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Ab initio calculation of structural, electronic and phonon properties of ZrRu and ZrZn in B2 phase

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ABSTRACT

The structural, electronic and dynamic properties of cesium chloride, ZrRu and ZrZn were studied by employing an *ab initio* pseudopotential method and a linear response scheme, within the generalized gradient approximation. The calculated lattice constant, bulk modulus and first-order pressure derivative of the bulk modulus were reported in B2 structure and compared with available experimental and other theoretical results. The electronic band structure, partial and total density of states were determined by using the Quantum-Espresso *ab initio* simulation package based on pseudopotential method. Phonon dispersion curves and density of states were calculated by employing a density functional perturbation theory.

1. Introduction

ZrRu and ZrZn have been used in nuclear power industry, because they exhibit fairly high melting point, high strength and oxidation resistance [1,2]. The fact that ZrRu and ZrZn exhibit a cesium chloride structure (B2) with space group $Pm\overline{3}m$ is well known by researcher. The structural, thermal and thermodynamic properties of ZrRu have been studied by several groups, employing different theoretical and experimental schemes [3–9]. The electronic structure of ZrRu alloy has been investigated using linear muffin-tin orbital (LMTO) method and a tight-bonding linear muffin-tin orbital (TB-LMTO) method calculation by Traiber et al. [10]. Arroyave et al. [11] studied on vibrational properties of ZrZn using the Vienna *ab initio* simulation package (VASP) code in the generalized gradient approximation (GGA). The authors in this study have concluded that ZrZn compound is dynamically stable at the equilibrium volumes. However, relatively less attention has been paid to the phonon properties of these alloys. The full phonon-dispersion curves are necessary for a microscopic understanding of the lattice dynamics. Knowledge of the phonon spectrum plays a significant role in determining various material properties such as phase transition, thermodynamic stability, transport and thermal properties. The aim of the present work is to investigate the structural, electronic and phonon properties of ZrRu and ZrZn alloys in the B2 phase by employing the density of functional theory (DFT).

2. Method

The calculations within the generalized gradient approximation (GGA) of DFT were carried out using the Quantum-ESPRESSO package [12]. The exchange-correlation term has been determined within the generalized gradient approximation (GGA) parameterized by Perdev–Burke–Ernzerhof [13]. The wave functions were expanded into plane waves with kinetic energies of up to 40 Ry. Self-consistent solutions of Khon–Sham equations were obtained by employing a set of 60 k-points within the irreducible part of the Brillouin zone (BZ). In order to obtain complete phonon dispersions and density of states, eight dynamical matrices were calculated on a $4\times4\times4$ q-point mesh. The dynamic matrices at arbitrary wave vectors were evaluated using Fourier deconvolution on this mesh.

3. Results

The theoretical equilibrium lattice constant is determined by fitting the total energy as a function of the volume to the Murnagan equation of states [14]. The calculated lattice constants a, bulk modulus, and the pressure derivative of the bulk modulus, dB/dP, for ZrRu and ZrZn alloys are presented in Table 1 along with the available experimental and other theoretical values

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Table 1
Calculated lattice constants (Å), bulk modulus (in Mbar), and pressure derivative of the bulk modulus dB/dP for ZrRu and ZrZn in B2 structure.

Materials	Reference	a	B	dB/dP
ZrRu	This work	3.262	1.813	3.91
	LAPW(LDA) [16]	3.22	2.28	3.6
	LAPW(GGA) [3]	3.22	–	–
	Theory [4]	3.241	1.10	–
	Exp. [4]	3.25	–	–
ZrZn	This work	3.336	1.010	4.11
	Theory(GGA) [11]	3.34	–	–
	Theory(LDA) [11]	3.267	–	–
	Theory [2]	3.336	–	–
	Exp. [17]	3.336	–	–

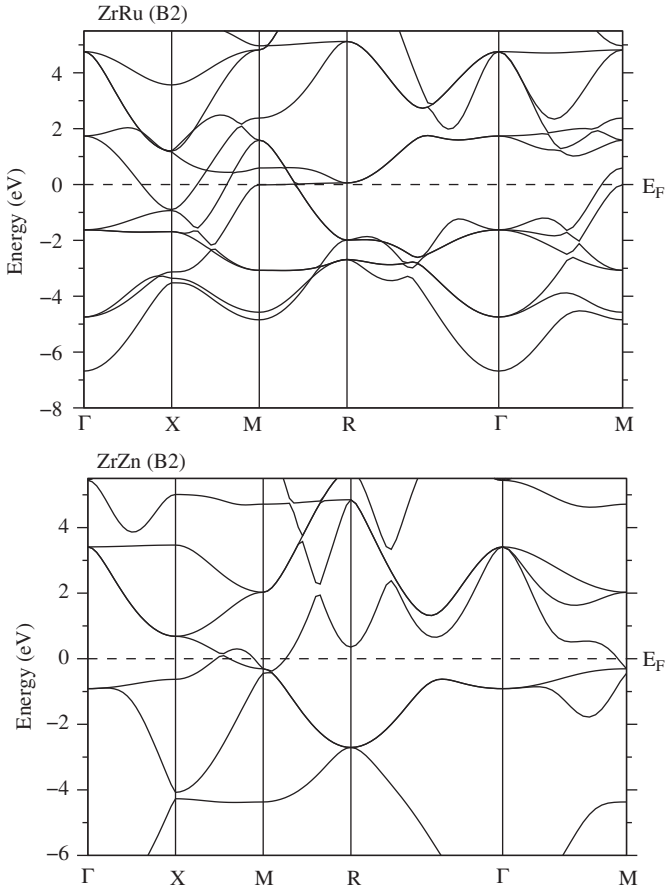

Fig. 1. Calculated electronic band structure for ZrRu and ZrZn in the B2 phase.

[2–4,11,15,16]. The calculated lattice constant for ZrRu is about 1% higher than the experimental value, yet this result is a usual feature of GGA calculations. There is no experimental or theoretical data reported for the bulk modulus of ZrZn while there are few available theoretical values for the bulk modulus of ZrRu. For the B2 structure of ZrRu, the calculated bulk modulus in the present study is less than theoretical value by about 25%. The calculated electronic structures for ZrRu and ZrZn in the B2 structure along high-symmetry directions that Fermi level as the energy zero are given in Fig. 1. The calculated electronic structures clearly show the metallic nature of both of the materials since the energy bands cross the Fermi level. The overall band profile of ZrRu is in agreement with the earlier work [10]. The total and partial DOS for ZrRu and ZrZn are plotted in Fig. 2. The density of states for ZrRu presents three peaks below the Fermi level. The energy values of these peaks are −3.71, −2.88 and −1.88 eV. All of them are mainly dominated by the Zr 4d and Ru 4d states with smaller contributions from the others states of Zr and Ru atoms. The density of states at the Fermi level is mainly determined by the Zr 4d and Ru 4d states. On the other hand, for ZrZn, the total DOS contains three peaks below the Fermi level, with −4.39, −1.7 and −0.6 eV. The characters of these peaks are dominated by Zr 4d states with smaller contributions from the Zr 5s and 5p states as well as the Zn 3d and 4s states. The density of states at Fermi level mainly come from the Zr 4d states. The phonon-dispersion curves and the density of states curves for ZrRu and ZrZn along several high-symmetry lines in the BZ are plotted in Fig. 3. The phonon properties of ZrRu and ZrZn were calculated within generalized gradient approximation in the CsCl(B2) structure with the space group symmetry Pm3m(2 2 1) in which the Zr atom is positioned at (0,0,0) and the Ru (Zn) at (0.5,0.5,0.5). In these materials, there are two atoms per primitive cubic unit cell. For both of the materials, the cesium chloride structure is dynamically stable since throughout the BZ all phonon frequencies are positive. There is no observed gap between the acoustic and optical branches in the phonon spectrum due to a small difference between the atoms of Zr and Ru (Zn). The sharp peaks at 5.15 and 4.26 THz in the phonon density of states for ZrRu and ZrZn are observed due to the longitudinal acoustic (LA), the transverse acoustic (TA) and the transverse optic (TO) phonon modes in all the directions. The optical phonon modes at the Zone centre of ZrRu and ZrZn were calculated to be 5.53 and 5.17 THz, respectively. We have compared our results of the phonon density of states of ZrZn with available theoretical result of Arroyave et al. and found a strong consistency among the studies.

4. Conclusions

In this research, using an *ab initio* pseudopotential method within a GGA of the density functional theory, the structural, electronic and dynamic properties of ZrRu and ZrZn in the B2 (CsCl) structure have been calculated. The structural properties including lattice constant, bulk modulus and first-order pressure derivative of bulk modulus were calculated. The calculated equilibrium lattice constant of ZrRu and ZrZn was compared with previous theoretical and available experimental results. The calculated electronic structures clearly show the metallic nature of both materials. The main contributions to the density of states at Fermi level come from the Zr 4d and Ru 4d states for ZrRu and the Zr 4d states for ZrZn. Moreover, the phonon spectrum and density of states in B2 phase have also been calculated using the density function perturbation method. There is no observed gap

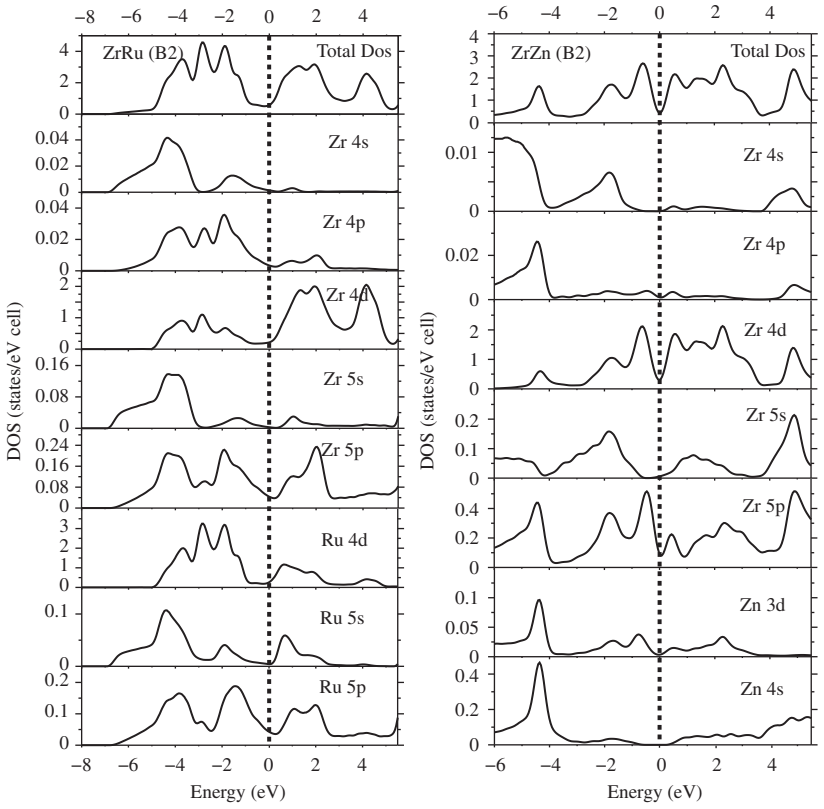

Fig. 2. Calculated partial and total DOS for ZrRu and ZrZn in the B2 phase along several lines of high symmetry in the Brillouin zone.

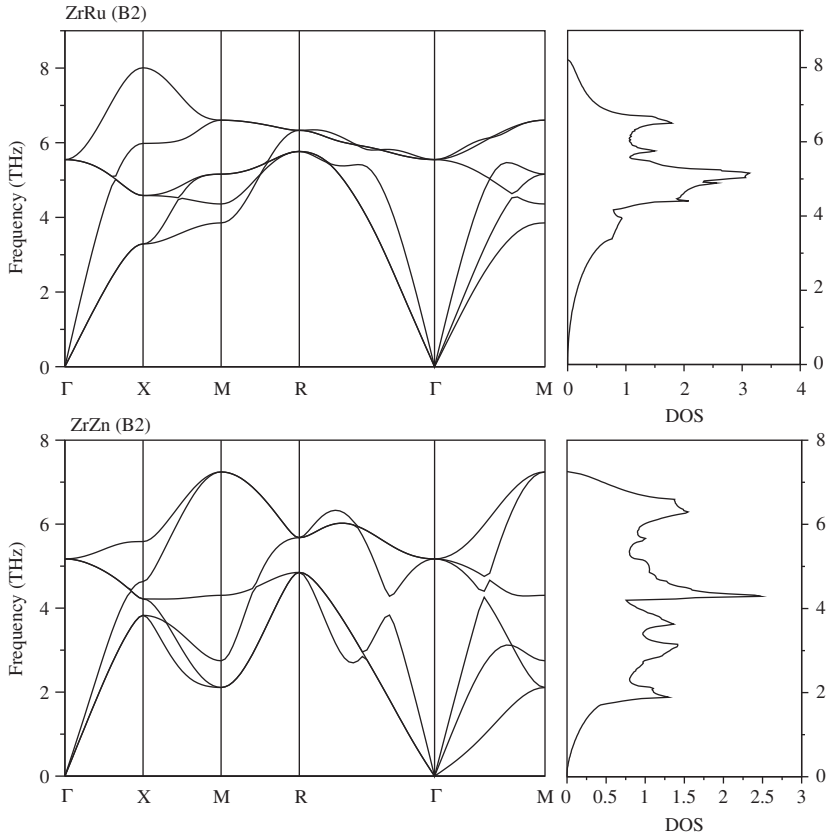

Fig. 3. Calculated phonon-dispersion curves and phonon densities of states for ZrRu and ZrZn in the B2 phase along several lines of high symmetry in the Brillouin zone.

between the acoustic and optical branches in the phonon spectrum due to a small difference between the atoms of Zr and Ru (Zn). The current phonon calculations of ZrRu and ZrZn will certainly be very useful for the interpretations of future experiments.

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