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First-principles study the structural, electronic, vibrational and thermodynamic properties of $Zr_{1-x}Hf_xCoH_3$

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ABSTRACT

The structural, electronic, vibrational and thermodynamic properties of $Zr_{1-x}Hf_xCoH_3$ ($x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0$) are investigated using first principles approach based on the virtual crystal approximation (VCA). The results indicate the series $Zr_{1-x}Hf_xCoH_3$ have the similar physical properties. When Hf concentration increases gradually, the lattice parameter reduces and the thermodynamic stability first decreases and then increases, respectively. The calculated results of charge distributions and electron localization function (ELF) suggest that the interactions of H–Co and H– $Zr_{1-x}Hf_x$ are primarily metallic with a small covalent component. The band structure and the corresponding density of states (DOS) around the Fermi level (E_f) indicate the metallicity enhances and the electrical conductivity is better with increasing Hf content. The phonon density of states imply that with the increase of Hf content, the covalent interactions between H($4c_2$) and $Zr_{1-x}Hf_x$ are weakened, while the covalent interactions between H($8f_1$) and $Zr_{1-x}Hf_x$ basically remained unchanged (H($4c_2$) and H($8f_1$) represent the hydrogen atoms occupying $4c_2$ and $8f_1$ site, respectively), which is consistent with the results of charge density. Finally, the thermodynamic properties are obtained and discussed on the base of the obtained vibrational properties.

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Introduction

The intermetallic compound ZrCo and its hydride $ZrCoH_3$ have gained considerable attention in the past decade because ZrCo has excellent hydriding/dehydriding property and some inherent excellent characters compared with uranium

conventionally served as a getter in the International Thermonuclear Experimental Reactor (ITER) project [1–7], which makes it be identified as a possible candidate for handling hydrogen isotopes tritium in ITER project [8,9].

Ideally, ZrCo alloy will completely transform into $ZrCoH_3$, and vice versa in the hydriding-dehydriding process. The

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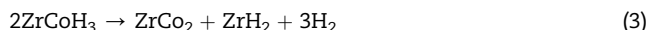
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chemical reaction exist in the hydriding -dehydriding process can be described by the following equation [10]:



Nevertheless, many experimental studies [5,11–16] have found that during its hydrogen desorption process, there is a disproportionation reaction described by the following equation:



This phenomenon make ZrCo lose its hydrogen isotope storage ability. A promising strategy to significantly improve the ability to resist the disproportionation reaction is that Zr or Co atom is partially substituted by other kind of atom M, such as Ti, Hf, Ni and Fe, which has been confirmed by many experimental studies [5,14–21]. For example, Peng L et al. [16] have investigated the influence of Hf substitution for zirconium in ZrCo on structure, hydrogen adsorption properties as well as hydrogen-induced disproportionation and discovered that $\text{Zr}_{0.7}\text{Hf}_{0.3}\text{Co}$ has much better ability of anti-disproportionation than ZrCo. Jat et al. [17] have studied the synthesis, characterization and hydrogen isotope storage properties of Zr–Ti–Co ternary alloys. It was found that Ti substituted alloys has favorable hydrogen isotope storage properties over pure ZrCo alloy for application in ITER SDS. In addition, Jat et al. [18] confirmed that $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Co}$ alloy has better durability against hydrogen induced disproportionation.

However, to the best of our knowledge, no theoretical ab-initio study on $\text{Zr}_{1-x}\text{Hf}_x\text{CoH}_3$ system has been reported except the ZrCoH_3 and HfCoH_3 . Gupta [22] has studied affection of the H–Zr interactions and found it playing a significant role in the stability of ZrCoH_3 system and the hydrogen site occupancy. D. Chattaraj et al. [23] reported the structural, electronic, vibrational, thermodynamic and elastic properties of ZrCoH_3 using first principles approach within the Vienna ab initio simulation package (VASP), in which the lattice constants, enthalpy of formation and bulk modulus of ZrCoH_3 have been determined and the character of chemical bonding in ZrCoH_3 has been analyzed. In addition, D. Chattaraj et al. [24] have investigated the dynamical, thermodynamic and elastic properties of ZrCoX_3 (X = H, D and T), which described the effect of isotopes on the vibrational and thermodynamic properties.

Here, we report theoretical study on the structural, electronic, dynamic and thermodynamic properties of $\text{Zr}_{1-x}\text{Hf}_x\text{CoH}_3$ ($x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0$, the x has the same meaning in this paper, unless otherwise stated) by first-principles. We hope that the calculated physical properties will provide some supportive data for further research.

The rest of the paper is arranged as follows: In Section Computational details, we give a detailed description of the computational method. In Section Results and discussions, the acquired results and their interpretation are given. Finally, a brief summary is given in Conclusions.

Computational method

All of ours calculations are performed based on density functional theory (DFT) and the density functional theory perturbation (DFPT) in the plane-wave pseudopotential approach using the ABINIT code [25]. The Generalized Gradient Approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [26] is employed for exchange–correlation energy, and the electronic pseudo-potentials performed for atoms are $\text{Zr-}4s^24p^64d^25s^2$, $\text{Co-}3s^23p^63d^74s^2$, $\text{Hf-}5s^25p^65d^26s^2$ and $\text{H-}1s^1$, respectively.

On the basis of our convergence test, an $6 \times 6 \times 6$ Monkhorst–pack k-point mesh in the Brillouin zone for a unit cell is adopted, and the energy cut-off is set to 30 hartree (1 hartree = 4.3597×10^{-18} J) to determine the number of plane waves in expansion which guarantees the total energy errors within 10^{-5} hartree in all our calculations.

After structural optimization, the electronic properties and vibrational properties are respectively obtained by the DFT and DFPT. Thereafter, the thermodynamic properties such as internal energy E , entropy S and specific heat C_V are predicted within the harmonic approximation (HA), then Gibbs free energy G is computed through the obtained internal energy E and entropy S .

The Virtual Crystal Approximation (VCA) [27,28] implemented in the ABINIT program is used to simulate the disordered alloy $\text{Zr}_{1-x}\text{Hf}_x\text{CoH}_3$. Compared with the supercell (SC) method, the VCA method has the advantages of simplicity and computational efficiency because it permit the crystal to continue to have the original periodicity but contain some fictitious “virtual” atoms whose potential is the average of those of the atoms in the parent compounds [29–31]. Therefore, the VCA method is a promising approach and has been successfully predicted the physical properties, such as structural, magnetic, electronic, piezoelectric, elastic, and dynamic properties of many disordered alloy systems [29,30,32–37].

Consequently, we believe that the VCA method can be used to predict the electronic, vibrational and thermodynamic properties of the ternary $\text{Zr}_{1-x}\text{Hf}_x\text{CoH}_3$ alloy. In $\text{Zr}_{1-x}\text{Hf}_x\text{CoH}_3$ system, the virtual pseudo-potential is constructed by assemblage of elemental ionic pseudo-potentials of ZrCoH_3 and HfCoH_3 within first-principles VCA schema, that is to say,

$$V_{\text{VCA}} = (1-x)V_{\text{ZrCoH}_3} + xV_{\text{HfCoH}_3} \quad (4)$$

where x is the Hf substitute fraction.

Results and discussions

Structure properties

The stable crystal structure of ZrCoH_3 and HfCoH_3 compounds and the mixed crystal $\text{Zr}_{1-x}\text{Hf}_x\text{CoH}_3$ are all simple orthorhombic ZrNiH_3 -type crystal structure with space group $\text{cmcm}(\text{SG}:63)$ as shown in Fig. 1, which contains two unit cells of $\text{Zr}_{1-x}\text{Hf}_x\text{CoH}_3$ [7,24,38].

The equilibrium lattice parameter is computed from the structural optimization, using the Broyden–Fletcher–Goldfarb–Shanno minimization [39–43]. The results of

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