

Pressure Induced Structural Phase Transition, Metallization and Superconductivity in Sodium Iodide (NaI)

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Abstract The structural phase transition and metallization of the simple alkali iodide, sodium iodide (*NaI*) is investigated through their band structures. The band structure, density of states (DOS) and total energy are computed as a function of volume for both NaCl and CsCl phases using the full potential linear muffin-tin orbital (FP-LMTO) method. The phase transition pressure (P_T) and the corresponding reduced volume (V_T) estimated in our calculation are 0.038 Mbar and 0.89 respectively. The metallization pressure P_M is 2.6259 Mbar and the corresponding reduced volume (V_M) is 0.36. The results of the metallization pressure in *NaI* are compared with that of other alkali iodide potassium iodide (KI) and RbI. It is found, that the charge transfer from *s* and *p* states to the *d* state will cause metallization and the metallization pressure increases with a decrease of the lattice constant. It is also confirmed that the metallization and structural phase transition do not occur simultaneously in ionic compounds.

Keywords Band Structure, Metallization, Structural Phase Transition, NaI, Density of States

achieved by Vohra [12]. But Eremets experimentally find the evidence for the metallization and superconductivity of CsI at high pressure. The ionic salt CsI is a metal under high pressure and as the pressure increases superconductivity sets in CsI [4]. In KI, Wier et al [13] experimentally reported the structural phase transition and metallization. In the present paper, we give more extensive discussion about the band structure, density of states and electronic charge distributions as a function of reduced volume. The structural phase transition, stability of the phase, equilibrium bulk modulus, metallization and superconductivity are reinvestigated and critically analyzed. The pressure dependence of the band gap and enthalpy calculations is performed at various high pressures. We give the details of the calculational procedure and electronic band structure corresponding to various pressure in section 2. In Section 3, the ground-state properties, structural phase transition and metallization are discussed. Concluding remarks are given in Section 4. These results lead us to expect superconductivity in other alkali halides under high pressure, especially those alkali iodides which have already become metals [1].

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 twenty three 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]. This material is a testing ground both for photo converters [3]. The metallization in CsI is experimentally

2. Band Structure and Density of States

2.1. Calculational Procedure

Sodium iodide crystallizes in rock salt structure under ambient conditions and undergoes structural phase transition from NaCl to CsCl structure. The electronic band structure calculations were performed for NaI corresponding to different reduced volumes both in NaCl to CsCl structures, by the first-principle linear muffin-tin orbital (FP-LMTO) method. We have used FP-LMTO method with generalized gradient approximation (GGA) [14,15]. It is based on the idea that one electron states of solids can be written as combinations of a small number of

states of the constituent atoms. Also the crystal potential is approximated by a series of non-overlapping atomic like spherically symmetric potentials and a constant potential between the spheres. This method has the advantage that the theory and the result are very easy to understand. For this reason most results of the electronic structures computed are interpreted in the light of full potential theory [16]. This full potential model assumes the solution to the time-independent single electron Schrödinger equation Ψ is well approximated by a linear combination of atomic orbitals. In this linear method, functions constructed from partial waves and their first energy derivatives obtained within the muffin-tin approximation are used as fixed basis. The chemical content of this technique acts as a guide to the non-specialist who wants to perform band structure calculations of his own. The problem of electronic structure involves the computation of eigen states for an infinite number of interacting electrons. This leads to the estimation called one electron approximation, which describes each electron as an independent particle moving in the mean field of the order electrons plus the field of the nuclei [16]. By standard variation technique one can obtain a set of linear equations, in terms of the Hamiltonian and overlap matrices to determine the eigen E and the expansion coefficients. Here the one electron energies are found by a single diagonalisation of the secular matrix [14,15].

We give here only the calculational details. The electronic configurations of Na is $[\text{Ne}] 3s^1 (Z=11)$ and for it is $[\text{Kr}] 4d^{10} 5s^2 5p^5 (Z=53)$. The valence electronic configurations of Na and I are $3s^1$ and $5s^2 5p^5$ respectively. There are 8 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) [17], to determine the bulk modulus and pressure derivative of bulk modulus B_0^1 . We have obtained,

- (i) Normal pressure band structure and density of states NaI (with NaCl structure)
- (ii) High pressure band structure and density of states of NaI (with CsCl structure)

The calculated total energies are fitted to Murnaghan's equation of states (EOS), to determine the pressure derivative of bulk modulus B_0^1 , phase-transition pressure and other ground – state pressure and other ground state properties [18,19]. The bulk modulus is a property of the material which defines its resistance to volume change when compressed. The cause for phase transition and the relation phase transition pressure and atomic radii are deduced from band structure investigation [10].

2.2. Band Structure and Density of States of NaI under Pressure

2.2.1. Band Structure and Density of States at Normal Pressure

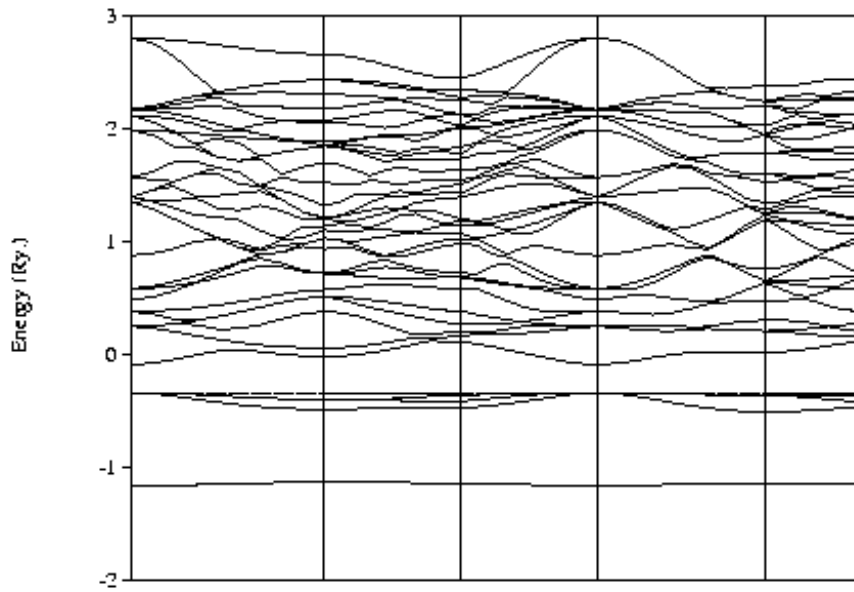
The normal pressure band structure of NaI (for NaCl

structure) is given in Fig.1. The overall topology of the band structure at $V/V_0=1$ is same for previous calculation. The three bands appearing just below the Fermi energy E_F are from Na- $3s^1$ and I- $5s^2, 5p^5$ electrons of NaI (Fig. 1). The empty conduction bands above the Fermi level are due to $3p^0, 3d^0$ states of Na and $5d^0, 6s^0, 6p^0$ states of I (Fig. 1). At normal condition, the band gap E_g is found to be 0.2480 Ry (3.373 eV) for NaI. The general features of band structures are similar to previous calculations. From our calculation, NaI is a direct band gap insulator at normal pressure. The density of histograms of NaI at normal pressure are given in Fig. 2. From the histogram, it is seen that at normal pressure the short spikes near E_F are due to Na- $3s^1, I-5p^5$ electrons (Fig. 2). The short spikes above the E_F are due to the $3p^0, 3d^0$ and $5d^0, 6s^0, 6p^0$ states of NaI (Fig. 2). At normal density of states histogram, the band gap E_g is found to be 0.2480 Ry (3.373 eV) for NaI. This value is agreement with the experimental value of 3.36 eV. The general features of density of states are similar to previous calculations [1].

2.2.2. Band Structure and Density of States at High Pressure

The high pressure band structure of NaI (for CsCl structure) is given in Fig. 3. Fermi level is indicated by dotted horizontal line. The overall topology of the band structure at $V/V_0=0.36$ is same as Fig. 1. But Fig. 3 represents metallic NaI and Fig. 1 represents insulating NaI. The triplet bands which are positioned at the bottom of valence band arise $3s^1$ electrons of Na (Fig. 3). A single band nearer to the triplet bands is due to I- $5s^2$ electrons (Fig. 3). The three bands appearing just below the Fermi energy E_F and touching Fermi energy E_F are from Na- $3s^1$ and I- $5p^5$ electrons of NaI (Fig. 3). The filled conduction bands above the Fermi level are due to $3p^0, 3d^0$ states of Na and $5d^0, 6s^0, 6p^0$ states of I (Fig. 3). In NaI, metallization takes place by the indirect closure (Fig. 3) of band gap between valence band maximum of Γ point and conduction band minimum at the H point. The metallization volume of NaI is $V/V_0=0.36$, which corresponds to the pressure $P_M=2.6259$ Mbar. The general features of high pressure band structure is similar to previous calculations [8-12]. From our calculation, in NaI direct closure of band gap occurs.

The density of states histograms of NaI at high pressure is given in Fig. 4. At this pressure NaI is in CsCl structure. From the histogram, it is seen that at high pressure the levels arising from Na- $3s^1$ (Fig. 4) electrons give a longest spike with fine width. The extended spike near the origin is due to I- $5p^5$ electrons and the dumpy spikes near E_F are due to Na- $3s^1, I-5p^5$ electrons (Fig. 4). The petite spikes above the E_F are due to the $3p^0, 3d^0$ and $5d^0, 6s^0, 6p^0$ states of NaI (Fig. 4). In Fig. 4 the heights of the spikes are considerably reduced when compared to Fig. 2. The reason is 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 $V/V_0=0.36$ (Fig. 4) indicating metallization in NaI.



ΓHNΓPN

Figure 1. Band structure of NaI at V/Vo=1.0 (NaCl structure)

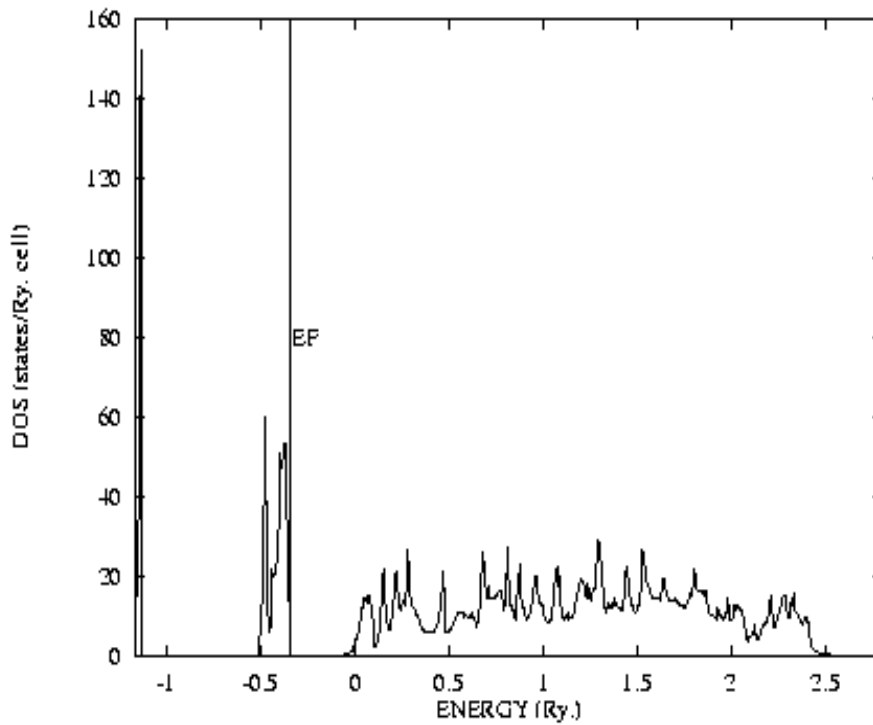


Figure 2. Density of states of NaI at V/Vo=1.0 (NaCl structure)

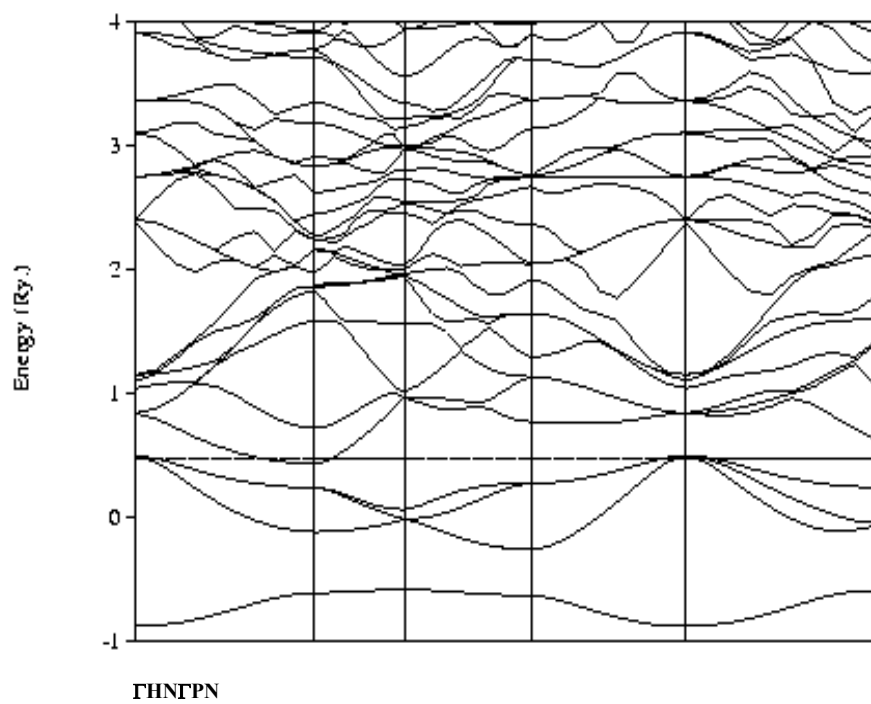


Figure 3. Band structure of NaI at $V/V_0=0.36$ (CsCl structure)

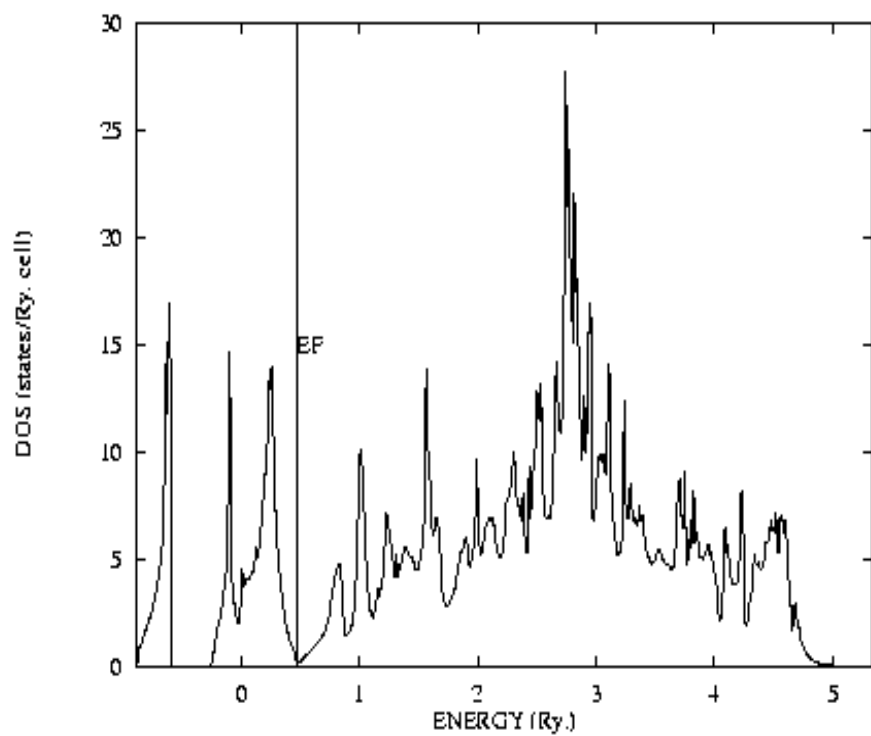


Figure 4. Density of states of NaI at $V/V_0=0.36$ (CsCl structure)

When pressure increases (reduced volume decreases) the value of the DOS at fermi energy, E_F ($N(E_F)$) increases [17]. The normal pressure DOS trend is changed under high pressure. The increase of pressure leads to the broadening of bands and decrease of states value in most of the energy regions. It also increases the width of the valance band and empty conduction bands [14,15]. When pressure increases, the value of E_F increases, whereas no density of states is available at the fermi level up to metallization pressure. Further increases in pressure leads to enhanced density of states at the fermi level which induces superconductivity [20].

3. Result and Discussion

3.1. Ground State Properties

From the total energies obtained from our calculation, the ground state properties and structural phase transition of NaI is studied. The total energy versus reduced volume

curve is given in Fig.5. The total energy is calculated as a function of reduced volume (V/V_0) for both NaCl and CsCl phases of NaI. 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 [14]

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

to obtain the pressure derivative of bulk modulus B_0^{-1} . The calculated reduced volumes, lattice constant and pressure values of NaI for different pressure are given in Table 1. The calculated total energies were fitted to Murnaghan's equation of state [8] to obtain the equilibrium lattice constant and other ground state properties. The values are given in Table 2. From the total energy as a function of reduced volume curve (Fig.5), it is found that, in NaI, up to $V/V_0 = 0.36$ ($P_T = 2.6259$ Mbar), NaCl structure has the lowest energy and on further reduction of volume CsCl structure becomes more stable in energy than the NaCl structure (Table.3).

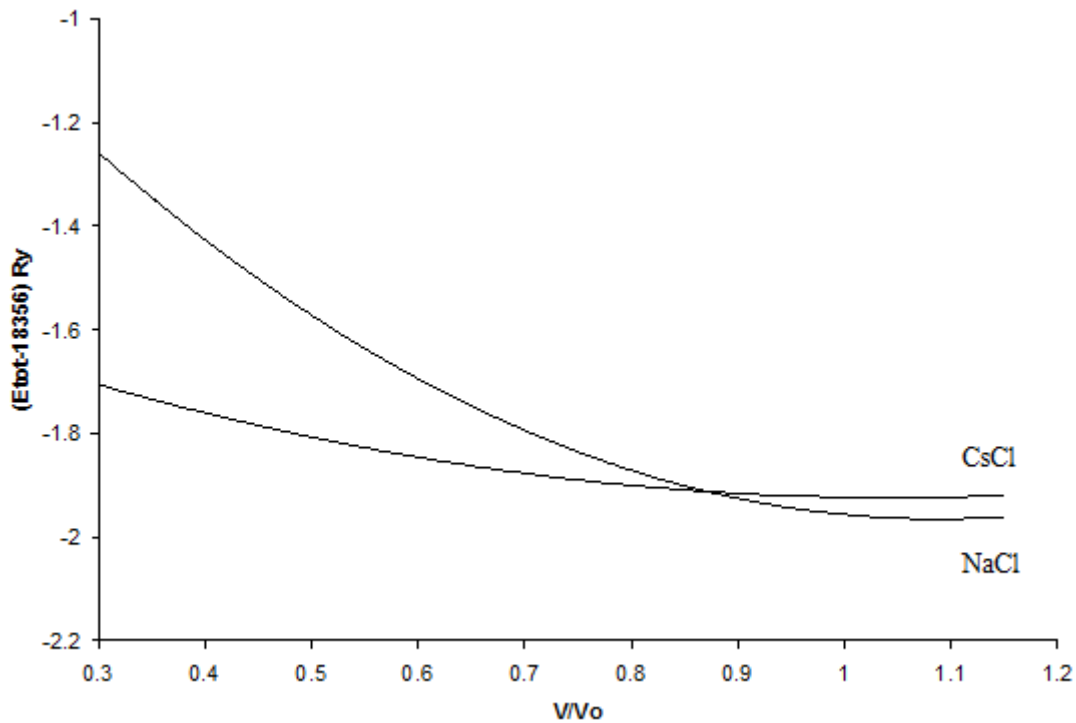


Figure 5. The relation connecting reduced volume and total energy of NaI

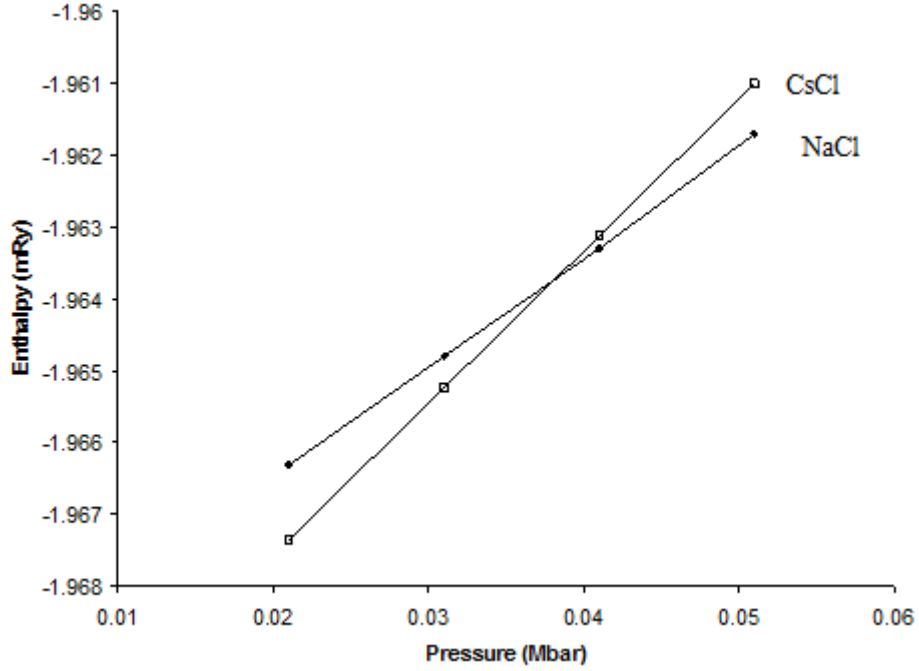


Figure 6. The relation connecting pressure and enthalpy of NaI

Table 1. Lattice constant (a) and Pressure (P) for different reduced volumes

V/V_0	a (a.u)	P (Mbar)	E_g (ev)
1	12.212	0	3.374
0.9	11.791	0.0214	3.346
0.8	11.366	0.0628	3.292
0.7	10.843	0.0920	3.254
0.6	10.299	0.3195	2.959
0.5	9.6293	0.7154	2.444
0.4	8.9979	1.7601	1.0859
0.36	8.687	2.6259	0.0001

Table 2. Equilibrium Lattice constant (a_0), Bulk modulus (B_0) and its Derivative (B_0')

Alkali iodide	a_0 (a.u)	B_0 (Mbar)	B_0'
NaI	12.212	0.151	5.59

Table 3. Metallization and Phase transition in Alkali iodides

COMPOUND	Lattice constant(au)	$(V/V_0)_M$	P_M Mbar
NaI	12.212	0.36	2.626
KI [4]	13.406	0.43	1.228
RbI[1]	13.967	0.4	1.157

3.2. Structural Phase Transition

At ambient pressure NaI is in the NaCl structure. The phase stability of the B1 (NaCl) and B2 (CsCl) structures of NaI is analyzed using the enthalpy calculation [18,19]. The enthalpy $H(P)$ is defined by

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

Where $E_{tot}(P)$ is the total energy of NaI as a function of pressure P and V is the volume of NaI at pressure P . The transition pressure corresponding to the phase transition from B1 to B2 is obtained from the relation

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

Where H_{B1} and H_{B2} are the enthalpies of the B1 and B2 phases respectively. The enthalpy versus pressure curve is given in Fig.6. In this figure, up to $P=0.038$ Mbar, NaCl has lowest energy. Further increase of pressure CsCl has lowest energy. The phase transition pressure (P_T) and the corresponding reduced volume (V_T) estimated in our calculation are 0.038 Mbar and 0.89 respectively. Our calculated phase transition pressure is in good agreement with the experimental value of 0.035 Mbar. However, there is no experimental or theoretical study available for comparison at these pressures in NaI. But experimental and theoretical studies are available for comparison with alkali iodides KI and RbI [Table. 4]

Table 4. Comparison of Metallization and phase transition in alkali iodides

Alkali iodide	Metallization		Phase transition	
	P_M Mbar	$(V/V_0)_M$	P_T Mbar	$(V/V_0)_T$
NaI	2.626	0.36	0.038	0.89
KI [4]	1.228	0.43	0.025	0.92
RbI [1]	1.157	0.4	0.0223	0.934

3.3. Metallization

At normal pressure, NaI is a wide gap insulator (Fig. 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. NaI becomes metal under pressure but before that it undergoes structural phase transition from B1 phase to B2 phase. The band structure and density of state corresponding to metallization of NaI is shown in Fig. 3 and 4. In NaI, metallization takes place by the indirect closure (Fig. 3) of band gap between valence band maximum at Γ point and conduction band minimum at the H point. The metallization volume of NaI is $V/V_0=0.36$ which corresponds to the pressure $P_M = 2.6259$ Mbar. The metallization occurs because of the closure of band gap between I-5p- like valence band and Na-3s- like conduction band (Fig. 3). 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 histograms. Thus in Fig. 4, the heights of the spikes is considerably reduced. When pressure is increased E_F increases whereas no density of states is available at the Fermi level up to metallization pressure [5]. There are appreciable values for DOS at $V/V_0=0.36$ (Fig. 4) indicating metallization in NaI. The comparison of Metallization and phase transition in alkali iodides are given in Table.4. From tables 3 and 4, it is noted that, when lattice constant decreases metallization pressure and phase transition pressure increases.

3.4. Superconductivity and Its Pressure Variation

The continuous promotion of s, p electron to d shell in solids under pressure is one of the factors which will induce superconductivity [11]. The theory of Gaspari and Gyoffy in conjunction with McMillan's formula is used to calculate T_c .

The electron-phonon mass enhancement factor, λ is

$$\lambda = N(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle \quad (4)$$

where M is the atomic mass, $\langle \omega^2 \rangle$ is an average of the phonon frequency square and $\langle I^2 \rangle$ is the square of the electron-phonon matrix element averaged over the Fermi surface. $\langle I^2 \rangle$ (in Rydbergs) can be written as [11].

$$\langle I^2 \rangle = 2 \sum_l \{ (l+1)/(2l+1)(2l+3) \} M_{l,l+1}^2 \{ N_l(E_F) N_{l+1}(E_F) / N(E_F)^2 \} \quad (5)$$

Where,

$$M_{l,l+1} = \Phi_l \Phi_{l+1} [(D(E_F)-1)(D_{l+1}(E_F)+1+2)+(E_F-V(S)S^2)] \quad (6)$$

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 band structure results[11]. We have calculated λ separately for Na and I atoms and for the T_c calculation (Eq.(7)) the mean value of is used

The average of the phonon frequency square is

$$\langle \omega^2 \rangle = 0.5 \theta_D^2 \quad (7)$$

The variation of Debye temperature with pressure $\theta_D(P)$ is given by [11]

$$\theta_D(P) = \theta_D^0 (a_0/a) (\sqrt{E_F}/\sqrt{E_F^0}) \quad (8)$$

where θ_D^0 , a_0 and E_F^0 are normal pressure quantities. McMillan's formula,

$$T_c = (\theta_D/1.45) \exp \{ -1.04 (1+\lambda) / [\lambda - \mu^* (1+0.62\lambda)] \} \quad (9)$$

gives the good estimate of the T_c value [31]. Here μ^* is the electron-electron interaction parameter which is estimated using the relation,

$$\mu^* = 0.26 N(E_F) / (1+N(E_F)) \quad (10)$$

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.(5-8) [21]. The value of T_c is determined at higher pressures also. The calculated values for θ_D , λ and T_c under various pressures are given in Table.5. In our calculation the highest T_c obtained is 1.18708 at 0.3 Mbar. The calculated T_c values depends more sensitive on λ rather than θ_D [21]. For NaI, no experimental T_c value available for comparison.

Table 5. T_c as a function of pressure for NaI

Pressure P Mbar	λ	θ_D K	μ^*	T_c K
3.6241	0.164	275	0.026	0.02467
4.0551	0.197	297	0.04	0.05717
4.5501	0.249	309	0.051	0.22688
45.1211	0.363	321	0.075	1.18708

4. Conclusions

The high pressure band structure, density of states, structural phase transition, metallization and superconductivity of NaI 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 $V/V_0=0.36$ (CsCl structure), and the corresponding pressure P_M is 2.6259 Mbar. In our calculation NaCl phase to CsCl phase transition occurs at 0.038 Mbar. This value is good agreement with the experimental value of 0.035 Mbar. It is also confirmed that the structural phase transition and metallization do not occur simultaneously in alkali iodide compounds [3].

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