

Pressure Induced Structural Phase Transition, Metallization and Superconductivity in RbBr

Y. Ramola^a, C. Nirmala Louis^{*a}, and A. Amalraj^b

^aResearch Center in Physics, Holy Cross College, Nagercoil 629 004, Tamil Nadu, India.

^bProfessor of Chemistry, St. Jerome's College, Ananthanadarkudy-629201 KK District, Tamilnadu, India

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Abstract:

The structural phase transition, metallization and superconductivity of the simple alkali bromide, Rubidium bromide (RbBr) is investigated through their band structures. Under high pressure RbBr undergoes a structural phase transition from the NaCl structure (B1) to the CsCl structure (B2). The band structure, density of states (DOS) and total energy are computed as a function of volume for both B1 and B2 phases using the full potential linear muffin-tin orbital (FP-LMTO) method. The ground state properties and band gap values are compared with the experimental results. The pressure corresponding to structural phase transition from NaCl structure (B1) to the CsCl structure (B2) is 0.028 Mbar in RbBr. The metallization pressure P_M is 1.172 Mbar. The superconducting transition temperatures (T_c) of RbBr is obtained as a function of pressure for both NaCl and CsCl structures. The highest T_c estimated is 2.151 K and the corresponding pressure is 4 Mbar in the NaCl structure and 0.819 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; high pressure

1. 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 [2]. The modern development in diamond anvil cell [3-11] enables the experimentalist to perform the investigation at very high value of pressure (5 Mbar). Already 23 new elemental superconductors were found at high pressure. In this list new compounds are now being included. One such compound is the simple ionic salt CsI [3].

Systems like oxygen [5], CsI [3], SnI₄ [7], selenium [8], phosphorous [9] and vanadium [10] are investigated under high pressure and these materials are found to become superconductors at very high pressures. In particular, there is a great interest in the pressure induced insulator –

metal transition and superconductivity of simple alkali halides. The alkali bromide RbBr 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 [11]. 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 bromides which have already become metals.

The electronic band structure calculations on alkali halides suggest that the insulator-metal transitions are due to the reordering of the energy bands [12] 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

*Corresponding author. E-mail:  nirmala_louis@yahoo.co.in

metallization of RbBr [13-20].

In 1973 Metallization of alkali halide crystals under super high pressure was reported by Zhdanov et al. [21]. The equation of states were obtained for both phases in a wide range of pressures from 0 to 2 Mbar. In 1984, pressure-induced structural transition of RbBr was reported by Huang et al. [22]. In this study a pressure-induced phase transition of RbBr was found by using energy dispersive X-ray diffraction with a synchrotron X-ray source. The cubic phase RbBr was found to undergo transformation to CsCl crystal structure under high pressure similar to that recently reported for KI [1]. In 1995, high pressure low- symmetry phases of rubidium halides was reported by Baroni and Giannozzi [23]. In this report the results for KI, KBr, RbBr 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 applied is 1.15 Mbar. RbBr is changed from cubic NaCl phase to CsCl phase at about 0.025 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 [25] 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 T_c which has been observed experimentally for CsI [3]. Hence, to gain a fundamental understanding of the structural phase transition, metallization and superconductivity of RbBr, 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 calculation procedure, electronic band structure and density of states corresponding to various pressures are given. 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 Ground state properties

The ground state properties of RbBr 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 RbBr ($V/V_0 = 1.0$ to 0.3 in steps of 0.05). Here V_0 is the experimental equilibrium volume corresponding to experimental equilibrium lattice constant $a_0 = 12.754$ a.u for RbBr. The calculated total energies were fitted to Murnaghan's equation of state [29] to obtain the equilibrium lattice constant and other ground state properties.

The variations of total energy as a function of reduced volumes for RbBr is shown in Fig. 1. Our estimated bulk modulus of RbBr is 0.143 Mbar. The compressibility decreases as the size of the cation decreases [1]. In Table 1, the equilibrium lattice constant, bulk modulus and band gap values are compared with experimental [22, 24] and previous theoretical works [25].

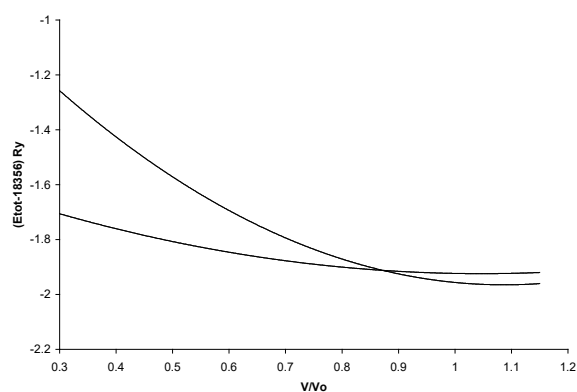


Figure 1. Total energy versus reduced volume curve for RbBr (B1 and B2 structures).

2.2 Structural phase transition

Under high pressure RbBr undergo a structural phase transition from the NaCl structure (B1) to the CsCl structure (B2). The phase stability of B1 and B2 structures of RbBr is analyzed using the enthalpy calculation. The enthalpy versus pressure plots of RbBr is given in Fig. 2. The phase transition pressure (P_T) and the corresponding reduced volume (V_T) estimated in our calculation are 0.028 Mbar and 0.87, respectively. Our calculated phase transition volume and pressure are in good agreement with

the experimental value of 0.025 Mbar [24]. The charge transfer causes the phase transition but the mechanism for the phase transition is a

geometric effect involving a change in coordination number from 6 in the NaCl phase to 8 in the CsCl phase.

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

Compound	Present work			Experiment [22, 24]			Previous theory [25]		
	a_0 a.u	B_0 Mbar	E_g eV	a_0 a.u	B_0 Mbar	E_g eV	a_0 a.u	B_0 Mbar	E_g eV
RbBr	12.754	0.143	6.254	12.956	0.149	7.200	12.556	0.133	6.207

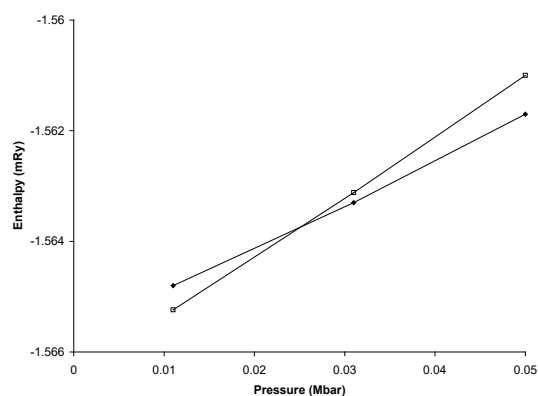


Figure 2. Enthalpy versus pressure curve for RbBr.

2.3 Metallization

At normal pressure, RbBr 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. RbBr 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 RbBr is shown in Figs. 3 and 4. In RbBr, metallization takes place by the indirect closure (Fig. 3) of band gap between valence band (at Γ -point) and conduction band (at H-point). The metallization volume of RbBr is $V/V_0 = 0.47$, which corresponds to the pressure $P_M = 1.172$ 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 Rb - 4d like conduction band (Fig. 3).

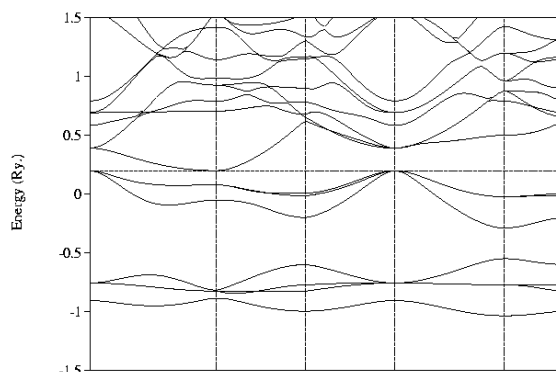


Figure 3. Band structure of RbBr at $V/V_0 = 0.47$ (CsCl structure).

Table 2. Metallization pressure for RbBr.

Compound	Lattice Constant a.u	Present study		Experiment [22, 24]		Previous theory [25]	
		$(V/V_0)_M$	P_M Mbar	$(V/V_0)_M$	P_M Mbar	$(V/V_0)_M$	P_M Mbar
RbBr	12.754	0.470	1.172	<0.460	>1.150	0.425	1.335

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. 4, 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 $V/V_0 = 0.47$ (Fig. 4) indicating metallization in RbBr. Further increase in pressure leads to enhanced density of states at the Fermi level which induces superconductivity in RbBr [30]. However, there are no experimental or theoretical study available for comparison at these pressures in RbBr. But experimental and theoretical studies are available for comparison with alkali iodides KI and CsI [1, 3].

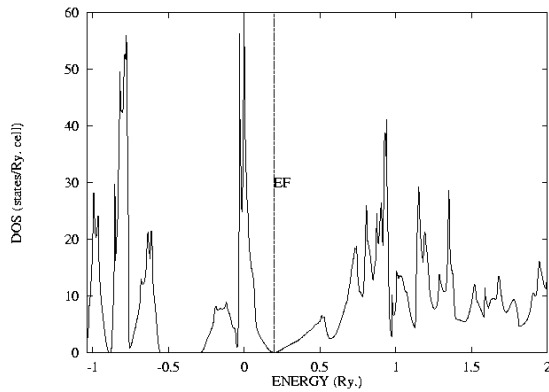


Figure 4. Density of states of RbBr at $V/V_0 = 0.47$ (CsCl structure).

3.4 Superconductivity

The factors which determine superconducting behaviour 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 continuous promotion of s, p electron to d shell in solids under pressure is one of the factors which will induce superconductivity [13, 14]. The theory of Gaspari and Gyoffy in conjunction with McMillan's formula is used to calculate T_c [31, 32].

The electron -phonon mass enhancement factor, λ is:

$$\lambda = N(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle \quad (1)$$

where M is the atomic mass, $\langle \omega^2 \rangle$ is an average of the phonon frequency square and $\langle I^2 \rangle$ is the square of the electron - phonon matrix element averaged over the Fermi surface. $\langle I^2 \rangle$ (in Rydbergs) can be written as [12]:

$$\langle I^2 \rangle = 2 \sum_l \{ (l+1) / ((2l+1)(2l+3)) \} M_{l,l+1}^2 \{ N_l(E_F) N_{l+1}(E_F) / N(E_F)^2 \} \quad (2)$$

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 to calculate $M_{l,l+1}$ are taken from the band structure results [1, 12, 13, 17, 18]. We have calculated λ separately for Rb and Br atoms and for the T_c calculation (Eq. 4) the mean value of λ is used [13].

The average of the phonon frequency square is:

$$\langle \omega^2 \rangle = 0.5 \theta_D^2 \quad (3)$$

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

$$\theta_D(P) = \theta_D^0 (a_0/a) (\sqrt{E_F} / \sqrt{E_F^0}) \quad (4)$$

where θ_D^0 , a_0 and E_F^0 are normal pressure quantities.

McMillan's formula [32],

$$T_c = (\theta_D / 1.45) \exp \{ -1.04(1+\lambda) / [\lambda - \mu^*(1+0.62\lambda)] \} \quad (5)$$

gives the good estimate of the T_c value [30]. Here μ^* is the electron-electron interaction parameter which is estimated using the relation [33]:

$$\mu^* = 0.26 N(E_F) / (1+N(E_F)) \quad (6)$$

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

The Fermi energy E_F (Ry) and density of states $N(E_F)$ (states/Ry.cell) are obtained from the self-consistent calculation and we have calculated the variation of θ_D , λ and T_c with pressure using Eqs. 1 - 6 [1]. The value of T_c is determined at higher pressures also. The calculated values for θ_D , μ^* , λ and T_c under various pressures are given in Table 3 (for NaCl structure) and Table 4 (for CsCl structure). The onset of superconductivity in RbBr is at 2.0 Mbar and thereafter T_c increases with pressure. From Tables 3 and 4, it is seen that T_c reaches a maximum value (T_c -max) of 2.151 K for RbBr in NaCl structure. But this value is 0.819 K for RbBr in the CsCl structure (Tables 3 and 4).

Our theoretical estimate for μ^* (Tables 4 and 5) 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 T_c under pressure lies in the direction of higher $\theta_{b\kappa}$. Also, the value of μ^* increases slightly with pressure whereas λ increases significantly with pressure. But the contribution from $\mu^*(P)$ to the variation of $T_c(P)$ is much less important than that of $\lambda(P)$. From this we concluded that, RbBr is electron-phonon mediated superconductors. The calculated λ values of RbBr 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 behaviour in alkali halides. From this, we concluded that alkali halides are pressure induced superconductors with low T_c values. Also, if RbBr is retained in the normal structure (NaCl) under high pressure then

the T_c 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 occurs simultaneously in RbBr.

Table 3. T_c as a function of pressure for RbBr (NaCl structure).

Pressure P Mbar	λ	$\theta_{b\kappa}$	μ^*	$T_{c\kappa}$
2.00	0.186	247.6	0.020	0.091
3.00	0.228	260.8	0.021	0.344
4.00	0.337	275.1	0.022	2.151

Table 4. T_c as a function of pressure for RbBr (CsCl structure).

Pressure P_{Mbar}	λ	$\theta_{b\kappa}$	μ^*	$T_{c\kappa}$
2.00	0.197	197.5	0.040	0.038
3.00	0.249	209.2	0.051	0.156
4.00	0.363	221.6	0.075	0.819

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

Compound	Metallization		Structural phase transition		Onset of superconducting transition		T_c -max K	
	P_M Mbar	$(V/V_0)_M$	P_T Mbar	$(V/V_0)_T$	P_s Mbar	$(V/V_0)_s$	NaCl (normal pressure structure)	CsCl (high pressure structure)
RbBr	1.172	0.47	0.028	0.87	2.0	0.39	2.151	0.819

3. Material and Methods

3.1 Computer methods

3.1.1 Band structure and density of states

3.1.1.1 Calculative procedure

The band structures of RbBr corresponding to various pressures are obtained in NaCl and CsCl structures using the full potential linear muffin-tin orbital (FP-LMTO) method with in generalized gradient approximation (GGA) [26, 27]. This method is well discussed in the literature [8, 1, 2, 28]. Here we have given only the computational details. The electronic configuration of Rb and Br are $[\text{Ar}] 5s^1 4p^6$ ($Z=37$) and $[\text{Ar}] 3d^{10} 4s^2 4p^5$ ($Z = 35$), respectively. The valence electronic

configurations of Rb and Br are $4p^6 5s^1$ 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 the Birch-Murnaghan's equation of state (EOS) [29], to determine the phase transition pressure and other ground state properties [30].

Birch-Murnaghan's equation of state is given by:

$$P = 1.5B_0 \left[(V_0/V)^{7/3} - (V_0/V)^{5/3} \right] \left[1 + 0.75 (B_0^{-1} - 4) \left\{ (V_0/V)^{2/3} - 1 \right\} \right] \quad (7)$$

to obtain the equilibrium lattice constant and other ground state properties. In our calculation we have chosen the NaCl structure for RbBr at

ambient pressure. The phase stability of the NaCl and CsCl structures of RbBr is analysed using the enthalpy calculation [1]. The enthalpy $H(P)$ is defined by:

$$H(P) = E_{\text{tot}}(P) + PV(P) \quad (8)$$

and the transition pressure corresponding to the phase transition from NaCl to CsCl is obtained from the relation:

$$H_{\text{NaCl}}(P) = H_{\text{CsCl}}(P) \quad (9)$$

where H_{NaCl} and H_{CsCl} are the enthalpies of the NaCl and CsCl phases respectively. The band structure results are used to compute the superconducting transition temperature (T_c) and its pressure variation [30-33].

3.1.2 The Band structure and Density of states of RbBr at normal pressure

The normal pressure band structure of RbBr (for NaCl structure) is given in Fig. 5. Fermi level is indicated by dotted horizontal line. The overall topology of the band structure at $V/V_0 = 1$ is same for previous calculations [25]. The triplet bands which are positioned at the bottom of valence band arise from $4p^6$ electrons of Rb (Fig. 5). A single band nearer to the triplet bands is due to $\text{Br-}4s^2$ electrons (Fig. 5). The three bands appearing just below the Fermi energy E_F are from $\text{Rb-}5s^1$ and $\text{Br-}4p^5$ electrons of RbBr (Fig. 5). The empty conduction bands above the Fermi level are due to $5p^0$, $4d^0$ states of Rb and $5s^0$, $4d^0$ states of Br (Fig.1). At normal condition, the band gap E_g is found to be 6.254 eV for RbBr. The experimental band gap is 7.2 eV for RbBr^{22} . The general features of band structures are similar to previous calculations on alkali halides [1]. From our calculation, RbBr is a direct band gap insulator at normal pressure.

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

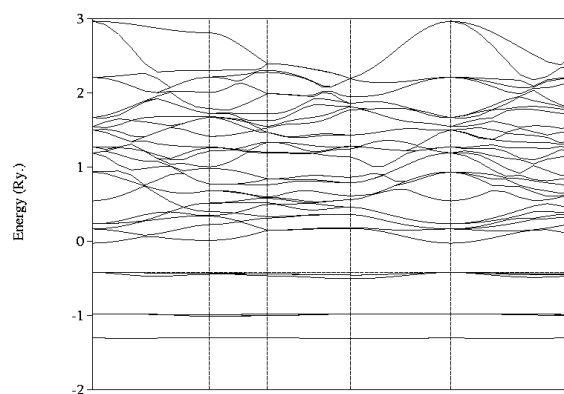


Figure 5. Band structure of RbBr at $V/V_0 = 1$ (NaCl structure).

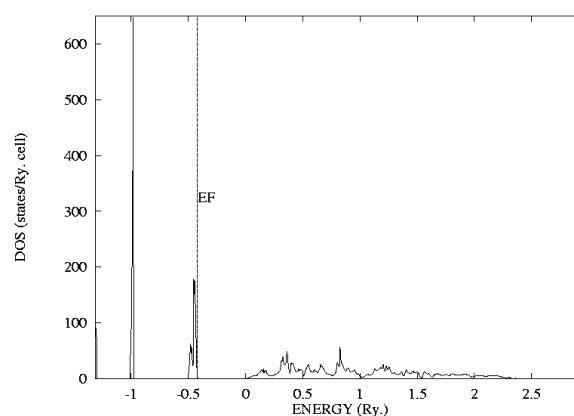


Figure 6. Density of states of RbBr at $V/V_0 = 1$ (NaCl structure).

4. Conclusions

The high pressure band structure, density of states, structural phase transition, metallization and superconductivity of RbBr is investigated. 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 (metallization). The metallization reduced volume is $V/V_0=0.47$ (CsCl structure), and the corresponding pressure P_M is 1.172 Mbar. In our calculation, NaCl phase to CsCl phase transition occurs at 0.028 Mbar. This value is good agreement with the experimental value of 0.025 Mbar. It is also confirmed that the structural phase transition, metallization and superconducting transition do not occur simultaneously in alkali bromide compounds [3].

Acknowledgments

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