High Pressure Electronic Band Structure and Metallization of Potassium Chloride

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Abstract-The structural phase transition and metallization of the simple alkali chloride potassium chloride (KCl) is investigated through their band structures. Under high pressure KCl undergoes a first order structural phase transition from the NaCl structure (B1) to the CsCl structure (B2). For both B1 and B2 phases, the band structure, density of states (DOS), and total energy are estimated as a function of volume. Birch-equation Murnaghan's of state is used to compute pressure values under reduced volume. The results of metallization pressure in KCl are compared to potassium iodide results (KI). Metallization is caused by charge transfer from the s and p states to the d state and the metallization pressure rises as the atomic radius lowers.

I. INTRODUCTION

The physical properties of materials undergo a variety of changes when they are subjected to high pressure [1-5]. Increased pressure causes a considerable reduction in volume, which leads to changes in electrical states and crystal structure. The recent development in diamond anvil cell [3] 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]. New compounds are now added in this list. The simple ionic salt CsI is one such compound [3]. With the advancement of high-pressure experimental techniques, researchers are focusing on pressure-induced structural phase transitions, insulator-metal transitions, and superconducting transitions. The pressure-induced metallization and superconductivity of simple alkali halides are of particular interest [6]. Because they are used in the construction of opto-electronic devices and serve as a model for other ionic compounds, the alkali iodide KCl is of tremendous physical interest [1]. As a result, electronic band structure studies of these materials are critical for gaining a fundamental knowledge of the structural phase transition and metallization of KCl, which drove the current study.

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II. DETAILS OF THE CALCULATION

Under ambient conditions, alkali iodide KCl crystallises in the NaCl structure, but under pressure, it transitions from NaCl to CsCl structure [3]. We have obtained, (i) normal pressure band structure and density of states of *KCl*   (with NaCl structure),(ii) high pressure band structure and density of states of *KCl* (with CsCl structure), Also, we have analyzed the structural phase transition from NaCl ☐ CsCl structure and metallization.

The electronic band structure and structural phase transition of KCl is studied using the first principle full potential linear muffin-tin orbital (FP-LMTO) method [2]. Relativistic contributions except spin-orbit coupling are included [1]. The exchange correlation scheme of von Barth and Hedin [7] is employed. E(k) was determined for the k-point placed at the centre of each volume element after the complete Brillouin zone was partitioned into 4096 cubical volume elements.However, due to symmetry concerns, only 145 k-points for the NaCl structure and 165 kpoints for the CsCl structure are uniformly distributed in the 1/48 th of the first Brillouin zone [1]. Within 10–5 Ry, the final convergence occurs. The tetrahedron method [2] is used to compute the partial and total density of states. The radii of the Wigner-Seitz sphere are chosen based on the charge transfer criterion from cation to anion.   The electronic configurations of K is [Ar] $4s^1$ (*Z*=19) and for Cl it is [Ne] $3s^2\,3p^5$ (*Z*=17). To determine the phase transition pressure and other ground state parameters, the calculated total energies were fitted to Murnaghan's equation of state (EOS) [8-13].

III. BAND STRUCTURE AND DENSITY OF STATES AT NORMAL PRESSURE

The normal pressure band structure of KCl (for NaCl structure) is given in Figure: 1. The dotted horizontal line represents the Fermi level. The overall topology of the band structure at V/Vo=1 is same for previous calculation. The three bands appearing just below the Fermi energy E_F are from $K\text{-}4s^1$ and $Cl\text{-}3p^5$ electrons of KCl (Figure: 1). The empty conduction bands above the Fermi level are due to $4p^0$, $3d^0$ states of K and $4s^0$,$3d^0$ states of Cl (Table: 1). At normal condition, the band gap Eg is found to be 0.3558 Ry (4.8388 eV) for KCl. The basic characteristics of band structures are similar to those found in prior calculations. From our calculation, KCl is a direct band gap insulator at normal pressure. The density of histograms of KCl at normal pressure are given in   Figure: 2. From the histogram, it is seen that at normal pressure the short spikes near E_F are due to $K\text{-}4s^1$, $Cl\text{-}3p^5$ electrons (Figure: 2). The 4p03d0 and 5s04d0 states of KCl are responsible for the brief spikes above the EF (Figure: 2). At normal density of states histogram, the band gap Eg is found to be 0.3558 Ry (4.8388 eV) for KCl.
The general features of density of states are similar to previous calculations [1].

IV. BAND STRUCTURE AND DENSITY OF STATES AT HIGH   PRESSURE

The high pressure band structure of KCl (for CsCl structure) is given in Figure: 3. Fermi level is indicated by dotted horizontal line. The overall topology of the band structure at V/Vo=0.52 is same as Figure: 1. But Figure: 3 represents metallic KCl and Figure: 1 represents insulating KCl. The triplet bands which are positioned at the

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bottom of valence band arise $3p^6$ electrons of K (Figure: 3). A single band nearer to the triplet bands is due to Cl-$3s^2$ electrons (Figure: 3). The three bands appearing just below the Fermi energy E_F and touching Fermi energy E_F are from K-$4s^1$ and Cl-$3p^5$ electrons of KCl (Table: 2).The filled conduction bands above the Fermi level are due to $4p^0,3d^0$ states of K and $4p^0,3d^0$ states of Cl (Figure: 3). In KCl, metallization takes place by the direct closure (Figure: 3) of band gap between valence band and conduction band. The metallization volume of KCl is V/Vo=0.52, which corresponds to the pressure P_M= 1.075 Mbar (Table: 3) The characteristics of the high-pressure band structure are similar to those found in prior calculations [8-12]. According to our calculations, the band gap in KCl closes directly. The density of states histograms of KCl at high pressure is given in Figure: 4. At this pressure KCl is in CsCl structure. From the histogram, it is seen that at high pressure the levels arising from K-$3p^6$ (Table: 4) electrons give a longest spike with fine width. The extended spike near the origin is due to Cl-$3s^2$ electrons and the dumpy spikes near E_F are due to K-$4s^1$, Cl-$3p^5$ electrons (Figure: 4). The petite spikes above the E_F are due to the 4p0 3d0 and $4s^0\ 3d^0$ states of KCl (Figure: 4). In Figure: 4 the heights of the spikes are considerably reduced when compared to Figure: 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/Vo= 0.52 (Figure: 4) indicating metallization in KCl [11,12] .

V. GROUND STATE PROPERTIES

The total energies derived from our computation are used to investigate the ground state characteristics of KCl. For both the B1 and B2 phases of KCl (V/Vo= 1.0 to 0.3 insteps of 0.1), total energy is determined as a function of reduced volume. Vo is the experimental equilibrium volume for KCl with an experimental equilibrium lattice constant of ao=11.8903 au. To determine the equilibrium lattice constant and other ground state parameters, the estimated total energies were fitted to Murnaghan's equation of state [8].

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

The structure of NaCl has the least energy at normal pressure, and the structure of CsCl has the least energy at high pressure [11, 12].

VI. STRUCTURAL PHASE TRANSITION

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

The enthalpy is defined by , $H(P)=E_{tot}(P)+PV(P)$ and the transition pressure corresponding to the phase transition from $B1$ to $B2$ is obtained from the relation [5], $H_{B1}(P)=H_{B2}(P)$ Where H_{B1} and H_{B2} are the enthalpies of the $B1(NaCl)$ and $B2\ (CsCl)$ phases respectively. The phase transition pressure ($P_{T)\ and}$ the corresponding reduced volume (V_T) estimated in our calculation are P_T = 0.06 Mbar and V_T =0.81 respectively. Our calculated phase transition volume and pressure are in good agreement with the previous theory and experiment [3]. The phase

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transition is caused by charge transfer, but the process is geometric effort, which involves a shift in coordination number from 6 in the B1 phase to 8 in the B2 phase [5].

VII.   METALLIZATION

KCl is a broad gap insulator at normal pressure (Figure: 1 and 2). As pressure rises, charge transfers from the s, p, and d states, widening the valence band and increasing the width of the empty conduction bands. The band gap narrows as a result of these changes, and the band gap closes at certain pressures. Under pressure, KCl becomes metal, but first it goes through a structural phase shift from B1 to B2 [11, 13]. Figures 3 and 4 depict the band structure and density of states associated with KCl metallization. The band gap between the valence and conduction bands is directly closed (Figure 3) during metallization in KCl. KCl has a $V/Vo=0.52$ metallization volume, which translates to a pressure of $PM =1.075$ Mbar (Table: 3). The band gap between the Cl-3p-like valence band and the K-4s-like conduction band is closed, resulting in metallization (Figure: 3). In most of the energy zones of DOS histograms, increasing pressure induces band broadening, which leads to a fall in density of states value. As a result, the spike heights in Figure 4 have been reduced significantly. As a result, the spike heights in Figure 4 are significantly lowered. When pressure is increased, EF increases, but up to metallization pressure, no density of states is available at the Fermi level [5]. At $V/Vo=0.52$ (Figure 4) there are significant DOS values, indicating metallization in KCl.

TABLE 1: Lattice constant (*a*) and Pressure (*P*) for different reduced volumes

V/Vo	a (a.u)	P (Mbar)
1	11.8903	0
0.9	11.480362	0.0243
0.8	11.038798	0.0709
0.7	10.558701	0.1629
0.6	10.030375	0.3547
0.5	9.4395180	0.7905
0.4	8.7635240	1.9188
0.3	7.9629540	5.5273

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TABLE 2: Equilibrium Lattice constant (a_o) Bulk modulus (B_o) and its Derivative (B_o^1)

IONIC COMPOUND	a_o (a.u)	B_o (Mbar)	B_{o1}
KCl	11.8903	0.1736	5.428

TABLE 3: Structural phase transition and Metallization pressures

IONIC COMPOUND	Structural Phase Transition NaCl→CsCl		Metallization	
	$(V/Vo)_T$	P_T(Mbar)	$(V/Vo)_M$	P_M(Mbar)
KCl	0.80798	0.06012	0.52048	1.07530

TABLE 4: Band gap closure as a function of pressure

V/Vo	a (a.u)	P (Mbar)	E_g (ev)
1	11.8903	0	4.8388
0.9	11.4803	0.0243	4.7294
0.8	11.0387	0.0709	4.5197
0.7	10.558	0.1629	4.1056
0.6	10.030	0.3547	3.2423
0.5	9.4391	0.7905	1.2816
0.52048	9.5645	1.0753	0

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Figure 1: Band structure of KCl at V/Vo=1.0 (NaCl structure)
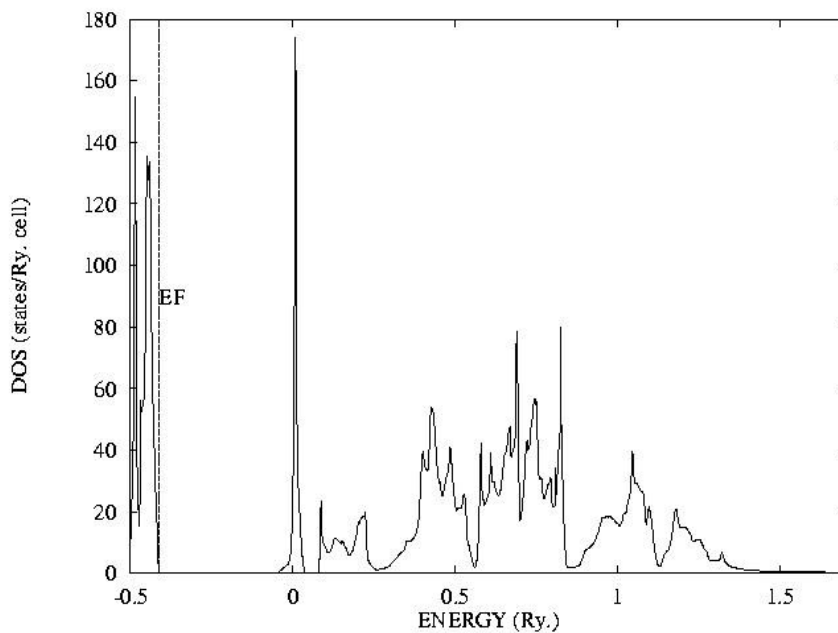
Figure 2: Density of states of KCl at V/Vo=1.0 (NaCl structure)

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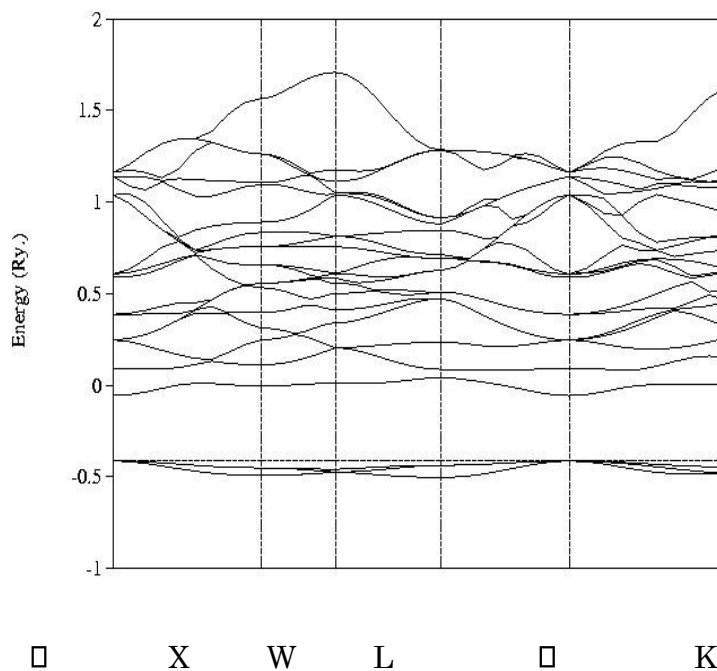
Figure 3: Band structure of KCl at V/Vo=0.52 (CsCl structure)
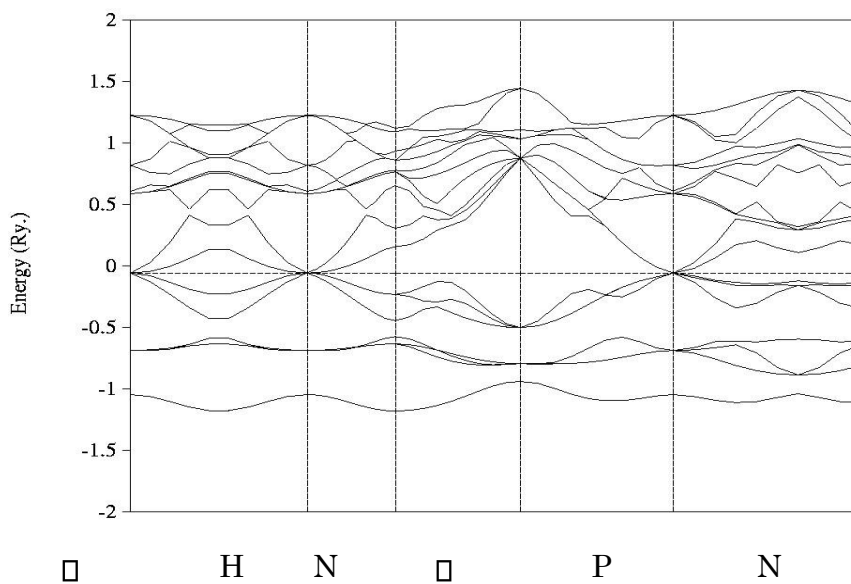
Figure 4: Density of states of KCl at V/Vo=0.52 (CsCl structure)

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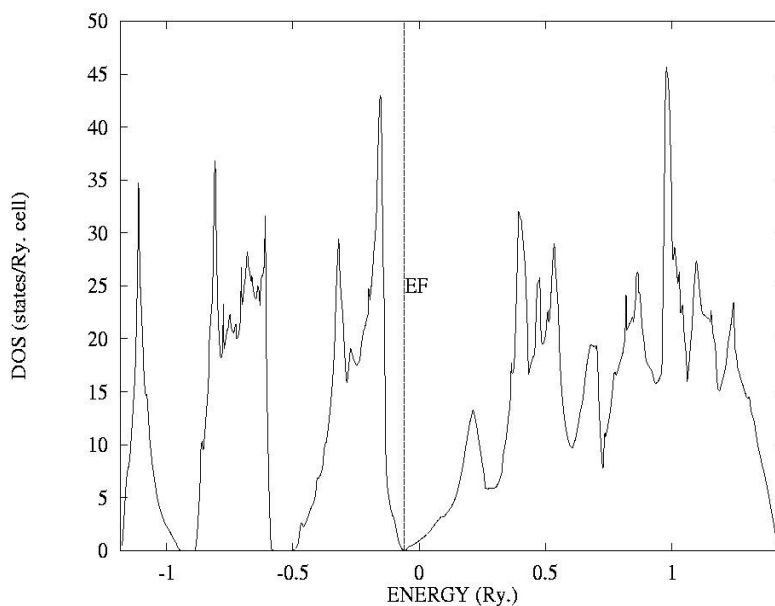
VIII.   CONCLUSION

In summary, we have investigated the pressure dependent band structure and density of states of KCl using FP-LMTO method. The total energies of KCl are computed and the results are used to study the structural phase transition and metallization under pressure. The structural phase transition from NaCl to CsCl is found to occur at 0.06 Mbar for KCl. Experimental phase transition pressure is 0.03 Mbar. Our calculated value is good agreement with the experimental value than the previous theoretical values (0.09Mbar). It is also confirmed that structural phase transition and metallization do not occur simultaneously in alkali halides.

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