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## **BAND STRUCTURE, METALLIZATION AND STRUCTURAL PHASE TRANSITION OF NABR UNDER HIGHPRESSURE**

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### **Abstract:**

*The metallization and the phase transition of the alkali bromide sodium bromide (NaBr) is investigated through its band structure. The equilibrium lattice constant, bulk modulus, pressure derivative of bulk modulus and the phase transition pressure at which the compound undergo structural phase transition from NaCl (B1) to the CsCl (B2) structure is predicted from the total energy calculations. The ground state properties and band gap values are compared with the experimental and other theoretical results. At normal pressure NaBr is a direct band gap insulator. When the pressure is increased there is enhanced overlapping between the wave functions of the neighboring atoms. As a result the widths of the valence and empty conduction bands increase. These changes lead to the narrowing and indirect closing of band gap in NaBr (metallization). It is also confirmed that the metallization and structural phase transition do not occur simultaneously in ionic compounds.*

**Keywords:** Band Structure; Metallization; Phase Transition.

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### **1. Introduction**

The physical properties of materials undergo a variety of changes when they are subjected to high pressure<sup>[1]</sup>. 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<sup>[2]</sup> enables the experimentalist to perform the investigation at very high value of pressure (5 Mbar). With the development of high pressure experimental techniques, investigations on pressure induced structural phase transition and insulator-metal transition are getting the attention of all. In particular, there is a great interest in the pressure induced metallization of simple alkali halides<sup>[3-6]</sup>.

The alkali halides are of great physical interest; since they find application in manufacture of opto-electronic devices and serve as a typical model for other ionic compounds<sup>[7]</sup>. The electronic band structure calculations on alkali halides suggest that the insulator - metal transitions are due to the reordering of the energy bands<sup>[8]</sup> 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 structural phase transition of NaBr<sup>[9-13]</sup>.

In 2014, band – gap and phonon distribution in alkali halides was reported by messaoudi et al<sup>[9]</sup>. In this study, a systematic first principles study was performed to calculate the structural, electronic, dynamical and thermodynamic properties of alkali halides NaF, NaCl, NaBr and NaI by means of both full potential linear augmented plane wave and plane wave pseudo potential method. In this study the temperature dependence of various quantities such as the mean – squared displacement and the heat capacity are computed using the quasi – harmonic approximation<sup>[9]</sup>. In 1998, conduction bands and invariant energy gaps in alkali bromides was reported by Boer and Groot et al. In this study the electronic structure calculations of the alkali bromides LiBr, NaBr, KBr, RbBr and CsBr are reported. It is shown that the conduction band has primarily bromine character<sup>[10]</sup>. In 1997, refractive index of the alkali halides and effect of pressure on the refractive index of 11 alkali halides was reported by P.G Johannsen et al. A recently developed comparative interferometric method for the determination of the refractive index at high pressure is applied to NaF, NaBr, NaI, KCl, KBr, KI, RbCl, RbI, CsCl, CsBr and CsI. In this study the refractive index of the sodium halide shows an almost linear density dependence, while the cesium halides exhibit strong nonlinear behavior<sup>[11]</sup>. In 1983, phase transitions and equations of state for the sodium halides: NaF, NaCl, NaBr and NaI was reported by Yosiko Sato Sorensen. In this study phase changes and equations of state of four sodium halides: NaF, NaCl, NaBr and NaI have been studied upto ~ 60 GPa at room temperature use of a diamond anvil cell. NaF and NaCl transform from the B1 phase to the B2 phase at ~ 23 GPa and ~ 29 GPa respectively. At ~ 33 GPa, NaBr transforms from the B1 phase to an unidentified phase with a lower symmetry than the B2 phase. NaI also transforms at ~ 32 GPa to a new phase which seems to have the same structure as that of high pressure phase of NaBr<sup>[12]</sup>. In 1973 metallization of alkali halide crystals under super high pressure was reported by Zhadnov et al. The equation of states were obtained for both phases in a wide range of pressures, from 0 to 2 Mbar<sup>[13]</sup>. In section 2, we give the details of the calculational procedure, electronic band structure and density of states corresponding to various pressures. The ground-states properties, structural phase transition and metallization are discussed in section 3. Concluding remarks are given in section 4.

## 2. Band Structure and Density of States

### 2.1. Calculational Procedure

Alkali bromide NaBr crystallizes in NaCl structure under ambient conditions and undergo structural phase transition from NaCl to CsCl structure under pressure<sup>[14]</sup>. We have obtained (i) normal pressure band structure and density of states of NaBr (with NaCl structure) and (ii) high pressure band structure and density of states of NaBr (with CsCl structure). Also, we have analyzed the structural phase transition from NaCl to CsCl structure and metallization. The electronic band structure calculations were performed for NaBr corresponding to different volumes in NaCl to CsCl structures, by the first-principle FP-LMTO method with in generalized gradient approximation (GGA)<sup>[13]</sup>.

The electronic configurations of Na ( $Z=11$ ) and Br ( $Z=35$ ) are  $[\text{Ne}] 3s^1$  and  $[\text{Ar}] 3d^{10} 4s^2 4p^5$  respectively. The valence electronic configurations of Na and Br are  $3s^1$  and  $4s^2 4p^5$  respectively. There are 8 electrons contribute to the valence band. The calculated total energies were fitted to murnaghan's equation of state (EOS) <sup>[16]</sup>, to determine the phase-transition pressure and other ground state properties.

## 2.2. Band Structure and Density of States of NaBr Under Pressure

The band structure and density of states of NaBr was computed for various reduced volumes ranging from  $V/V_0=1.0$  to 0.3 in steps of 0.05. Even though we have obtained the band structure for  $V/V_0$  values from 1.0 to 0.3, we have presented here the band structures of NaBr along the symmetry directions  $\Gamma$ -X-W-L- $\Gamma$ -K and  $\Gamma$ -H-N-P- $\Gamma$ -N and the corresponding density of states of NaBr (Figures 1 to 4). The normal pressure band structure and density of states of NaBr is given in figures 1 and 2 respectively. It is seen that the band structure exhibits characteristic features similar to CsBr. In figure 1, the single band, which is positioned at the bottom of valence band, arises from Br- $4s^2$  electrons. The three bands appearing just below the Fermi energy  $E_F$  are from Na- $3s^1$  and Br- $4p^5$  electrons of NaBr. At normal pressure, the direct band gap  $E_g$  is found to be 7.1 eV for NaBr. The levels arising from Br- $4s^2$  electrons give the longest spike (Figure 2). The short spikes near  $E_F$  are due to Na- $3s^1$ , Br- $4p^5$  electrons. 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 <sup>[14,15]</sup>.

At normal pressure, the band gap of NaBr is direct with valence band maximum at  $\Gamma$  point and conduction band minimum at  $\Gamma$  point with band gap value 7.1 eV (figure.1). The calculated energy gap is in agreement with the experimental value (Table 1). As pressure increases the width of the valence band and the empty conduction band get widened <sup>[16]</sup>. 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 CsBr<sup>[17]</sup>. This trend 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 available at the Fermi level up to metallization pressure. In Figure 4, there is appreciable value for  $N(E_F)$  at  $V/V_0=0.308$ , for NaBr in CsCl structure, which indicates metallization in NaBr.

Table 1: Equilibrium lattice constant ( $a_0$ ), Bulk Modulus ( $B_0$ ) and its pressure derivative ( $B_0'$ ) of NaBr in NaCl structure

Ground state properties	NaBr		
	Present work	Experimental works [4]	Previous theoretical works [7]
$a_0$ a.u.	11.2854	11.34215	10.9641
$B_0$ Mbar	0.199	0.21	0.28
$B_0'$	5.49	5.46	5.48
$E_g$ eV	7.1	7.102	5.84

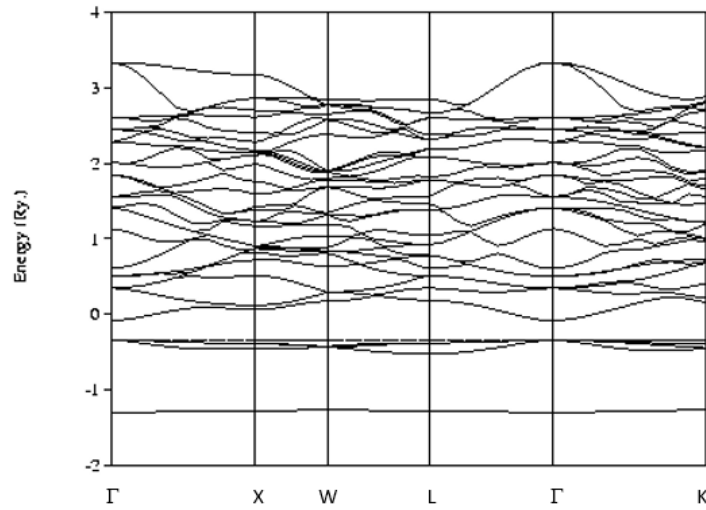


Figure 1: Band structure of NaBr at V/Vo=1 in NaCl structure (normal pressure)

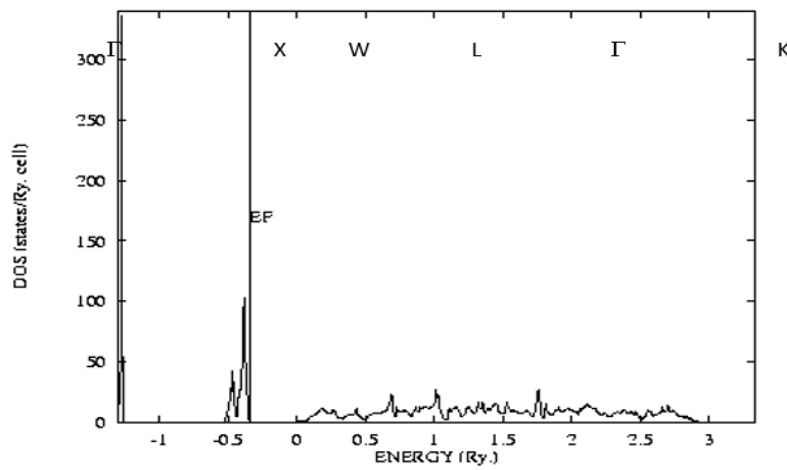


Figure 2: Density of states of NaBr at V/Vo=1 in NaCl structure (normal pressure)

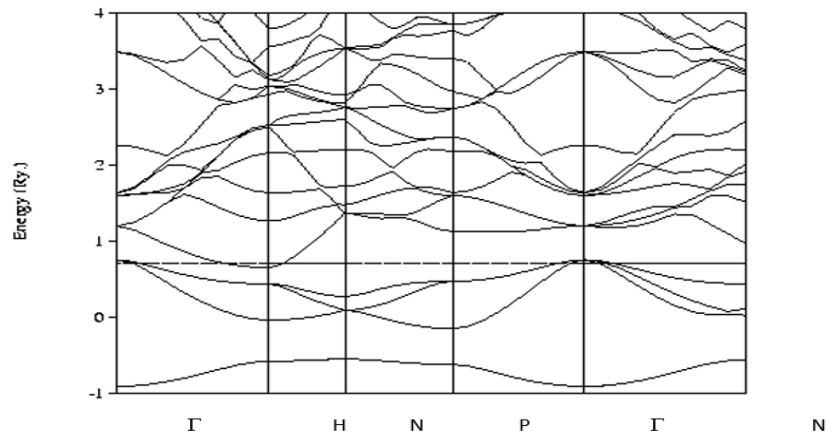
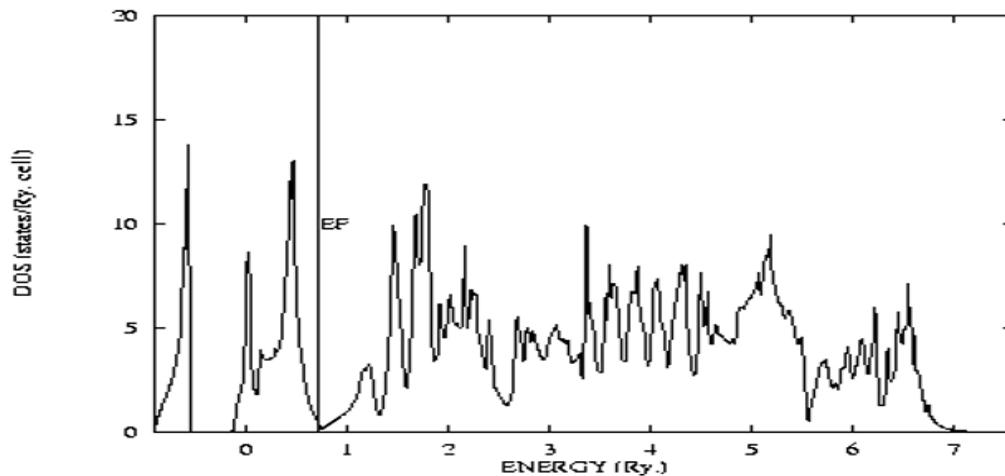


Figure 3: Band structure of NaBr at V/Vo=0.308 in CsCl structure

Figure 4: Density of states of NaBr at  $V/V_0=0.308$  in CsCl structure

### 3. Results and Discussion

#### 3.1. Ground State Properties

The ground state properties and structural phase transitions of NaBr are studied from its total energy obtained from our calculation. Relation connecting pressure and reduced volume of NaBr is given in figure 5. In this figure, when the volume decreases pressure increases. Relation connecting pressure and band gap ( $E_g$ ) of NaBr is given in figure 6. In this figure, when the pressure increases the band gap decreases and  $E_g=0$  at metallization pressure. Relation connecting reduced volume and lattice constant of NaBr is given in figure 7. In this figure, when the volume decreases lattice constant decreases. The total energy versus reduced volume curve is given in figure 8. The total energy is calculated as a function of reduced volume ( $V/V_0$ ) for NaCl and CsCl phases of NaBr. Here,  $V_0$  is the experimental equilibrium volume corresponding to the experimental equilibrium lattice constant. The calculated total energies were fitted to Murnaghan's equation of state<sup>[16]</sup>

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

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

The variation in the total energy as a function of reduced volume for NaBr is calculated. In table 1, the equilibrium lattice constant ( $a_0$ ), band gap ( $E_g$ ), bulk modulus ( $B_0$ ) and its pressure derivative ( $B_0'$ ) values are compared with experimental and previous theoretical works<sup>[9-13]</sup>. From the total energy as a function of reduced volume curve (Figure 8), it is found that, in NaBr, upto  $V/V_0=0.63$  ( $P_T=0.50$ ), NaCl structure has the lowest energy and on further reduction of volume CsCl structure becomes more stable in energy than the NaCl structure (Table 2).

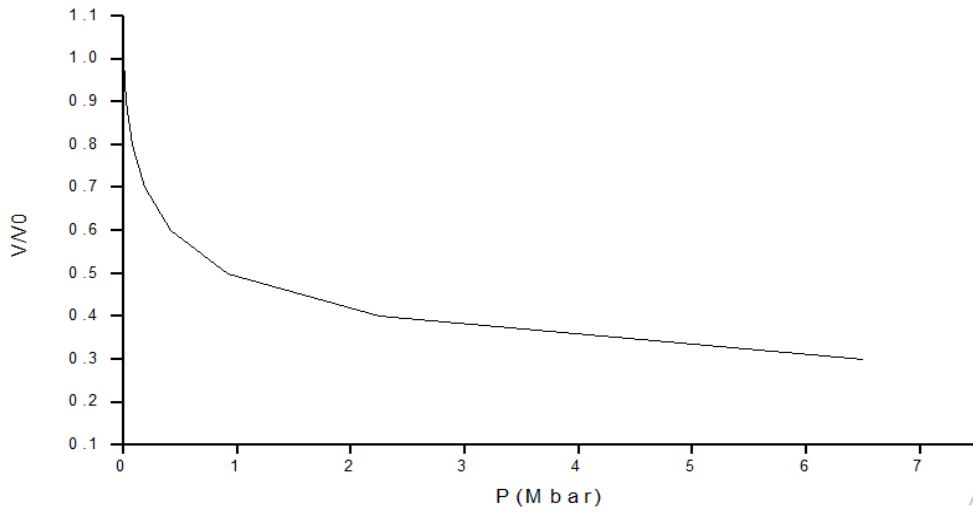


Figure 5: Relation connecting pressure and reduced volume of NaBr

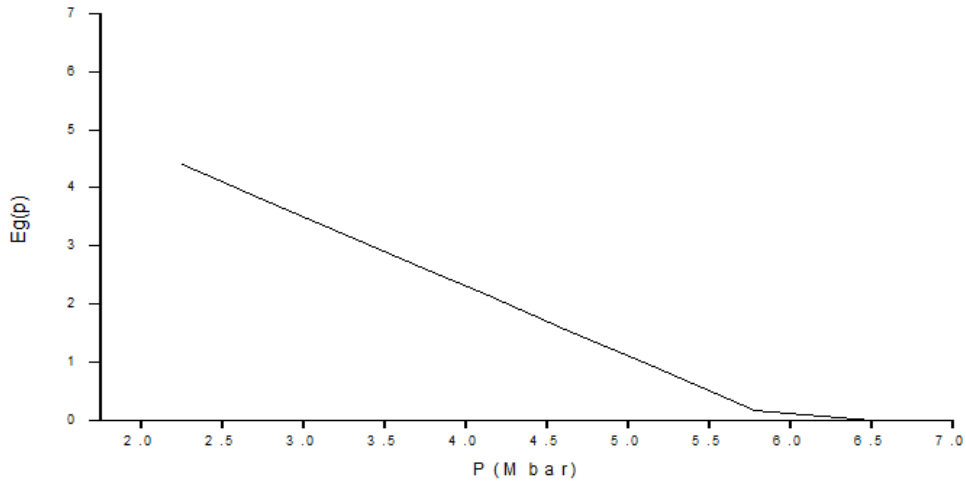


Figure 6: Relation connecting pressure and energy gap of NaBr

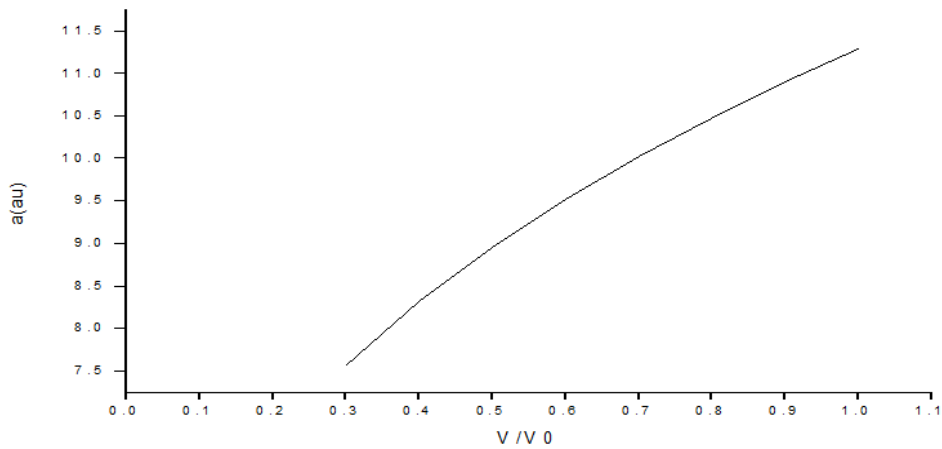


Figure 7: Relation connecting reduced volume and lattice constant of NaBr

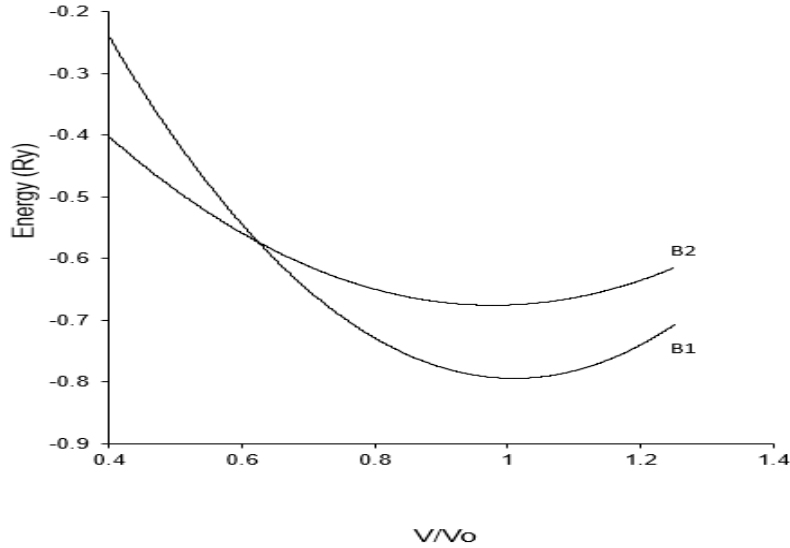


Figure 8: Relation connecting reduced volume and total energy of NaBr

Table 2: Metallization and Phase transition in NaBr

Sodium Compound	Metallization		Phase transition NaCl to CsCl	
	$P_M$ Mbar	$(V/V_0)_M$	$P_T$ Mbar	$(V/V_0)_T$
NaBr	5.9117	0.308	0.50	0.63

### 3.2. Structural Phase Transition

In our calculation we have chosen the NaCl structure for NaBr at ambient pressure. The phase stability of the NaCl and CsCl structure of NaBr is analysed using the enthalpy calculation<sup>[13]</sup>. The enthalpy  $H(P)$  is defined by

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

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

$$H_{NaCl}(P) = H_{CsCl} \tag{3}$$

Where  $H_{NaCl}$  and  $H_{CsCl}$  are the enthalpies of the NaCl and CsCl phases respectively. The pressure versus enthalpy curve for NaBr is given in Figure 9. The phase transition pressure ( $P_T$ ) and the corresponding reduced volume  $(V/V_0)_T$  estimated in our calculation are given in table 2. For NaBr, our calculated phase transition pressure is in good agreement with the experimental and previous theoretical results.

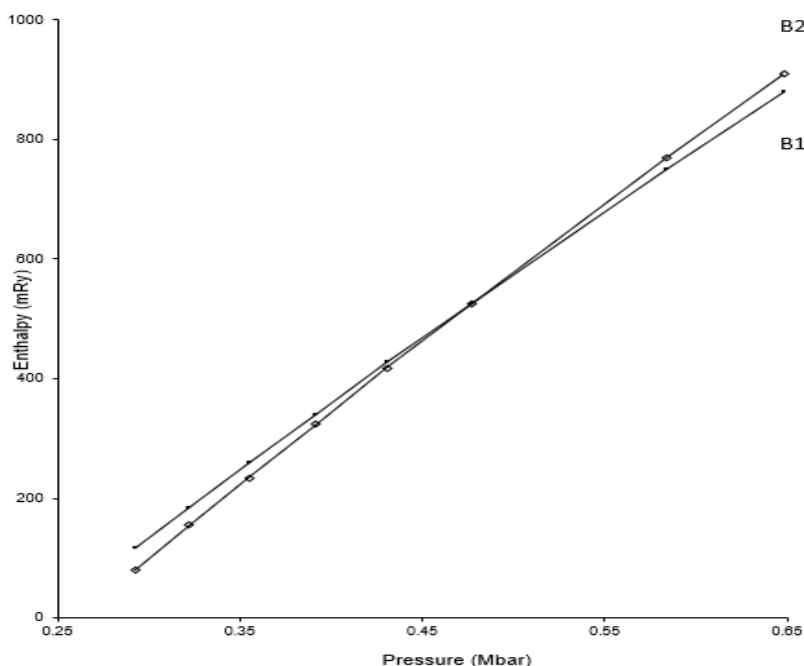


Figure 9: Relation connecting pressure and enthalpy of NaBr

### 3.3. Metallization

At normal pressure NaBr 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 of metallization NaBr are shown figures 3 and 4 respectively. In NaBr, the metallization occurs through indirect closing of the band gap between valence band maximum at  $\Gamma$  point and conduction band minimum at H point. The metallization volume of NaBr is  $V/V_0 = 0.308$  (CsCl structure), which corresponds to the pressure  $P_M = 5.9117$  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 just set in NaBr (figure 4).

### 4. Conclusion

In the present investigation, the pressure dependent band structures and density of states of NaBr are computed and the results are used to study the metallization and structural phase transition under high pressure. When the pressure is increased there is enhanced overlapping between the wave functions of the neighboring atoms. As a result the widths of the valence and empty conduction band increase. These changes lead to the narrowing and closing of band gap in NaBr (metallization).

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