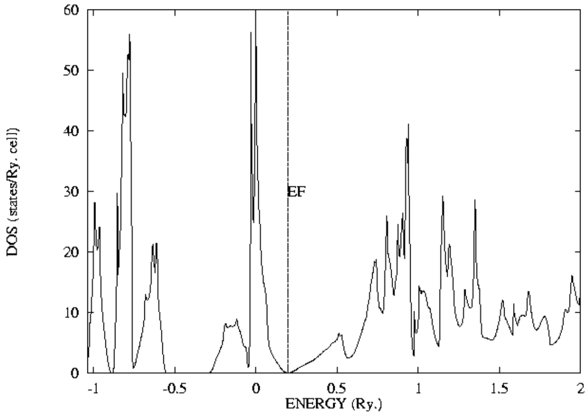

Figure 6. Density of states of KBr at $V/V_o = 0.45$ (CsCl structure).

Table 2. Metallization pressure for KBr.

Compound	Lattice constant a.u	Present study		Experiment [22,24]		Previous theory [25]	
		$(V/V_o)_M$	P_M Mbar	$(V/V_o)_M$	P_M Mbar	$(V/V_o)_M$	P_M Mbar
KBr	12.379	0.450	1.274	<0.460	>1.150	0.435	1.475

3.4 Superconductivity

The factors which determine superconducting behavior in alkali halides are electron - phonon mass enhancement factor λ, electron-electron interaction parameter μ^*, Debye temperature θ_D, $s, p \rightarrow d$ electron transfer and the *d* electron delocalization. The calculated values of θ_D, λ, μ^* and *Tc* under various pressures for KBr in NaCl and CsCl structures are given in tables 3 and 4. The onset of superconductivity in KBr is at 2.5 Mbar and thereafter *Tc* increases with pressure. From tables 3 and 4, it is seen that *Tc* reaches a maximum value (*Tc-max*) of 5.911 K for KBr in NaCl structure. But this value is 0.897 K for KBr in the CsCl structure (tables 3 and 4).

Table 3. *Tc* as a function of pressure for KBr (NaCl structure).

Pressure ***P* Mbar**	λ	θ_D K	μ^*	*Tc* K
2.50	0.286	528	0.101	0.122
3.00	0.343	671	0.112	0.546
4.50	0.431	732	0.124	2.203
5.00	0.527	868	0.138	5.911

Table 4. *Tc* as a function of pressure for KBr (CsCl structure).

Pressure ***P* Mbar**	λ	θ_D K	μ^*	*Tc* K
2.50	0.165	489.4	0.046	0.008
3.00	0.170	551.9	0.046	0.014
4.50	0.219	621.0	0.047	0.203
5.00	0.254	647.4	0.038	0.897

Our theoretical estimate for μ^* (Table 4) in CsCl structure is small when compared to the standard value ($\mu^* = 0.1$) used for metals. This is because the DOS at E_F ($N(E_F)$), on which μ^* depends, is zero to start with and increases slowly with pressure in alkali halides. The path to the enhancement of *Tc* under pressure lies in the direction of higher $\theta_D(P)$. Also the valus of μ^* increases slightly with pressure whereas λ increases significantly with pressure. But the contribution from $\mu^* (P)$ to the variation of *Tc(P)* is much less important than that of $\lambda (P)$. From this we concluded that, KBr is electron-phonon mediated superconductors. The calculated λ values of KBr is small, thus one can expect measurable superconductivity at low temperature as we have predicted [1]. The growth of the anion - *d* electron number with pressure (more itinerant than its previous status) is attributed to the superconducting behavior in alkali halides. From this, we concluded that alkali halides are pressure induced superconductors with low *Tc* values. Also, if KBr is retained in the normal structure (NaCl) under high pressure then the *Tc* value is comparatively high (tables 3 and 4). From Table 5, it is seen that the metallization, structural phase transition and onset of superconductivity does not occur simultaneously in KBr.

Table 5. Metallization, phase transition and superconducting transition pressures.

Compound	**Metallization**		**structural phase transition**		**Onset of superconducting transition**		***Tc-max* K**	
	P_M Mbar	$(V/V_o)_M$	P_T Mbar	$(V/V_o)_T$	P_S Mbar	$(V/V_o)_S$	NaCl (normal pressure structure)	CsCl (high pressure structure)
KBr	1.274	0.45	0.0254	0.88	2.5	0.35	5.911	0.897

4. Conclusions

In the present investigation, the pressure dependent band structures and density of states of KBr are computed and the results are used to study the structural phase transition, metallization and superconductivity under pressure. Our calculation confirms the structural phase transition from NaCl structure to CsCl structure in KBr under pressure. The calculated metallization pressure P_M is in better agreement with the experimental observation than the previous theoretical calculations. In KBr, both NaCl and CsCl structures give increasing of *Tc* with increase of pressure. In our calculation the highest *Tc* obtained is 5.911 K for KBr in NaCl structure and 0.897 K for KBr in the CsCl structure. The calculated Tc values depends more sensitively on λ rather than θ_D. So, KBr comes under an electron-phonon mediated superconductor. For KBr, no experimental Tc value available for comparison. The structural phase transition (0.0254 Mbar), metallization (1.274 Mbar) and onset of superconductivity (2.5 Mbar) do not occur simultaneously in ionic salts is confirmed in the simple ionic salt KBr.

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