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HIGH PRESSURE BEHAVIOR OF KCl: STRUCTURAL AND ELECTRONIC PROPERTIES

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Abstract

The high pressure behavior of the structural and electronic properties of KCl is studied with use of the density functional pseudopotential method within local-density approximation. At zero pressure, the rocksalt phase is found to be lower in energy than CsCl structure. However, we predict a phase transition into CsCl structure at a pressure of about 1.5 GPa. The calculated ground state properties such as lattice constant, bulk modulus, and its pressure derivative are in reasonable agreement with experiment. The electronic band structure at normal and high pressures is also calculated. It is found that metallization occurs for rocksalt and CsCl structures at ultrahigh pressures.

I. Introduction

The study of the structural and electronic properties of KCl under high pressure has attracted a great deal of interest for many years. Although the ionic solid has rocksalt (B1) structure at ambient pressure, a solid-solid phase transition to CsCl structure (B2) has been experimentally observed at about 2 GPa [1]. The insulator to metal transition, so called metallization of alkali halides under high pressure, is also of considerable interest [2]. Such a transition in general occurs as a result of progressively stronger interactions between the atomic valence orbitals which broaden the bands and ultimately close the energy gap between the valence and the conduction bands [3].

A number of theoretical calculations have been done to study the structural and electronic behavior of KCl at ambient and also high pressures. Perrot [4] has used the APWHF method to calculate the Hartree-Fock band structures of alkali chlorides. Cohesive properties of alkali halides have also been studied by using the standard self-consistent KKR method within the limit of the local densitv approximation [5]. Although thier calculated values for the equilibrium lattice parameter, the total energy and the bulk modulus are in good agreement with experimental results, contrary to the experimental facts their theory gives a lower energy to the B2 structure of KCl compared to its rocksalt structure even at ambient pressure. This inconsistency was attributed to the underestimate of the total energy calculated by muffin-tin approximation.

Our calculations are based on the well-established methodology of density functional theory in the local-density approximation (LDA), combined with the pseudopotential technique [6-8]. The purpose of this paper is twofold: First, we calculate different structural parameters such as lattice constant, bulk modulus, and its pressure derivative by applying different proposed equations of state to our data. Comparing the new data with experimental results is valuable not only for testing the range of validity of some of the well used empirical and semiempirical equations of state but additionally because it provides insight into the nature of solid-state theories. Secondly, we have investigated the effect of pressure on the electronic structure of KCl. In addition to analyzing the change of band structure under pressure, the metallization pressure is also calculated and compared with the phenomenological Herzfeld criterion [9].

Keywords: Ab initio calculations; Structural and electronic properties

The theoretical and computational techniques used in this work are summarized in section II. The results of the calculations at normal and high pressures are presented in section III. Finally, section IV deals with conclusions.

II. Procedure

The calculations were performed using the CASTEP code, which has been explained in detail elsewhere [10, 11]. The code is based on *ab-initio* total energy pseudopotential method. Density functional theory with the local density approximation (LDA) for exchange and correlation energies are used to model the electron-electron interactions. The electronic wavefunctions in the Kohn-Sham equations are expanded in a plane-wave basis set with periodic boundary conditions.

The pseudopotential theory is used to replace the strong electron-ion interaction with a much weaker potential. This weaker potential allows the plane-wave basis set to be cut off at 250 eV. Figure 1 indicates that further increase of the cut off energy does not change the results significantly. Our norm-conserving, nonlocal pseudopotential of the Kleinmann-Bylander [12] was generated by Lin and coworkers [13] using the method of Kerker [14].

As the conventional matrix diagonalization to calculate the self-consistent Kohn-Sham eigenstates and eigenvalues are severely restricted by the size of the system, the CASTEP code has used the recently developed preconditioned conjugate-gradients technique [10, 15] for minimizing the Kohn- Sham energy functional. Important features of the method are that the orbital coefficients are updated in a band-by-band manner, which allows a substantial saving of memory compared with other methods [15], and the variation of the Kohn-Sham Hamilto
during the minimization search is fully included, w
avoids the problem of "charge sloshing" [10]. This
iterative approach is much better suited to performing
energy pseudopotential calculations because
computational time and memory requirements scale r
slowly with the size of the system, allowing calcula
on larger and more complex systems than can be stu
using conventional matrix diagonalization technique

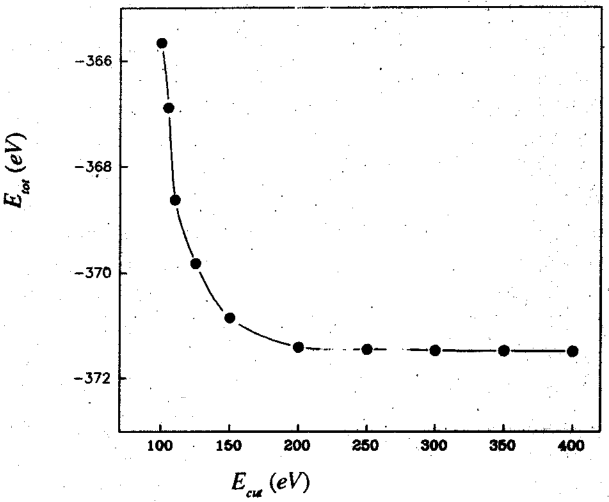

Figure 1. Total energy per unit cell for rocksalt structure at ambient pressure vs. plane waves cut off energy

Our calculational approach incorporates two key i
of the Car-Parrinello method [16]. First, the ground
is determined by global minimization of the en
functional with respect to the plane-wave coefficien
the occupied orthonormal orbitals. A second con
borrowed from the Car-Parrinello method is tha
repeated transformation of orbitals from real to recipr
space and back. This exploits the fact that the ki
energy is diagonal in reciprocal space and most o
potential energy operator is diagonal in real space. Bec
of these repeated transformations, the calculations
heavily on efficient fast-Fourier methods.

The Bloch theorem allows us to change the proble
calculating an infinite number of electronic wavefunct
for a bulk solid to one of calculating a finite numbe
electronic wavefunctions at an infinite number of k po
As the electronic wavefunctions at k points that are c
together can be considered nearly identical, hence
sufficient to calculate the total energy of the solid at
a finite number of k points in the Brillouin zone. Bec
of the high degree of symmetry, the charge density
calculated at only 4 special k points in the Brillouin z
as suggested by Chadi and Cohen [17]. To be sure tha
k point sampling was sufficient we also calculated
equilibrium lattice parameter with a set of 20 k points
significant difference was observed. Subsequ
calculations using very many k points to determine b
structures further suggested that the 4 k point set is suffic
for relaxation purposes. We find that the energy conve
to about 0.01 eV per atom.

In order to obtain the minimum energy configurat
both the atomic postitions and unit cell dimensions hav
be relaxed. Relaxation of the atomic postitions was d
directly, using Hellmann-Feynman forces and a stee
descents algorithm, but relaxation of the unit cell
achieved by performing a series of runs at various lat
parameters, in each case relaxing the atomic position

III. Results and Discussion

A. Structural Properties

Figure 2 shows the total structural energy as a funct
of volume for the rocksalt and CsCl structure. In acc
with experimental results, we find that the rocksalt ph
is lower in energy than the CsCl stucture at zero press

The equilibrium lattice parameter for two phases which are their values at minimum energy was calculated by fitting the data with Murnaghan equation of state [18]. The results are compared with experimental and theoretical values in Tables I and II. Our calculated lattice parameter for rocksalt structure is about 3% above the experimental value. This overestimation, which has also been observed by others [1], is not unusual in applying LDA for highly ionic systems with full shells of electrons. As the CsCl structure is not metastable at zero pressure [19], the experimental equilibrium lattice parameter for this phase is undetermined. Meanwhile, Campbell *et al.* [19], by fitting their high pressure experimental data with Birch-Murnaghan and Universal equation of state and extrapolation to zero pressure, obtained $V_{02}/V_{01}=0.848$, where V_{02} and V_{01} indicate CsCl and rocksalt equilibrium volumes, respectively. Based on the Murnaghan equation of state, we extract a value of 0.846 which is in excellent agreement with their result. It is seen that our calculated bulk modulus is significantly higher than the experimental values. This is probably due to linear assumption of bulk modulus with pressure, which presumably is not correct for a wide range of pressures. Hence, in order to calculate the bulk modulus and its pressure derivative more accurately we fitted our data with two more equations of state proposed for compressed solids [20, 21]. Because the graphs for both structures are similar, we will only show the results for rocksalt phase in Figures 3 and 4. The B and B' obtained by different equations of state are summarized in Tables I and II. It is seen that the results obtained from the last two equations of state, especially the Parsafar equation, are in

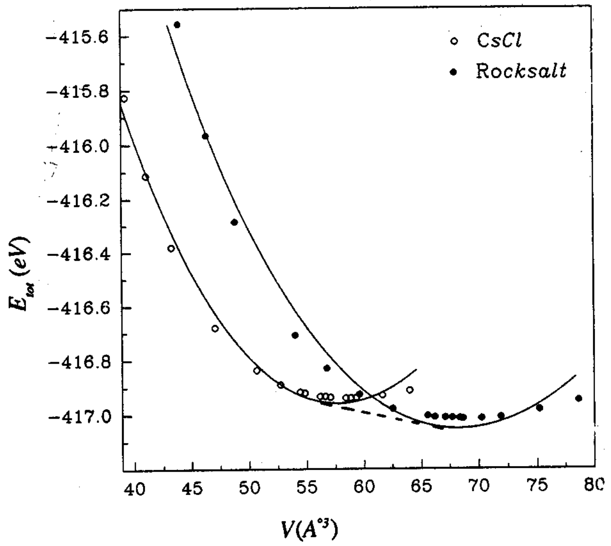

Figure 2. Calculated total energies per unit cell for CsCl and rocksalt structures as a function of volume. The solid lines are the best fits to the Murnaghan equation of state. The dashed line is the common tangent line.

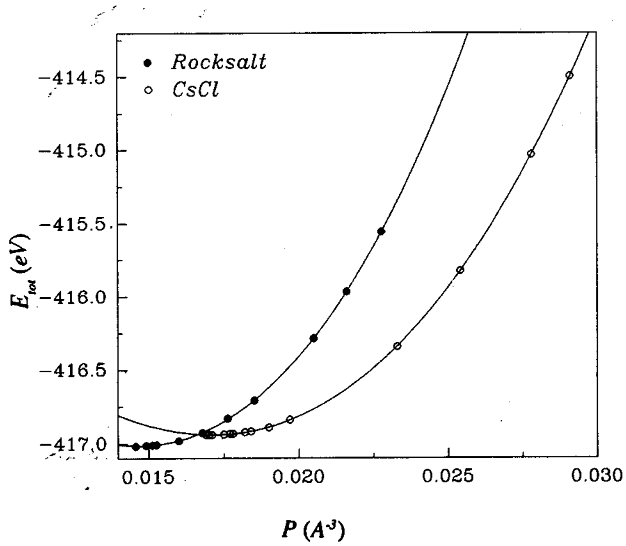

Figure 3. Total energy is plotted vs ρ where ρ = 1/V to evaluate B and B' for the Parsafar equation of state [20].

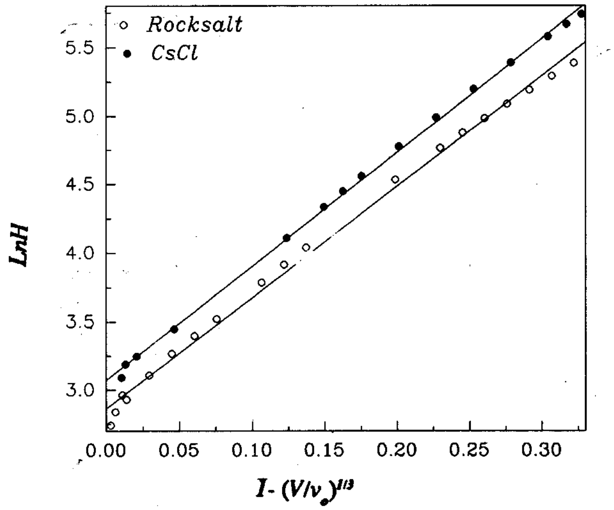

Figure 4. Ln H is plotted vs $1-(V/V_0)^{1/3}$ to evaluate B and B' for the Vinet equation of state [21]. Values of B and B', as determined from the intercept and slope of a least squares linear fit are given in Tables I and II.

Table I. Lattice parameter, bulk modulus and its pressure derivative for rocksalt structure

	a_0 (Å)	B (GPa)	B'
This study:			
Murnaghan EOS [18]	6.48	42.55	---
Parsafar EOS [20]	6.48	19.64	5.73
Vinet EOS [21]	6.48	18.46	6.27
Froyen and Cohen [1]	6.30	22.6-24.8	---
Experimental	6.24^a	19.7^b	---

a Reference [25], b Reference [26]

much better agreement with experimental results than they are with Murnaghan's results.

Figure 2 shows that the difference in the cohesive energy between the two phases at ambient pressure is about 0.09 eV. As the system is compressed (the volume is decreased) the total energy difference between two phases decreases, so that around V=0.88 V_0 the energy in the CsCl phase is lower than that in the rocksalt and the rocksalt structure transforms into the CsCl phase. It should be mentioned that V_0 throughout this paper is the rocksalt equilibrium volume. The slope of the common tangent line (dashed line in Fig. 2) which indicates the rocksalt-CsCl phase transition is about 1.5 GPa.

Alternatively, we calculated the Gibbs free energy (E_{tot}+PV) at different pressures for two phases and plotted the results in Figure 5. It is seen that at a pressure of about 1.5 GPa, the two Gibbs free energy become equal which can be considered as the phase transition pressure. Beyond this pressure, the CsCl phase is stabilized with respect to rocksalt structure. Our calculated pressure for phase transition is in reasonable agreement with experimental results, 2 GPa [1].

Table II. Lattice parameter, bulk modulus and its pressure derivative for CsCl structure

	a_0 (Å)	B (GPa)	B'
This study:			
Murnaghan EOS [18]	3.86	49.70	---
Parsafar EOS [20]	3.86	24.71	5.71
Vinet EOS [21]	3.86	24.11	6.27
Campbell [19]	3.75	27.9-28.7	4.0-4.38
Yagi [24]	---	18.7-24.20	4.0-5.75
Froyen [1]	---	26.37	4.42

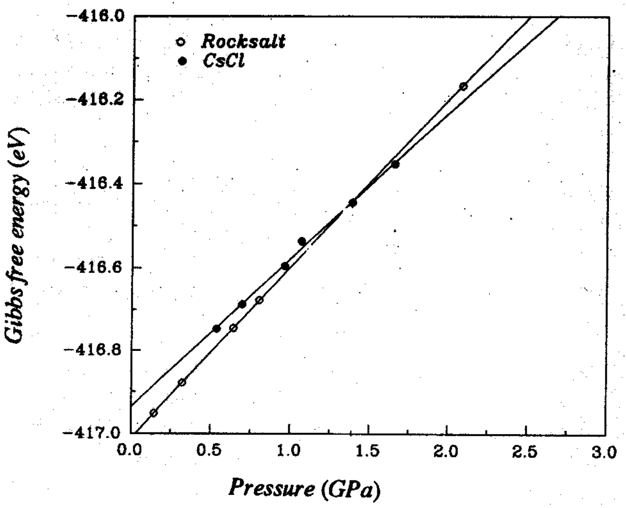

Figure 5. Zero-temperature Gibbs free energies per unit cell as a function of pressure for CsCl and rocksalt structures.

B. Electronic Properties

The calculated band structure for CsCl and rocksalt at different pressures is shown in Figures 6-9. It is seen that

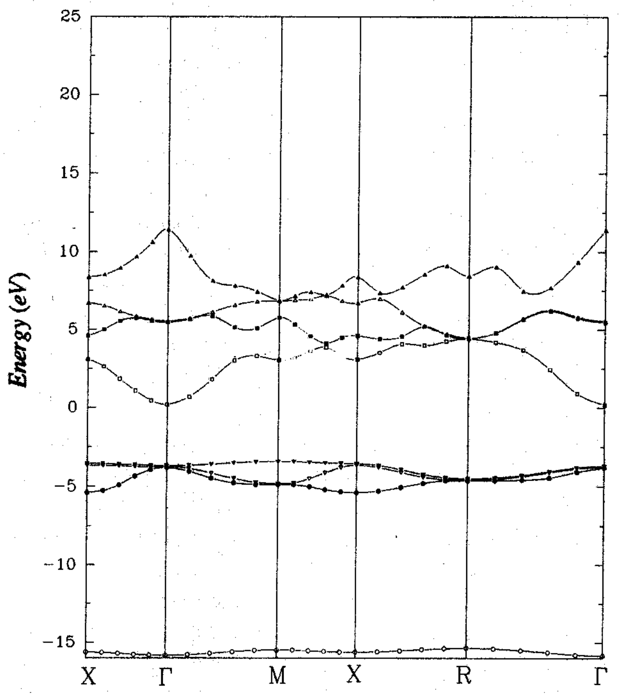

Figure 6. Electronic band structures for CsCl phase at zero pressure (V=V_0). The band gap is indirect (Γ-M) with a value of 3.6 eV.

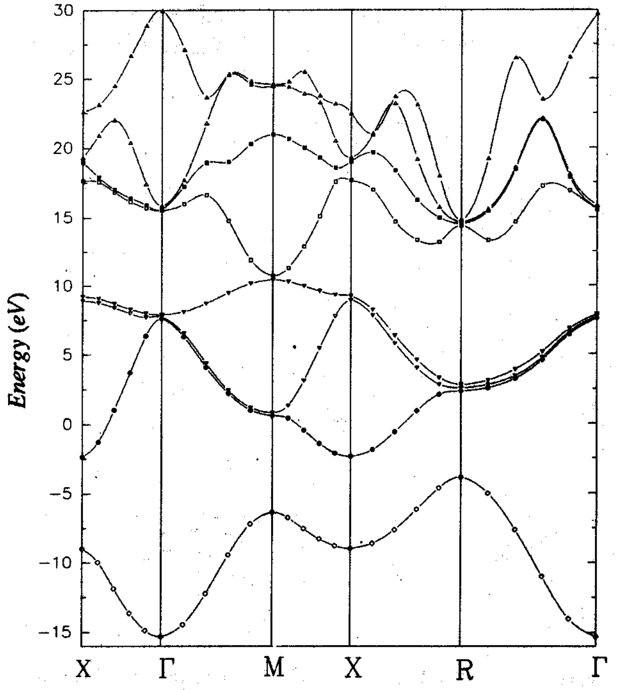

Figure 7. Electronic band structures at ultra-high pressure (V=0.22 V_0 which is equivalent to P=990 GPa). The band gap is direct (M-point) with a value of 0.3 eV.

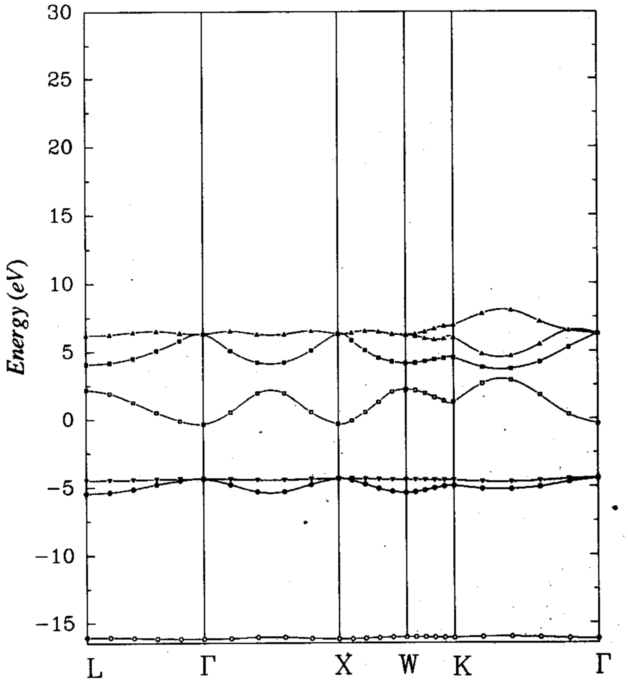

Figure 8. Electronic band structures for rocksalt phase at zero pressure ($V=V_0$). The band gap is direct (Γ-point) with a value of 4.01 eV.

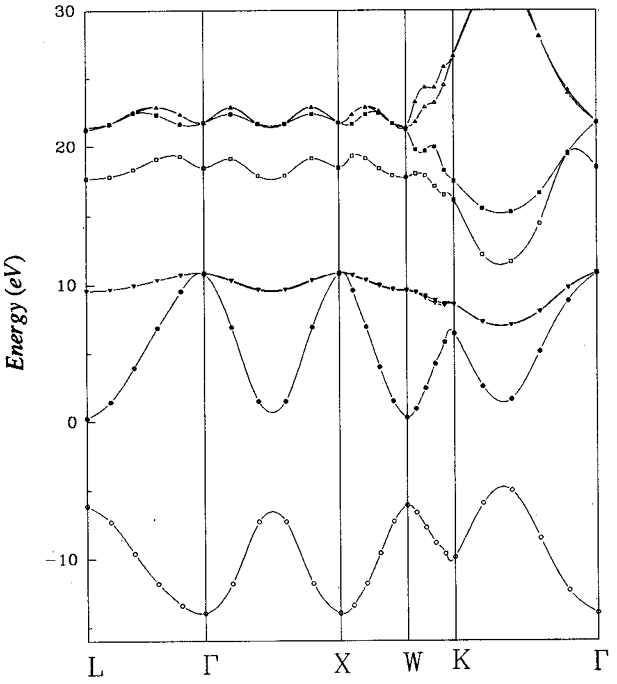

Figure 9. Electronic band structure at ultra-high pressure ($V=0.2 V_0$ which is equivalent to p=1400 GPa). The band gap is indirect with a value of 0.77 eV.

the band gap of the CsCl at zero pressure is indirect (Γ-M) with a value of 3.6 eV. As pressure is applied, the gap initially increases so that at $V=0.47 V_0$ the indirect gap has a value of 5.5 eV. Applying more pressure changes the fundamental gap from indirect to direct at the M symmetry point in the Brillouin zone. Compressing the crystal even further will decrease the direct band gap in a systematic way so that at $V/V_0 = 0.22$, which is equivalent to a pressure of around P=1000 GPa, the gap practically vanishes. Figure 8 shows that the band gap of the rocksalt structure at zero pressure is direct (Γ-point) with a value of 4.01 eV which is about 45% lower than experimental results [22]. Such an underestimation is not unusual in calculations based on local density approximation and is attributed to the rise of the valence band due to the self-interaction of the valence electrons [23]. Increasing the pressure initially enhances the direct band gap at Γ point. Further increase of the pressure not only changes the gap to indirect but systematically decreases the gap value so that at about P=1300 GPa the gap is practically zero. Such insulator-conductor transitions, so called metallization, have been experimentally observed and theoretically predicted for different materials [2, 23]. Feldman and coworkers [2] have investigated the metallization pressure for NaCl in the CsCl structure. They used the linear augmented plane wave (LAPW) and APW (within the muffin-tin approximation) methods for determining the metallization volume. Their calculation predicts a direct band gap closer (M-point) at a volume of $V/V_0=0.285$. For comparison, the Herzfeld criterion of metallization for KCl has been reported [9] to be about $V/V_0 = 0.29$.

Finally, it is seen that the conduction and valence band widths in both structures increase by increasing pressure. This systematic increase in the band dispersion is attributed to the stronger interatomic interaction under high pressure [23].

IV. Conclusion

Our calculations indicate that KCl should transform from the rocksalt to the CsCl structure at a pressure of about 1.5 GPa. Our calculated lattice parameter for rocksalt structure is about 3% above the experimental value. This is due to the fact that the local density approximation is expected to give accurate results only for systems with slowly varying charge density, while KCl is a highly ionic crystal with a rapid variation in its charge density.

We also calculated the electronic band structure and its behavior under high pressure. Finally, we report the metallization pressure for rocksalt and CsCl structure.

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