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Structural, electronic and elastic properties of alkali hydrides (MH: M = Li, Na, K, Rb, Cs): *Ab initio* study

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ABSTRACT

The structural, electronic and elastic properties of alkali metal hydrides (MH: M = Li, Na, K, Rb, Cs) are investigated by first principles calculation using the Vienna *ab initio* simulation package. The lattice constants, bulk modulus and the density of states are obtained. The calculated lattice parameters are in good agreement with the available results. A structural phase transition from NaCl to CsCl phase is predicted under high pressure. The electronic structure reveals that these materials are non-metallic at normal pressure. The computed elastic constants indicate that these hydrides are mechanically stable at ambient pressure. The calculated Debye temperature values are in good agreement with experimental results.

1. Introduction

The metal-hydrogen systems have received wide attention due to their large number of technical applications [1]. The metal hydrides are potential materials for portable fuel cell applications [2]. Perrot [3] predicted a structural phase transition from NaCl (B1) to CsCl (B2) phase for LiH at a pressure of 200 GPa. Loubeyre [4] investigated the various physical properties of LiH and LiD under high pressure using single crystal X-ray diffraction method. With the development of the high pressure experimental techniques, investigations of structural phase transition, insulator–metal transition and superconducting transition under pressure were widely carried out [5,6]. The X-ray experimental study [7] showed that LiH, NaH, KH, RbH and CsH crystallize with the rock salt (B1) structure at room temperature. A structural phase transition from NaCl to CsCl phase was observed in CsH [8], NaH [9] and KH, RbH [10] at high pressure. To the best of our knowledge the electronic and elastic properties of the high pressure phase (CsCl) of alkali hydrides are not yet reported.

In the present work, we have investigated the structural phase transition, density of states (DOS), and elastic properties of the alkali hydrides MH (M = Li, Na, K, Rb, Cs) in both NaCl and CsCl phases, under normal and high pressures.

2. Computational details

The total energy calculations are performed in the frame work of density functional theory as implemented in the VASP code [11–13]. Both the local density approximation (LDA) [14] and generalized gradient approximation (GGA) [15–17], are used for the exchange and correlation. Ground state geometries are determined by minimizing stresses and Hellman–Feynman forces using the conjugate-gradient algorithm with force convergence less than 10^{-3}eV Å^{-1} and the Brillouin zone integration is performed with a Gaussian broadening of 0.1 eV. The cutoff energy for plane waves in our calculation is 400 eV. The valence electron configurations are Li $2s^1$, Na $3s^1$, K $4s^1$, Rb $5s^1$, Cs $6s^1$ and H $1s^1$ atoms. Brillouin zone integrations are performed on the Monkhorst–Pack K-point mesh [18] with a grid size of 12 × 12 × 12 for structural optimization and the total energy calculation. The unit cell structure of the proposed phases of alkali metal hydrides are shown in Fig. 1.

The Murnaghan's second order equation [19,20] is used to calculate accurate pressure corresponding to the desired volume and it is given as,

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

where P is the pressure, B_0 and B_0' are the bulk modulus and its first pressure derivative respectively. $V/V_0 = 1.0$ is the primitive cell volume corresponding to normal pressure, where 'V_0' is the volume

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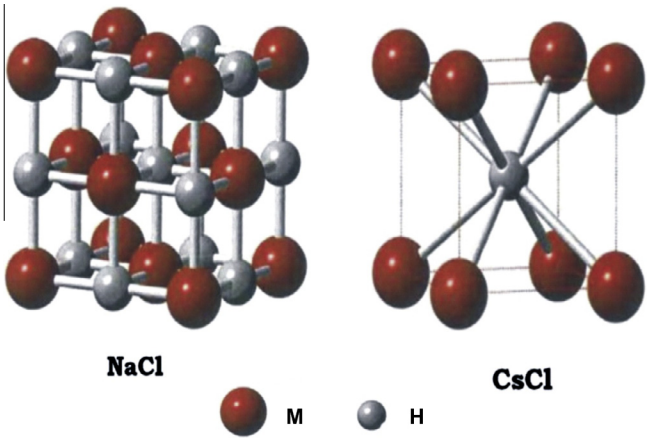

Fig. 1. Unit cell for the NaCl and CsCl phases of alkali hydrides.

corresponding to normal pressure and 'V' is the volume for pressure P. This equation of state (EOS) has been found to give a good estimate of pressure values. Therefore, in this work, we have used the Murnaghan's EOS formula for the pressure calculations. The total energy calculation is performed as a function of reduced volume (V/V_0) which ranges from 1.0 to 0.4.

3. Results and discussion

3.1. Geometric properties of alkali hydrides

The lattice constants for both NaCl and CsCl structures of alkali hydrides MH (M = Li, Na, K, Rb, Cs) are optimized and their total energies (per unit cell) are calculated. The calculated ground state properties like lattice constant a_0 (Å), cell volume V_0 (Å^3), valence electron density ρ (electrons/ Å^3), energy band gap E_g (eV), bond distance M–H (Å), bulk modulus B_0 (GPa) and its derivative B_0' for

Table 1
Calculated lattice parameter a_0 (Å), equilibrium volume V_0 (Å^3), valence electron density ρ (electrons/ Å^3), energy gap E_g (eV), bond length M–H (Å), bulk modulus B_0 (GPa), pressure derivative B_0' for the alkali hydrides with NaCl structure.

NaCl type		LiH	NaH	KH	RbH	CsH
a_0	GGA	4.0811	4.8511	5.7210	5.9918	6.344
	LDA	3.651	4.381	5.551	6.0611	6.551
		4.075[21][a], 4.084[22][a]	4.880[21][a]	5.70[21][a]	6.037[21][a]	6.376[21][a], 6.38[8][a]
		4.069[23][a], 3.92[24][b]	4.775[24][b]	5.701[24][b]	6.199[24][b]	6.407[24][b]
V_0	GGA	16.99	28.54	46.81	53.78	63.83
	LDA	12.17	21.02	42.76	55.67	70.29
ρ	GGA	0.1177	0.0700	0.0427	0.0371	0.0313
	LDA	0.164	0.0951	0.0441	0.0359	0.0284
E_g	GGA	4.6723	4.8560	3.5992	3.0255	2.4472
	LDA	3.1	4.501	3.21	2.201	2.0
		4.4[25][a], 9.2[26][a]	1.52[28][b]	3.203[35][b]	2.96[35][b]	2.80[36][b]
		3.31[27][a], 6.61[28][b]	3.46[35][b]			
		9.15[29][b], 4.92[32][b]	5.68[34][b]			
		4.99[30,31][a]				
		4.64[32][b], 5.24[33][b]				
		5.37[34][b]				
M–H	GGA	1.5801	1.962	1.9843	2.2004	2.01
	LDA	1.5105	1.628	1.892	1.95	1.92
B_0	GGA	33	26	16	14.1	12
	LDA	43.8	33.53	19.6	15.34	11.18
		32.2[8][a], 32.3[37][b]	14.3[41][a], 19.4[9][a]	15.6[41][a]	10.0[41][a]	7.6[41][a], 11.9[40][b]
		40.5[38][b], 34.1[39][b]	29.6[24][b], 30.8[42][b]	17.3[40][b]	14.7[40][b]	8.8[38][b], 8.0[8][a]
		33.6[27][b], 40.5[40][b]	19.7[39][b], 27.4[38][b]	16.3[38][b]	14.1[39][b]	
		34.24[23][a]	23.5[36][b]			
			22.8[32,34][b]			
B_0'	GGA	4.9	3.62	2.955	2.8402	3.0365
	LDA	4.2	3.81	3.61	3.21	2.95
		3.95[43][a]	4.40[9][a]	4.00[10][a]		4.00[44][a]

[a] Experimental estimates.
[b] Other theoretical findings.

Table 2
Calculated lattice parameter a_0 (Å), equilibrium volume V_0 (Å^3), valence electron density ρ (electrons/Å^3), energy gap E_g (eV), bond length M–H (Å), bulk modulus B_0 (GPa), pressure derivative B_0' for the alkali hydrides with CsCl structure.

CsCl type		LiH	NaH	KH	RbH	CsH
a_0	GGA	2.458	3.010	3.520	3.81	3.84
	LDA	2.316	2.668	3.398	3.68	4.088
			3.094[9][a],4.838[45][b]			
			4.955[46][b]			
V_0	GGA	14.87	27.21	43.62	55.35	56.72
	LDA	12.44	18.99	39.23	49.35	68.32
			29.07[9][a]			
			28.35[47][b]			
ρ	GGA	0.1344	0.0735	0.0458	0.03613	0.03526

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