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Ab initio investigations of the perovskite and K_2NiF_4 phases in the Cs–Ca–H system

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This paper is dedicated to Bernard Darriet and to the memory of Michel Pezat.

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ABSTRACT

Deriving the energy–volume equation of state within DFT for $CsCaH_3$ and Cs_2CaH_4 has allowed predicting significant changes within the ionic behavior of hydrogen. In Cs_2CaH_4, apical H1 and equatorial H2 are found as less and more ionic respectively as compared to the perovskite hydride. This leads to a larger overall binding both from energy differences and chemical bonding analysis.

1. Introduction

Several binary and ternary ionic hydrides exist; many of them based on alkali- and alkaline-earth metals. They are characterized by nearly fully anionic hydrogen and large band gaps. The strong bonding of hydrogen with the metal matrix such as in MgH_2 hinders their use as hydrogen storage for energy sources under normal conditions. However they are envisaged for such applications at elevated temperatures [1].

The original investigations within the Cs–Ca–H system by Park, Pezat and Darriet [2] suggested the existence of $CsCaH_3$ with orthorhombic $GdFeO_3$-type perovskite structure. However Bronger and Breil [3] proposed that the synthesized phase was actually Cs_2CaH_4 with a K_2NiF_4-type structure, and provided X-ray diffraction analysis with atomic positions. The structure is shown in Fig. 1 with corner sharing CaH_6 octahedra interlayered with CsH rocksalt like entities. Hereafter, the apical hydrogen is called H1 and the equatorial one, H2. Nevertheless a cubic perovskite was identified later on by Gingl et al. [4]. On the electronic structure side, a number of ternary hydrides with perovskite structure were investigated by Sato et al. [5]. In view of the presence of two ternary hydrides within the Cs–Ca–H ternary, $CsCaH_3$ and Cs_2CaH_4, we engaged a comparative study of their electronic structure for establishing trends of stability and change of ionic behavior of hydrogen, using complementary computational methods within the well established quantum theoretical density functional DFT [6].

2. Computational methodology

Within DFT, a pseudo-potential approach within the VASP code [7,8] is used firstly to geometry optimize atomic positions and lattice parameters. Then the respective equations of states (EOS) are obtained through energy–volume curves fitted with Birch EOS [9]. For these purposes, we use the accurate projector augmented wave (PAW) method [8,10] with potentials built within the generalized gradient approximation (GGA) for an account of the effects of exchange and correlation [11]. The calculations are converged at an energy cut-off of 95.45 eV for cubic perovskite $CsCaH_3$ and 159 eV for Cs_2CaH_4. The *k*-point integration is carried out with a starting mesh of 4 × 4 × 4 up to 8 × 8 × 8 for best convergence and relaxation to zero strains. The Brillouin zone integrals are approximated using a special *k*-point sampling following Blöchl [10].

For a full description of the electronic band structures and of chemical bonding, the scalar relativistic all-electrons augmented

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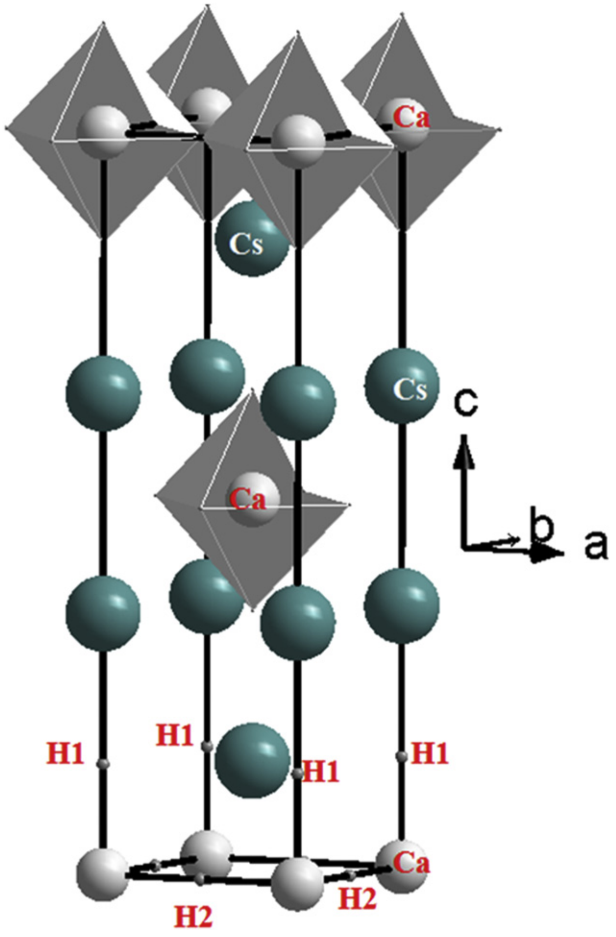

Fig. 1. The body centered tetragonal structure of Cs_2CaH_4.

spherical wave (ASW) [12,13] method is used. Like in the calculations with pseudo-potentials, the exchange and correlation effects are accounted for within GGA functional [11]. In the ASW method, the wave function is expanded in atom-centered augmented spherical waves, which are Hankel functions and numerical solutions of Schrödinger's equation, respectively, outside and inside the so-called augmentation spheres. In order to optimize the basis set, additional augmented spherical waves are placed at carefully selected interstitial sites (IS). The choice of these sites as well as the augmentation radii are automatically determined using the sphere-geometry optimization algorithm [14]. Self-consistency is achieved by a highly efficient algorithm for convergence acceleration [15]. The Brillouin zone integrations are performed using the linear tetrahedron method [10]. In the minimal ASW basis set, we have chosen the outermost shells to represent the valence states using partial waves up to $l_{max.} + 1 = 2$ for Ca, Cs, H and IS. The completeness of the valence basis set is checked for charge convergence. The self-consistent field calculations are run to a convergence of $\Delta Q = 10^{-8}$ for the charge density and the accuracy of the method is in the range of about 10^{-7} eV regarding energy differences. The relative magnitude of the chemical bonding is obtained based on the covalent bond energy ECOV approach which merges both overlap and Hamiltonian population analysis (resp. S_{ij}, and H_{ij}, i,j being two chemical species) [16]. The ECOV are constructed by considering s and p-like valence states of Cs, Ca and H. In the plots negative, positive and zero ECOV magnitudes indicate bonding, anti-bonding and non-bonding interactions respectively.

3. Geometry optimization and equations of state

Starting from the internal lattice coordinates of literature for the ternary hydrides [3,4], we carried out a full geometry optimization. The optimized lattice parameters, shown in Tables 1 and 2, are in good agreement with experimental data. Also the Ca–H distances are smaller than Cs–H ones in both varieties. It will be shown hereafter that they indicate prevailing Ca–H bonding which is differentiated between the two H sites in the K_2NiF_4-type structure of Cs_2CaH_4.

3.1. Equations of state

In order to extract energies to compare the binding within the two ternary hydrides, one needs establishing the energy–volume equation of state (EOS). In fact the calculated total energy pertains to the cohesive energy within the crystal because the solution of the Kohn-Sham DFT equations yield the energy with respect to infinitely separated electrons and nuclei. In as far as the zero of energy depends on the choice of the pseudo-potentials, somehow it becomes arbitrary; i.e. it is shifted but not scaled. However the energy derivatives as well as the EOS remain unaltered. For this reason one needs to establish the EOS and extract the fit parameters for an assessment of the equilibrium values. This is done from (E,V) set of calculations around minima found from geometry optimization. The resulting E = f(V) curves have a quadratic variation which can be fitted with energy–volume Birch EOS to the 3rd order [12]:

$$E(V) = E_o(V_o) + [9/8]V_oB_o\left[([(V_o)/V])^{[2/3]} - 1\right]^2 + [9/16]B_o(B' - 4)V_o\left[([(V_o)/V])^{[2/3]} - 1\right]^3,$$

where E_o, V_o, B_o and B' are the equilibrium energy, the volume, the bulk modulus and its pressure derivative, respectively.

Also for a test of Park et al. hypothesis of a $GdFeO_3$-type $CsCaH_3$ [2] its EOS was calculated beside the cubic one. The two curves together with the fit results in the inserts are shown in Fig. 2a. In this panel and in following ones relevant to the EOS, low residue χ^2 values ($\sim 10^{-6}$) are indicative of good fits. It can be seen that the system is slightly more stable in the cubic structure with a volume per formula unit (fu) in closer agreement with experiment than from geometry optimized value in Table 1. In as far as the main difference between cubic perovskite and orthorhombic one is in the tilting of the CaH_6 octahedra in the latter which is a stabilizing factor leading eventually to a transformation to post-perovskite in oxides (covalent) under pressure [17], then (ionic) hydride systems behave oppositely; i.e. a non tilted sequence of octahedra is preferred. The zero pressure bulk modulus of $B_0 = 23$ GPa (in both varieties), is in agreement with literature [5]. It indicates a soft, highly compressible material in comparison with oxides based on transition metals [17], despite the three dimensional structure. Note that all chemical elements in presence are s-like, i.e. with non directional (p or d) orbitals.

Table 1
Crystal characteristics of cubic perovskite $CsCaH_3$ from geometry and comparison with literature data.

$CsCaH_3$ *Pm-3m* #221 Z = 1	This work	Ref. [4]
Cs	0, 0, 0	0, 0, 0
Ca	½, ½, ½	½, ½, ½
H	½, ½, 0; 0, ½, ½; ½, 0, ½	½, ½, 0; 0, ½, ½; ½, 0, ½
a (Å)	4.54	4.61
Volume (Å^3)	80.0	97.9
d (Ca–H) (Å)	2.29	2.30
d (Cs–H) (Å)	3.12	3.15