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Density functional study of vibrational, thermodynamic and elastic properties of ZrCo and $ZrCoX_3$ (X = H, D and T) compounds

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The dynamical, thermodynamic and elastic properties of ZrCo and its hydrides $ZrCoX_3$ (X = H, D and T) are reported. While the electronic structure calculations are performed using plane wave pseudopotential approach, the effect of isotopes on the vibrational and thermodynamic properties has been demonstrated through frozen phonon approach. The results reveal significant difference between the $ZrCoH_3$ and its isotopic analogs in terms of phonon frequencies and zero point energies. For example, the energy gap between optical and acoustic modes reduces in the order of $ZrCoT_3 > ZrCoD_3 > ZrCoH_3$. The vibrational properties shows that the intermetallic ZrCo is dynamically stable whereas $ZrCoX_3$ (X = H, D and T) are dynamically unstable. The calculated formation energies of $ZrCoX_3$, including the ZPE, are -146.7, -158.3 and -164.1 kJ/(mole of $ZrCoX_3$) for X = H, D and T, respectively. In addition, the changes in elastic properties of ZrCo upon hydrogenation have also been investigated. The results show that both ZrCo and $ZrCoH_3$ are mechanically stable at ambient pressure. The Debye temperatures of both ZrCo and $ZrCoH_3$ are determined using the calculated elastic moduli.

1. Introduction

The ZrCo-X_2 (X = H, D and T) systems have gain considerable attention because of its use in the hydrogen isotopes storage in the International Thermonuclear Experimental Reactor (ITER) project [1]. Tritium is one the most important isotopes of hydrogen which is going to be used as fuel in fusion reactor. But, this radioactive isotope is a beta emitter and required to be stored safely in a suitable matrix. The solid state storage of hydrogen isotopes is quite reliable, safe and advantageous compared to gaseous or liquid form of storage [2–4]. Metal hydrides are unique choice as a solid state storage material for tritium [5]. Development and delivery of such systems for tritium are of urgent requirement in the ITER project. Conventionally, uranium is used as getter bed for tritium as it has high absorption capacity at room temperature, low equilibrium pressure (<1 bar at 550–680 K) which prevents the accidental release of tritium into atmosphere, fast kinetics of hydrogen absorption–desorption and large cyclic life [6]. However, uranium hydride is pyrophoric in nature and uranium is a nuclear material. So investigation for finding out an alternate material for tritium storage is in progress. Several experimental and theoretical studies are reported on the uranium based intermetallics for this purpose [7–9]. Presently, the intermetallic ZrCo have been found to be suitable for the safe storage, supply and recovery of hydrogen isotopes in the ITER [1,10–14]. ZrCo intermetallic has good hydriding/dehydriding property which can serve as a substitution of uranium [15]. Also it is not pyrophoric and easy to handle as it is not a nuclear material [10,13]. However, the major drawback of ZrCo is that its absorption–desorption cycle become poor on prolonged thermal cycling [16–18] which is due to the disproportionation of its hydride ($ZrCoH_x$ ($x \leqslant 3$) into the stable hydride phase ZrH_2 and the hydrogen non-absorbing phase $ZrCo_2$. Most recently, several experimental studies are reported on the substitution of a third element into ZrCo intermetallic to improve its cyclic life stability [19,20].

Experimental investigation of thermo-physical, vibrational and mechanical properties of metal and alloy tritides are difficult compared to hydrides and deuterides because tritium is radioactive in nature. A special experimental facility is required for the safe handling of tritides. The computational techniques based on first principles method are helpful for this purpose. The theoretically calculated thermo-physical properties of radioactive tritides will be helpful for predicting the behavior of the material where there is lack of experimental facility for handling radioactivity. The computed properties will also serve as supportive data for further experimental findings. In this context, the structural, dynamical,

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thermodynamic and elastic properties of ZrCo and its hydrides $ZrCoX_3$ (X = H, D and T) are calculated using the DFT based *ab initio* method.

Very few literatures on theoretical studies of ZrCo-hydrogen system [21–23] are available though there are plenty of experimental data on this system. Gupta [22] has investigated that the Zr–H bonding contribution plays a crucial role in the stability of the hydride $ZrCoH_3$ and also has important role in the hydrogen site occupancy. In our previous study, the structural, electronic and thermodynamic properties of the ZrCo and its hydride $ZrCoH_3$ are reported [23]. The ground state properties like equilibrium lattice constants, bulk modulus and enthalpy of formation of ZrCo and $ZrCoH_3$ have been determined by optimizing the atomic and electronic structure of the compounds. The nature of chemical bonding in ZrCo and $ZrCoH_3$ has been depicted in terms of electronic density of states spectrum and charge density contour. The scope of studying isotope effect, vibrational, thermodynamic and elastic properties of ZrCo and $ZrCoH_3$ is fulfilled here. Recently, the isotope effect of ZrX_2 compounds is reported using first principles method [24]. In that study, the isotope effect of ZrX_2 (X = H, D and T) compounds are depicted in terms variation of phonon frequencies and zero point energies. Li et al. [25] have reported the structural, vibrational and thermodynamic properties of ZrCo by first principles method and density-functional perturbation theory (DFPT). The phonon frequency (ω) at the Brillouin zone center, Phonon dispersion curve and phonon density of state for ZrCo have been determined. Zero point energy and the phonon contribution to the thermodynamic properties such as Helmholtz free energy, internal energy, entropy and constant-volume specific heat of ZrCo are calculated from 300 to 1000 K within the harmonic approximation [26]. Regarding the elastic properties of ZrCo and its hydride, Agosta et al. [27] have experimentally investigated the variation of elastic properties of ZrCo as a function of temperature using ultrasonic pulse echo method. Very few literatures are available on the elastic properties of ZrCo and $ZrCoH_3$.

As $ZrCoX_3$ (X = H, D and T) are isoelectronic compounds, therefore the electronic properties are similar. Hence, it is of interest to investigate the hydrogen isotope effect on their vibrational and thermodynamic properties through phonon frequencies. The results of this study could provide useful information which could be valuable for the design of tritium storage bed.

2. Computational details

All the present calculations are performed using the plane wave-pseudopotential method under the framework of density functional theory as implemented in the Vienna *ab initio* simulation package (VASP) [28–30]. The electron–ion interaction and the exchange correlation energy are described under the projector-augmented wave (PAW) [31,32] method and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [33], respectively. The valence electronic configuration of Zr, Co and H are set to $5s^14d^3$, $4s^13d^8$ and $1s^1$, respectively. The energy cut off for the plane wave basis set is fixed at 500 eV. The ionic optimization is carried out using the conjugate gradient scheme and the forces on each ion was minimized up to 5 meV/Å [34,35]. The *k*-point sampling in the Brillouin Zone (BZ) has been treated with the Monhorst-Pack scheme [36], using a $4 \times 4 \times 4$ k-mesh. Total energies of each relaxed structure using the linear tetrahedron method with Blöchl corrections are subsequently calculated in order to eliminate any broadening-related uncertainty in the energies [37]. To begin with the dynamical calculations, the lattice parameters of ZrCo and $ZrCoH_3$ have been optimized using VASP code and the optimized structures are used for phonon calculation.

The phonon frequencies of ZrCo and $ZrCoX_3$ (X = H, D and T) are calculated by the PHONON program [38] using the forces based on the VASP package. A $3 \times 3 \times 3$ supercell of ZrCo containing total 54 atoms and a $3 \times 1 \times 2$ supercell of $ZrCoX_3$ (X = H, D and T) containing 120 atoms have been used for the phonon calculations. A small displacement of 0.02 Å have been given to the atoms present in the supercell of ZrCo and $ZrCoX_3$ (X = H, D and T) compounds. The phonon dispersion curves and temperature dependent thermodynamic functions of these compounds are obtained by using the calculated phonon frequencies. The temperature-dependent thermodynamic functions of a crystal, such as the internal energy (E), entropy (S), Helmholtz free energy (F) and constant volume heat capacity (C_V) can be calculated from their phonon density of states as a function of phonon frequencies. In the present study, the phonon contribution to Helmholtz free energy F, internal energy E, entropy S and constant volume specific heat C_V, at temperature T are calculated within the harmonic approximation using the following formulas [39]:

$$F = 3nNk_BT \int_0^{\omega_{\max}} \ln\left\{2\sinh\frac{\hbar\omega}{2k_BT}\right\} g(\omega)d\omega \tag{1}$$

$$E = 3nN\frac{\hbar}{2} \int_0^{\omega_{\max}} \omega\coth\left(\frac{\hbar\omega}{2k_BT}\right) g(\omega)d\omega \tag{2}$$

$$S = 3nNk_B \int_0^{\omega_{\max}} \left[\frac{\hbar\omega}{2k_BT}\coth\frac{\hbar\omega}{2k_BT} - \ln\left\{2\sinh\frac{\hbar\omega}{2k_BT}\right\}\right] g(\omega)d\omega \tag{3}$$

$$C_V = 3nNk_B \int_0^{\omega_{\max}} \left(\frac{\hbar\omega}{2k_BT}\right)^2 \operatorname{csc}h^2\left(\frac{\hbar\omega}{2k_BT}\right) g(\omega)d\omega \tag{4}$$

F and the E at zero temperature represents the zero point energy, which can be calculated from the expression as $F_0 = E_0 = 3nN\int_0^{\omega_{\max}}\left(\frac{\hbar\omega}{2}\right)g(\omega)d\omega$, where n is the number of atoms per unit cell, N is the number of unit cells, ω is the phonon frequencies, $\omega_{\max}$ is the maximum phonon frequency, and $g(\omega)$ is the normalized phonon density of states with $\int_0^{\omega_{\max}} g(\omega)d\omega = 1$.

The total energy of hydrogen molecule (H_2) and zero point energy of X_2 ($X = H_2$, D_2 and T_2) molecules are calculated using DFT which is described earlier [24]. The elastic properties of ZrCo and its hydride $ZrCoH_3$ were also calculated using an efficient stress–strain method [40] implemented in VASP.

3. Results and discussion

3.1. Structural properties

The crystal structure of ZrCo is CsCl-type cubic (bcc) with lattice parameter a = 3.196 Å [41,42] as shown in Fig. 1a. In ZrCo, the Zr atom occupies 1*a* (0,0,0) and Co atom occupies 1*b* (0.5,0.5,0.5) Wyckoff site. The hydride $ZrCoH_3$ favors a simple orthorhombic $ZrNiH_3$-type crystal structure as shown in Fig. 1b with the room temperature lattice parameters listed in Table 1 [43,44]. The crystal structure shown in Fig. 1b contains two unit cells of $ZrCoH_3$. To obtain the ground state structural parameters, the ionic and electronic structure of the ZrCo and $ZrCoH_3$ have been optimized by varying the lattice parameters. The ground state crystal structures data and the optimized lattice parameters of ZrCo and $ZrCoH_3$ are summarized in Table 1. The lattice parameters are found to be within ±1% accuracy from the experimental data. The good agreement between calculated lattice parameters and the experimentally reported values establishes the accuracy and reliability of the present computational method. The calculated ground state structure of ZrCo and $ZrCoH_3$ are considered for the calculation of vibrational and elastic properties.

3.2. Vibrational properties

The dispersion relation between vibrational frequency ω and wave vector q can be expressed as [45]:

$$\omega = \omega_j(q) \tag{5}$$

The subscript j is the branch index. Generally, a crystal lattice with n atoms per unit cell has $3n$ branches, three of which are acoustic modes and the remainders are optical modes. The lattice vibration mode with $q \approx 0$ plays an important role for Raman scattering and infrared absorption [46]. So, the vibrational frequency with $q = 0$, i.e. at the center Γ point of the first Brillouin zone, is called as normal mode of vibration. The crystal structure of ZrCo contains 2 atoms per unit cell, so there are six normal modes of vibrations, which includes three low frequency acoustic modes and three high frequency optical modes. As the $ZrCoX_3$ (X = H, D and T) compounds contains two unit cell having total number of 10 atoms, there are 30 normal vibrational modes among which three are acoustic and the remainder are optical modes. The light atom H has larger displacement amplitude which corresponds to