

The novel structure and superconductivity of zirconium hydride



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ARTICLE INFO

Article history:

Received 19 December 2016

Received in revised form 9 March 2017

Accepted 11 March 2017

Keywords:

Phase stability
Electron-phonon coupling
Superconductivity
Electronic structure

ABSTRACT

The combined method of first principles calculations with structure searching is employed to study the phase stability of stoichiometric ZrH_x system with $x = 1-3$. A new zirconium hydride structure of $P6_3/mmc$ ZrH_3 is predicted to be thermodynamically stable at ambient pressure. Compared to ZrH and ZrH_2 , the electron-phonon coupling (EPC) in the phonon DOS of the hexagonal phase $P6_3/mmc$ ZrH_3 is much stronger. The superconductivity of the $P6_3/mmc$ - ZrH_3 has been predicted with a critical temperature T_c of 11.7 K, indicating perspectives in the interpretation of zirconium hydrides for the inherent properties and potential applications.

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1. Introduction

Zirconium and its alloys are essential structural materials within the fuel region of nuclear reactors. They can meet the comprehensive requirement of mechanical and corrosion resistance at reactor-operating temperature while keeping good compatibility with fuel materials [1–3]. The working environment of fuel cladding is in contact with water coolant, which promotes the oxidation of zirconium and its alloys. In the corrosion process, the hydrogen is generated, a portion of which can diffuse into the alloy to form zirconium hydrides when the hydrogen solubility limit is exceeded. These zirconium hydrides can precipitate out in the material and play important roles in fuel performance [4–6]. The wide usage of zirconium alloys has motivated numerous studies devoting to the phase diagram, structural, mechanical, and thermodynamic properties of zirconium and zirconium hydrides both from experiments and theory [7–14].

Zirconium hydrides have been reported to experience a phase transition as a function of hydrogen concentration [7]. At ambient condition, zirconium hydrides crystallize in a tetragonal phase ϵ - ZrH_2 with $I4/mmm$ space group [8]. As the hydrogen concentration decreases, the ϵ - ZrH_2 transforms to a nonstoichiometric bcc phase δ - $ZrH_{1.5}$ with $Fm\bar{3}m$ space group or a metastable tetragonal γ - ZrH phase with $P4_2/n$ space group [9]. However, except these well known atomic structures, whether or not the Zr-H clusters constituting other crystallographic phases remains until now an open

question. The efforts to searching for unknown zirconium hydride phases have been carried out. Recently, a new zirconium hydride ζ - Zr_2H , belonging to the trigonal crystal system with space group $P3m1$, has been identified and characterized experimentally [10]. As the fuel rod cladding materials in nuclear reactors, the superconductivity of zirconium hydrides is of great significance, however, the reported phases and compounds of zirconium hydrides show non-superconducting properties. Except for the experimental efforts, as the development of algorithm in theory, the structure prediction for the potential new structures of given compounds becomes possible.

In this paper, we focus the structure search on the ZrH_x ($x = 1-3$) compounds using the CALYPSO code combined with the Vienna ab initio simulation package (VASP) [15]. CALYPSO has been used to investigate a great variety of materials at different pressures [16–21]. Structure searching was performed and one new zirconium hydrides of ZrH_3 ($P6_3/mmc$) is predicted at ambient pressure, whose crystallographic structure has never been reported in the literatures. The fundamental properties including the electronic band structure, phonon dispersions, and superconductivity of this new phase are then studied, where the metallicity and superconductivity have been revealed. The electron-phonon coupling (EPC) calculations were performed by linear response theory, leading to a critical temperature T_c of 11.7 K for this H-rich phase. Compared to the 0.55 K of pure hcp Zr [22], the superconducting transition temperature increases ~ 11 K. In addition, for zirconium hydrides, the isotope effect is considered and the T_c of 9.21 K is obtained for ZrD_3 . Note that, it is the first zirconium hydride of the superconducting properties to date, which opens a potential application field of zirconium hydrides.

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2. Computational method

The structure relaxations and energetic calculations were performed using density functional theory (DFT), as implemented in the VASP code. [15] The electron-ion interaction is described by the projector-augmented-wave (PAW) potential methods [23] with the $1s^1$ and $4s^2 4p^6 5s^2 4d^2$ configurations treated as valence electrons for H and Zr, respectively. The exchange and correlation effects are described by generalized gradient approximation in the Perdew-Burke-Ernzerhof (PBE) form [24] and the plane-wave basis set is limited by the cutoff energy of 500 eV. In the Brillouin zone (BZ) integration, we use a $21 \times 21 \times 15$ grid with the Monkhorst-Pack scheme [25] to ensure the energy convergence to less than 1 meV/atom. The phonon spectrum and EPC were calculated within the framework of linear response theory by the Quantum-ESPRESSO code [26]. The superconductivity calculations are based on the microscopic theory of Bardeen, Cooper, and Schrieffer (BCS) [27] as generalized by Migdal and Eliashberg [28,29]. Critical temperatures were estimated using the modified approximate McMillan equation [30].

3. Results and discussion

We performed evolutionary variable cell structure prediction simulations from one to four ZrH_x ($x = 1-3$) formula units (f.u.) per cell. Besides the two well known phases of zirconium hydrides (γ -ZrH and ϵ -ZrH₂), the structure searching predicts a new low-enthalpy stoichiometric phases, i.e., the hexagonal ZrH₃. The atomic structures are depicted in Fig. 1 and the corresponding parameters are listed in Table 1. As is shown in Fig. 1, the H-rich ZrH₃ phase crystallizes in a hexagonal structure with space group P6₃/mmc, the unit cell of which contains two Zr atoms and six H atoms. The Zr atoms locate at 2d Wyckoff sites, while the six H atoms locate at two different Wyckoff sites, i.e., the 2b and 4f sites respectively, as listed in Table 1. The Zr atoms locate at the center of hexahedron formed by its surrounding five neighbor hydrogen

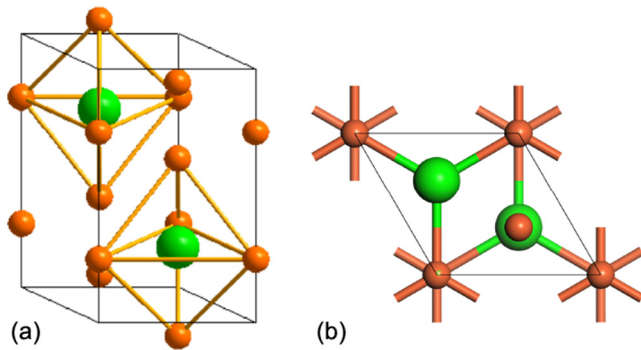


Fig. 1. Crystal structures of P6₃/mmc ZrH₃ for side view (a) and top view (b). The large green balls represent the Zr atoms and small orange balls stand for H atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Structural information of our predicted P6₃/mmc-ZrH₃ structure.

Phase	Lattice parameter	Wyckoff positions	Atomic coordinates (fractional)
ZrH ₃ (P6 ₃ /mmc)	$a = b = 3.472$ (Å)	Zr 2d	$\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$
	$c = 5.904$ (Å)	H 2b	$0, 0, \frac{1}{4}$
	$\alpha = \beta = 90^\circ$	H 4f	$\frac{1}{3}, \frac{2}{3}, 0.402$
	$\gamma = 120^\circ$		

atoms (three first nearest neighbor ones and two second nearest neighbor ones), as depicted in Fig. 1(a). The bonding length of Zr–H is ~ 2.00 Å, which is shorter than that of γ -ZrH (~ 2.05 Å) and ϵ -ZrH₂ (~ 2.09 Å), indicating the stronger Zr–H interaction in ZrH₃. The phase stabilities are checked by calculating the enthalpy difference with respect to pure hcp Zr metal and H₂, as well as γ -ZrH and ϵ -ZrH₂ (Fig. 2(a)). It is found that P6₃/mmc-ZrH₃ is easy to be synthesized at ambient condition and high pressures considered here (up to 50 GPa) due to the much lower enthalpy. The phase stability is also confirmed by calculating the phonon dispersion relations, as shown in Fig. 2(b). There are no imaginary frequencies in the whole Brillouin zone, indicating the dynamical stability of this phase. The phonon frequencies of the crystalline structure are closely related to the phonon density of states (DOS) and Eliashberg EPC spectral function $\alpha^2F(\omega)$, which will be discussed below.

The band structure and electronic density of states for P6₃/mmc ZrH₃ at ambient pressure are shown in Fig. 3. The electronic band structures of ZrH₃ exhibit metallic features, in agreement with previous experimental observations for γ -ZrH, δ -ZrH_{1.5} and ϵ -ZrH₂ [2,31–36]. Evidently, the conduction band is strongly marked by Zr-d orbitals. For γ -ZrH, δ -ZrH_{1.5} and ϵ -ZrH₂, a band gap about 4 eV below the Fermi level divides the DOS into two parts, which has been observed experimentally [31–33]. However, P6₃/mmc ZrH₃ exhibits a continuous distribution of density of states in the whole energy domain. From previous XPS measurements [31,32], a hump centered at -6.5 eV below the Fermi level is observed

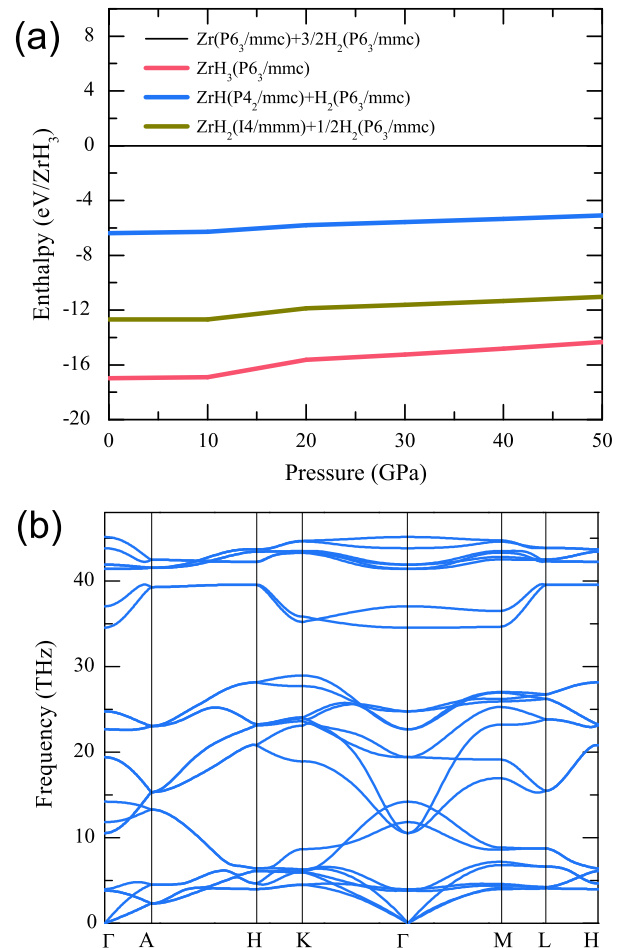


Fig. 2. (a) Enthalpy difference of P6₃/mmc-ZrH₃ with respect to pure hcp Zr metal and H₂, and γ -ZrH and ϵ -ZrH₂. (b) Phonon dispersion curves of P6₃/mmc-ZrH₃ along the high symmetry \mathbf{q} points in Brillouin zone.

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