



High-pressure structural phase transitions and electronic properties of the alkali hydride compounds XH (X=K, Rb and Cs)

Raed Jaradat ^a, Mohammed Abu-Jafar ^{a,*}, Issam Abdelraziq ^a, Saad Bin Omran ^b, Diana Dahliah ^a, Rabah Khenata ^c

^a Physics Department, An Najah National University, Nablus, Palestine

^b Department of Physics and Astronomy, College of Science, King Saud University, P.O.Box 2455, Riyadh 11451, Saudi Arabia

^c Laboratoire de Physique Quantique de la Matière et de la Modélisation, Mathématique (LPQ3M), Université de Mascara, Mascara, 29000, Algeria

H I G H L I G H T S

- mBJ-GGA and YS-PBE0 convert the CsCl structure from semiconductor to insulator for KH and RbH.
- mBJ-GGA and YS-PBE0 convert the CsCl structure from semiconductor to wide energy-band gap semiconductor for CsH.
- Three phase transitions have been predicted in this work, from RS to CsCl, RS to ZB and RS to WZ, for each compound.
- Under low pressure, the RS structure expands and transforms into WZ and ZB only when V/V_0 is greater than one.

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The equilibrium structural parameters, structural phase transition as well the electronic properties of XH compounds have been computed by using the first-principles calculations based on density-functional theory (DFT) and the full-potential linearized augmented plane-wave (FP-LAPW) method. The generalized gradient approximation (GGA) has been used for the exchange-correlation potential. The equilibrium structural parameters such as the lattice constant, the bulk modulus and the pressure-induced phase transition were calculated for rocksalt (RS), cesium chloride (CsCl), zincblende (ZB) and wurtzite (WZ) structures. The GGA, modified Becke-Johnson (mBJ-GGA) and Yukawa screened hybrid functional (YS-PBE0) schemes have been used to calculate the electronic properties. The mBJ-GGA and YS-PBE0 schemes have been found to be more accurate than GGA in computing the energy-band gap. An agreement of our results with the experimental and results of the other theoretical work indicate its reliability. The compounds under our investigation are found to be wide band gap semiconductors within the GGA, and insulators using the mBJ-GGA and YS-PBE0 approaches.

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1. Introduction

Hydrogen is the lightest element in the periodic table, that is why alkali hydrides XH (X = Li, Na, K, Rb and Cs) have the simplest structures. These compounds have diverse technological applications such as hydrogen storage and high-energy fuels [1]. Generally, these types of compounds are, soft solids: their bulk moduli gradually decrease from Li to Cs, while their lattice constant increases. From the previous experimental work it has been reported that these types of compounds crystallize in the rocksalt structure

at atmospheric pressure and room temperature. The structural phase transition of NaH, KH, RbH and CsH compounds from the low-pressure rocksalt (B1) structure to the high-pressure cesium chloride (B2) structure has been observed in diamond-anvil-cell high-pressure experiments, while the B1 to B2 phase transition in LiH has not yet been observed [2–4]. The transition pressures for these compounds decreases as the alkali atomic mass increases. NaH has a huge transition pressure compared to the others, which is approximately 30 GPa, and a volume fraction $V/V_0 = 0.61 \pm 0.01$ [3]. The KH, RbH and CsH transition pressures are 4.0, 2.2 and 1.2 GPa, respectively [4]. The transition pressures of CsH, RbH, and KH are found to be 28 GPa measured by performing the high-pressure energy-dispersive X-ray studies [4], which is in excellent

* Corresponding author.

E-mail address: mabujafar@najah.edu (M. Abu-Jafar).

agreement with the result obtained from the equation of state. However the calculation of transition pressure of NaH is excluded in their experiment. Sudha et al. [5] used the Vienna package to investigate the structural, electronic, elastic and their related properties of the alkali hydrides XH ($X = \text{Li, Na, K, Rb, Cs}$) in the rocksalt and cesium chloride structures; these compounds were reported to be semiconductors with the CsCl structure. The B1 to B2 transition pressures were predicted to be 208.0, 37.0, 3.5, 3.0 and 2.1 GPa for LiH, NaH, KH, RbH and CsH, respectively, using the GGA approach [5]. Xiao-Wei et al. [6] used an ab initio plane-wave pseudo-potential density-functional theory method to investigate the phase transition from the B1 to B2 structures and the bulk modulus of NaH; the transition pressure was predicted to be 32 GPa, and the bulk modulus was found to decrease as the temperature increases. Saitta et al. [7] carried out DFT calculations within the local-density approximation (LDA) and its gradient-corrected (GC) generalization using pseudo-potentials to calculate the transition pressure for CsH from the B1 to B2; pressures of -0.8 and 1.5 GPa were obtained using the LDA and GC approaches, respectively. Rodriguez et al. [8] applied an improved linear muffin-tin orbital atomic-sphere approximation-energy approach to investigate the static structural properties and the pressure-induced phase transition from B1 to B2 for the NaH and KH compounds; the estimated transition pressures were found to be 30.7 and 2.0 GPa for NaH and KH, respectively. Ahuja et al. [9] used the full-potential linear-muffin-tin-orbital (FP-LMTO) method to theoretically investigate the LiH, NaH, KH and RbH compounds. These authors predict that RbH and KH will transform to CsCl structure, while their calculations predict CrB crystal structures at high pressure for RbH and KH but not for the light alkali compounds, NaH and LiH. Jaradat et al. [10] used the full-potential linearized augmented plane wave (FP-LAPW) method implemented in Wien2k package to investigate the structural, electronic properties and the pressure-induced phase transition of alkali hydrides XH ($X = \text{Li, Na}$) in the rocksalt, cesium chloride, zinc-blende and wurtzite structures; these compounds were predicted to be semiconductors with the CsCl structure and the pressure-induced phase transition from the RS to CsCl were found to be 211.8 and 34.26 GPa for LiH and NaH, respectively, while from the RS to ZB were found to be -3.83 and -1.94 GPa for LiH and NaH, respectively and from RS to WZ were -2.4 and -1.57 GPa for LiH and NaH, respectively.

From the above discussions, we can see that the researchers have studied these compounds in the rocksalt and cesium chloride structures, but there are no previous reports on these types of compounds in the zincblende (ZB) and wurtzite (WZ) phases. The structural, electronic properties as well as the structural phase transitions of the alkali hydrides XH ($X = \text{K, Rb and Cs}$) are investigated in this work in the RS, CsCl, ZB and WZ structures using the full-potential linearized augmented plane-wave method (FP-LAPW) in order to complement existing theoretical works on alkali hydride compounds.

2. Methods of calculations

The first-principles calculations of the alkali hydrides are performed in four different structures (RS, CsCl, ZB and WZ) using the (FP-LAPW) method [11] based on the density-functional theory (DFT) [12] and implemented in WIEN2k code [13]. Generalized gradient approximation (GGA-PBE) [14] has been used to predict the pressure-induced structural transitions from RS to the other structures and to calculate the structural properties. The modified Becke-Johnson (GGA-mBJ) [15,16] and Yukawa screened hybrid functional (YS-PBE0) [17] approaches have also been used to

overcome the severe underestimation of the excited-state properties using GGA approach, such as the band-gap values for many semiconductors and insulators.

To study the region near the nucleus without introducing pseudo potential, the basis set must be efficient. Therefore, the atomic space is divided into the following two regions: the muffin-tin region and the interstitial region. The muffin-tin region is the space occupied by spheres of radius R_{MT} , one around each atom; these spheres are often called muffin-tin (MT) spheres. The remaining space outside the spheres is called the interstitial region. The product of the spherical-harmonic expansion and the radial function, along with their first derivatives, are linearized to form the basis functions used inside the MT spheres, and plane-wave basis set is used in the interstitial part of the unit cell. The muffin tin radii (R_{MT}) used in the present calculations for the H, K, Rb and Cs atoms are 1.4a.u., 2.6a.u., 2.67a.u and 2.76a.u., respectively. The charge density was Fourier expanded up to $G_{\text{max}} = 20$ in RS, CsCl and ZB, and up to $G_{\text{max}} = 14$ in the WZ structure. The plane-wave cutoff was chosen such that $R_{\text{MT}} \cdot K_{\text{max}} = 5$.

The basis functions, charge density and potential are expanded inside the muffin-tin spheres in combination with the spherical harmonic functions, with a cut-off $l_{\text{max}} = 12$ for the WZ structure and $l_{\text{max}} = 6$ for the cubic structures. For energy convergence, the full Brillouin zones (FBZ) were sampled at 1331 k-points for the three cubic structures, RS, CsCl and ZB, with a grid size of $11 \times 11 \times 11$, which is reduced to 56 special k-points in the irreducible Brillouin zones (IBZ); and 3700 k-points for the WZ structure with a grid size of $18 \times 18 \times 10$, which is reduced to 222 special k-points in the IBZ [18]. The iteration process was repeated until the calculated total energy of the crystal converged to less than 10^{-5} Ry/unit cell.

3. Results and discussions

3.1. Structural properties

The ground-state properties of alkali hydrides for each structure have been estimated by calculating the total energy at different unit-cell volumes and fitting the calculated energy versus volume (E-V) curves to Murnaghan's equation of state (EOS) [19], as shown in Figs. 1–3 for the KH, RbH and CsH compounds, respectively, with RS, CsCl, ZB and WZ structures. It is clearly seen from these curves that the rocksalt structure has the lowest energy minimum at ambient pressure, which means that it is the most stable structure at normal conditions.

The calculated equilibrium lattice constant a_0 , bulk modulus B_0 and first-order pressure derivatives of the bulk modulus B'_0 for KH, RbH and CsH in the RS, CsCl, ZB and WZ phases, along with the available experimental [2,4,20–22] and theoretical [5,23–26] results are listed in Tables 1–3. It is clear that the lattice constants for all phases increase as the X radii increase, while the bulk moduli decrease. Table 1 shows that the calculated structural parameters for KH, RbH and CsH in RS structure are in good agreement with the experimental results. From Table 2, it is clear that the calculated structural parameters for KH, RbH and CsH in the CsCl structure are in good agreement with the results of Sudha et al. [5].

The calculated structural parameters for KH, RbH and CsH in the ZB structure are presented in Table 3: the lattice constant increases as the alkali radius increases, while the bulk modulus decreases. Table 4 displays the structural parameters for the alkali compounds in the WZ structure. We can see that the lattice constant and c/a ratio increase as the alkali radius increases; the c/a ratios are approximately 1.5142, 1.5265 and 1.5480 for KH, RbH and CsH, respectively.

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