



Structural, electronic, elastic properties and stabilities of hexagonal ZrNiAl alloy and its hydride ZrNiAlH_{0.67} under pressure

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ABSTRACT

The structural, electronic, elastic properties and stabilities of hexagonal prototype alloy ZrNiAl and its saturated hydride ZrNiAlH_{0.67} are investigated using the pseudopotential plane wave method within the generalized gradient approximation (GGA). The calculated structural parameters are in good agreement with the available experimental data. Partial covalent characters on ZrNiAl and ZrNiAlH_{0.67} are verified by the calculations of PDOS (partial density of states) and overlap population. Band structures show both ZrNiAl and ZrNiAlH_{0.67} belong to metals. The elastic constants and their pressure dependences are calculated using the static finite strain technique. From the analysis of the mechanical stabilities, hexagonal ZrNiAl is unstable at higher pressure than 29.34 GPa; that its hydride ZrNiAlH_{0.67} is stable up to 50 GPa is similar with the experimental result of isostructural LaNiInD_{1.63-x}. Hydrogenation not only leads to strong lattice anisotropy but also leads to strong mechanical anisotropy.

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1. Introduction

The hexagonal ZrNiAl (space group *p*-62*m*) is a prototype alloy for a large family of ternary alloys XTM (X = early transition metal, lanthanide metal, or actinide metal; T = late transition metal; and M = element of the third, fourth, or fifth main group) [1]. In the large family, more than 300 examples were recorded [2], and their structural, electronic, magnetic and transport properties have been intensively investigated in the recent tens of years [1–11]. Unusual physical properties, particularly a variety of magnetic behaviors are exhibited [1,4,8,11]. But physical properties of prototype alloy ZrNiAl itself are, however, relatively less known.

Early in 1967, Kripyakevich et al. [3] correctly and carefully reported the crystal structure of the hexagonal ZrNiAl by extensive experiment work for the first time. In their reports, the hexagonal ZrNiAl is built of two types of basal-plane layers, containing Zr–Ni1 and Al–Ni2, alternating along the crystal *c*-axis [Fig. 1a]. Later, their results were confirmed again by Yoshida et al. [5] in 1995 and Zumnick et al. [7] in 1999. Yoshida et al. [5] further investigated the hydrogen storage capacity of hexagonal ZrNiAl alloy and the structure of its hydride. In 2000, Nowak and Hayashi [1] investigated the factors about the strength of interactions affecting the

Al nuclei by Al NMR study in ZrNiAl. They mentioned that ZrNiAl undoubtedly has a partial covalent character in term of the distances of atoms, and very small values of Al-*s* and Al-*p* densities of states at the Fermi level because of slow relaxation rate of Al nuclei in ZrNiAl. For other properties, such as elastic properties, structural stability, to the best of our knowledge, neither experimental nor theoretical details are available for the hexagonal ZrNiAl alloy. Furthermore, there are also no investigations about the pressure effects on its physical properties.

On the other hand, there has been increasing interest in intermetallic alloys for hydrogen (H) storage in application for energy conversion systems [2,12–19]. One type of known hydrogen storage intermetallic alloys are equiatomic ternary alloys with hexagonal ZrNiAl structure, such as MNiAl (M = Y, Gd, Dy, Er, Sm, Lu, U) [12–14], whose hydrides comply with “2-Å rule” [20]; RTIn (R = La, Ce, Pr, Nd; T = Ni, Pd, Pt) [2,15–19], whose hydrides violate “2-Å rule”. Regardless of complying with or violating “2-Å rule”, the structures of most of these hydrides (such as UNiAlH_{1.9} [13], CeNiInH_{1.33} [15]) are characterized by a hexagonal (space group *P*6̄2*m*) ZrNiAlH_{0.67} crystal structure [3] shown in Fig. 1b.

Clearly, hydrogen atom is at the trigonal-bipyramidal site, and surrounded by two Ni and three Zr atoms. Although the “ZrNiAlH_{0.67}-type” hydrides, especially for violating “2-Å rule” hydrides were intensively researched on their structural, electronic and bonding properties in the recent years [15–19], their elastic properties and structural stabilities under pressure were also less known. To our best knowledge, only Stange et al. [16] investigated

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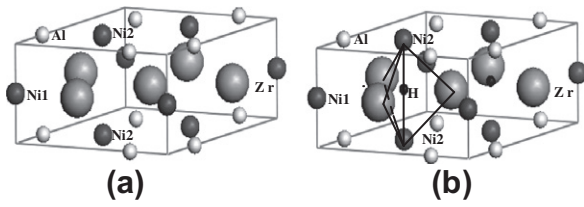


Fig. 1. (a) The crystal structure of hexagonal ZrNiAl and (b) the crystal structure of hexagonal ZrNiAlH_{0.67}.

the stability of LaNiInD_{1.632-x} in experiment, and concluded LaNiInD_{1.632-x} is stable up to 40 GPa.

To understand the stability of metal hydrides is a key to rationally investigate and design potential hydrogen-storage materials. Further, theoretical high pressure studies on metal hydrides assume additional importance as the high pressure X-ray and neutron diffraction studies have difficulties to establish the positions of hydrogen (deuterium) atoms [18]. At the same time, in practice, for hydrogen storage alloy hydride, the plateau pressure is required to range from 0.1 to 20 MPa from room temperature to 100 °C [13]. Apparently, high pressure studies, especially structural stabilities studies under pressure for these hydrides are necessary. For ZrNiAlH_{0.67}, not only elastic/mechanical properties but also electronic properties are not known at 0 and high pressure.

Hence, in this work, we will systematically investigate the structural, electronic, elastic properties of hexagonal ZrNiAl alloy and its saturated hydride ZrNiAlH_{0.67} under pressure up to 50 GPa using first-principles calculations. From the calculated elastic constants, we will investigate their mechanical stabilities and anisotropic behaviors as well as the bulk modulus, shear modulus, Young's modulus, Poisson's ratios and Debye temperatures. In order to explore the effect of hydrogenation, the results of hexagonal ZrNiAl and its hydride ZrNiAlH_{0.67} are analyzed contrastively. In Section 2, we give the brief descriptions of theoretical methods. The results of structural, electronic, elastic properties and stabilities of the hexagonal ZrNiAl alloy and its hydride ZrNiAlH_{0.67} under pressure are presented in Section 3. A summary is given in the last Section.

2. Calculation methods

2.1. Total energy electronic structure calculations

We calculate the electronic structures of hexagonal ZrNiAl alloy and its saturated hydride ZrNiAlH_{0.67} using the plane-wave pseudopotential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) code [21,22] together with the generalized gradient approximation (GGA) for exchange–correlation function in the scheme of Perdew–Bueke–Ernzerhof (PBE) [23]. The Kohn–Sham equation was solved by means of the ultrasoft pseudopotentials introduced by Vanderbilt [24]. Pseudo-atomic calculations were performed for Zr 4s²4p⁶4d²5s², Ni 3d⁸4s², Al 3s²3p¹, and H-1s¹. A plane-wave basis set with energy cut-off 450 eV was applied. For the Brillouin zone sampling, we used a 6 × 6 × 12 Monkhorst–Pack mesh. The self-consistent convergence of the total energy was 10⁻⁶ eV/Atom. These parameters are applied not only for hexagonal ZrNiAl but also for its hydride ZrNiAlH_{0.67}.

To verify that these parameters are sufficient in leading to well converged total energy, tests of convergence have been conducted. First, let 6 × 6 × 12 grid keep constant, for 300, 350, 400, 450 and 500 eV cut-off energies, the total energies differences of the hexagonal ZrNiAl (ZrNiAlH_{0.67}) unit cell relative to that at the 550 eV cut-off energy are 0.221 (0.249), 0.017 (0.032), 0.018 (0.015), 0.008

(0.005), 0.001 (0.003) eV, respectively. Second, let 450 eV cut-off energy keep constant, for 3 × 3 × 6, 4 × 4 × 8, 5 × 5 × 10, 6 × 6 × 12 and 7 × 7 × 14 grids, the total energies differences of the hexagonal ZrNiAl (ZrNiAlH_{0.67}) unit cell relative to that at the 8 × 8 × 16 grid are 0.004 (-0.014), 0.009 (0.009), -0.016 (-0.001), -0.036 (0.003), 0.001 (0.004) eV, respectively. These tests affirmed that an adequate convergence of total energy is achieved with the energy cut-off of 450 eV and 6 × 6 × 12 *k*-point grid.

2.2. Elastic properties

The elastic stiffness tensor is related to the stress tensor and the strain tensor by Hooke's law. The elastic constants are calculated as the second derivatives of the internal energy with respect to the strain tensor. The elastic stiffness tensor c_{ijkl} can be expressed as [25–27]:

$$c_{ijkl} = \left(\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}} \right)_x \quad (1)$$

with e_{kl} , σ_{ij} , X , x are Eulerian strain tensor, applied stress, the coordinates before and after deformation, respectively. Since the stress and strain tensors are symmetric, the most general elastic stiffness tensors have only 21 non-zero independent components. For a hexagonal crystal, they are reduced to five components, i.e. C_{11} , C_{12} , C_{13} , C_{33} and C_{44} . These elastic constants can be determined by computing the stress generated by applying a small strain to an optimized unit cell [28]. In practice, the maximum strain amplitude was set from -0.003 to 0.003 with the step of 0.001, all forces on atoms are converged to less than 0.006 eV/Å. Before the calculations of elastic constants of different pressures, we firstly obtained a corresponding equilibrium structure. For the acquisition of zero pressure equilibrium structure, we adapted the method introduced in Section 3; for the acquisition of non-zero hydrostatic pressure equilibrium structure, we adapted the BFGS algorithm [29] (proposed by Broyden, Fletcher, Goldfarb, and Shanno), which provides a fast way of finding the lowest energy structure and the optimized cell at different hydrostatic pressures. Hydrostatic pressure is introduced by the set of the parameters in the CASTEP software.

The adiabatic bulk B and the shear modulus G for hexagonal crystal structure are taken as [30,31]:

$$B_V = \frac{1}{9} [2(C_{11} + C_{12}) + C_{33} + 4C_{13}]. \quad (2)$$

$$G_V = \frac{1}{30} (C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 12C_{66}). \quad (3)$$

$$B_R = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}. \quad (4)$$

$$G_R = \frac{5}{2} \frac{((C_{11} + C_{12})C_{33} - 2C_{13}^2)^2 C_{44}C_{66}}{3B_V C_{44}C_{66} + ((C_{11} + C_{12})C_{33} - 2C_{13}^2)^2 (C_{44} + C_{66})} \quad (5)$$

where

$$C_{66} = \frac{1}{2} (C_{11} - C_{12}). \quad (6)$$

The arithmetic average of the Voigt and the Reuss bounds is commonly used to estimate the elastic moduli of polycrystals. In the terms of the Voigt–Reuss–Hill approximations [32]:

$$B = (B_V + B_R)/2. \quad (7)$$

$$G = (G_V + G_R)/2. \quad (8)$$

Then, Young's modulus E and Poisson's ratio σ can be calculated by:

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