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Induced changes in vibrational properties of NaH and KH under hydrostatic pressure

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ABSTRACT

The pressure induced phase transition from the NaCl to CsCl structure in NaH and KH has been investigated by means of first-principles calculations, and density functional linear-response theory. A pressure-induced soft-acoustic phonon mode is identified at 30 GPa, and 7.5 GPa for NaH and KH respectively. Phonon calculations suggest that the pressure induced instabilities of the transverse acoustic modes at the [ε00], and [εε0] directions are responsible for the phase transition of NaH and KH. Furthermore charge density analysis shows that there is charge transfer from the alkali ion to hydrogen (i.e., Na→H, K→H) inducing B1–B2 phase transition.

1. Introduction

Hydrogen, the simplest and the lightest element of universe still fascinating to physicists community. From a fundamental point of view, and inspite of the simplicity of its electronic structure, there are many unanswered questions about the fundamental properties of H, especially at high pressure, for example metallic and superconducting hydrogen remains elusive, despite considerable ongoing experimental effort up to pressure of 342 GPa [1,2]. From a technical point of view hydrogen is considered to be one of the most promising clean energy sources with the capability of replacing fossil fuels. The use of hydrogen-based energy in practical applications such as fuel cell vehicles, however, requires the development of safe and efficient hydrogen storage technology.

The hydrogen can form compounds with elements from many column in the periodic table, with chemical bonding ranging from strong to modest hydrogen bonds, having large crystal structure. As a proper reference material alkali-metal hydrides NaH and KH having the NaCl (B1) structure at ambient conditions.

Considerable progress has been made in the theoretical description [3–5] of the structural electronic, bonding, and related properties of NaH and KH. However, little is known about the pressure-induced phase transformations in alkali hybrids NaH and KH.

Theoretical studies [6] show that NaH and KH have been found to undergo first-order phase transition from the sixfold-coordinated NaCl structure to the eightfold coordinated CsCl structure under high and moderate pressure. Diamond-anvil-cell high pressure experiments [7,8] have been applied to characterize the pressure phase of NaH and KH. The phase transition from NaCl · (B1)→CsCl · (B2) was observed at high pressure of 29.3 GPa [8] for NaH and at low pressure of 4 GPa [8] for KH.

Motivated by recent theoretical studies [4–6], already mentioned concerning the pressure induced NaCl→CsCl phase transition in NaH and KH, we attempt here to complete the previous studies. In particular we address in more details, the pressure inducing dynamic instabilities, the driving mechanisms of these transitions and the related electronic properties of NaH and KH by means of the state of art first-principles pseudopotential method.

The rest of the paper is organized as follows: in Section 2, we briefly describe the computational techniques used in this work. Results and discussion will be presented in Section 3. Finally, the conclusion will be given in Section 4.

2. Method

Total energy and dynamical calculations are performed using the generalized gradient approximation (GGA) [9] for NaH, and local density approximation (LDA) [10] for KH, within the plane wave pseudopotential method as implemented in the pwscf code [11]. For K atom, we have used Troullier and Martin norm-conserving pseudopotentials [12], with nonlinear core corrections. For Na atom, we used ultrasoft Vanderbilt pseudopotentials [13], with nonlinear core corrections; while for hydrogen we used

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projected augmented plane wave method (PAW) pseudopotentials [14]. The electron wave functions were expanded with a plane wave basis set with a kinetic energy of 65 Ry, and an energy cutoff of 500 Ry were included for the charge density. The *k*-space integration on the Brillouin zone (BZ) for the self-consistent calculations was calculated with $8\times8\times8$ *k*-points mesh of Monkhorst-Pack [15]. The lattice dynamics properties are calculated using the density functional perturbation theory (DFTP) [16]. In particular$4\times4\times4$ *q*-points mesh of MP was used. These matrices were then Fourier interpolated to obtain the phonon dispersion curves.

3. Results

Fig. 1 shows the total energy as a function of volume of NaH and KH for the rocksalt, and CsCl phases. The calculated total energies are fitted with the Murnaghan's equation of states [17], to obtain structural parameters. The calculated structural parameters for the ground state phases, namely the equilibrium lattice parameter *a*, and the bulk modulus *B*, are given in Table 1, with available theoretical and experimental values. Comparing our results with data of experimental measurements [7–8] and other first-principles calculations [5], we find good agreements. The rather underestimation of the lattice constants of KH is a well-known feature of the local density approximation. Fig. 1 shows that under ambient conditions, the B1 phase is the ground-state phase of NaH and KH; while at high pressure, the B2 phase would be favoured.

The calculated phonon dispersion curves of NaH and KH in the ground state NaCl structure along the principal symmetry direction of the Brillouin zone are displayed in Fig. 2; while projected phonon density of states (PPDOS) is given in Fig. 3.

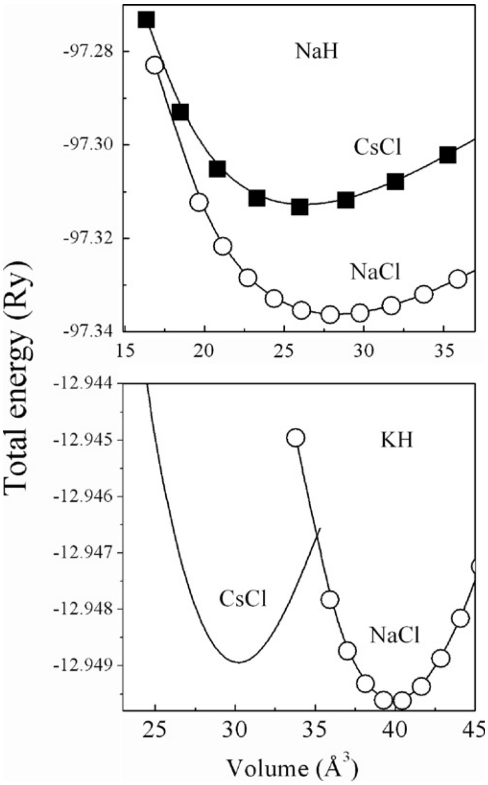

Fig. 1. Total energy versus volume for the CsCl, and rocksalt phases of NaH and KH.

Table 1
Calculated lattice parameter *a*, and the bulk modulus *B* of NaH and KaH.

		a **(Å)**	***B*** **(GPa)**
NaH	Present cal. Pseudopotential-GGA	4.834	23.1
	Other cal.[a]	4.773	21.6
	Exp.[b]	4.878	19.4
KH	Present cal. Pseudopotential-LDA	5.426	17.0
	Other cal.[a]	5.699	13.3
	Exp.[c]	5.730	15.6

[a] Ref. [5].
[b] Ref. [8].
[c] Ref. [7].

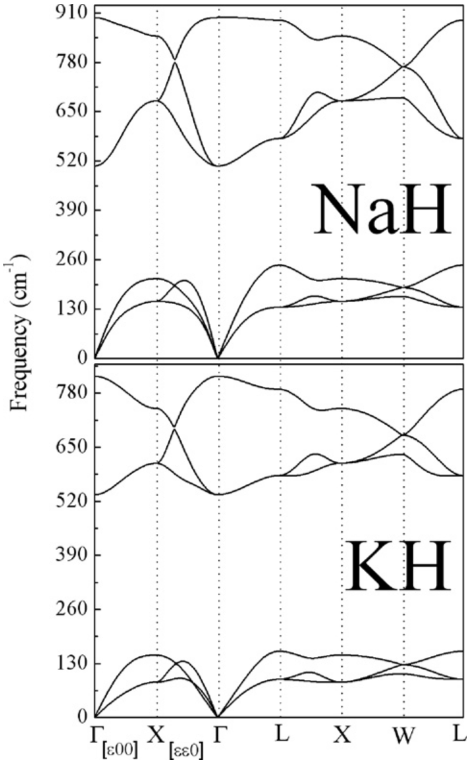

Fig. 2. Phonon band structure of the rocksalt phase at equilibrium volume of NaH and KH.

The phonon band structure of NaH and KH shows that the longitudinal acoustic (LA) and transverse acoustic (TA) phonon modes have small variation along a large part of the BZ, principally along the $L\rightarrow X\rightarrow W\rightarrow L$ direction. As a consequence, we observe very sharp peaks for the acoustic modes in the PPDOS. The optical phonon modes show strong dispersion along the BZ and because of the flatness, we do not observe sharp peaks in the optical region of the PPDOS, except for the transverse optical mode of KH.

The PPDOS shows that the Na and K atoms dominate the low frequency vibrations, while the hydrogen mainly contributes to the high frequency vibrations because of its weak atomic mass. Because of the strong mass mismatch between Na, K and H, we found that KH and to less extent NaH show a noticeable gap ($\sim$253 cm^{-1}, for NaH, and $\sim$392 cm^{-1} for KH) between optical and acoustic modes.

The calculated acoustic phonon dispersion curves of the B1 phase of NaH and KH at different pressure are shown respectively in Figs. 4 and 5. At volume of $0.60V_0$ for NaH and $0.75V_0$ for KH (V_0 is the calculated equilibrium volume of the B1 phase of NaH and KH) corresponding to a pressure of 30 GPa for NaH and 7.5 GPa for KH.