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First-principles structural, electronic and vibrational properties of zinc-blende zirconium carbide

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ABSTRACT

We have systematically studied the structural, elastic, electronic, dynamical and thermodynamical properties of zirconium carbide in zinc blende (ZB) phase using ab-initio calculations based on density-functional theory. The calculated structural parameters, such as the lattice constant, bulk modulus and elastic constants, are in good agreement with available theoretical data. The calculated bulk modulus and shear modulus show that ZB-ZrC is softer than RS-ZrC. Further, the anisotropic factor, Poisson's ratio, and Young's modulus are also calculated and discussed. ZB-ZrC is anisotropic. Electronic band structure indicates narrow bandgap semiconducting nature of ZrC in ZB phase. In the phonon dispersion curves of ZB-ZrC all phonon frequencies are positive and hence indicate that the compound is dynamically stable. Temperature variations of thermodynamical functions such as free energy, internal energy, entropy and lattice specific heat at constant volume are also calculated and discussed. The elastic and dynamical stability is independent of pseudo-potentials.

1. Introduction

Zirconium carbide (ZrC) is important for basic research and several technological applications such as cutting tools, high temperature and thermal protection material due to its unusual macroscopic property arising from three different types of binding mechanism. ZrC possesses promising characteristics such as high stiffness, high hardness, high thermal conductivity and high melting temperature. These properties are responsible for making zirconium carbide an ultra-hard and high thermal protection material [1–3]. The NaCl (B1) type structured compound is very common in alkali halides, alkaline-earth metal oxides and transition metal compounds. The tracks along the B1 → B2 (CsCl-type) phase transition under pressure were widely reported [4–6]. Recently, the transition metal zirconium carbide has been synthesized rock salt (RS) structure and found to be non-stoichiometric owing to carbon-vacancy defects, which has been followed by several theoretical studies [2]. Grossman et al. [7] reported experiments on ZrC for the high temperature thermo-physical properties. Using full-potential linearzied augmented plane waves Stampfl et al. [8] investigated the electronic structure and physical properties of early transition metal nitrides in B1 structure. A series of investigations for RS and CsCl phases of ZrC have been carried out mainly focusing on the electronic, structural and lattice dynamical properties at ambient condition but there is no understanding of its non-stoichiometric structure and probable stable phases of ZrC. Recently, we have performed a first principles study of compression, structural, elastic, electronic and vibrational properties of rock salt and high pressure CsCl phases of ZrC to understand the mechanism of pressure induced phase transitions and superconductivity [4]. However, ZrC in another cubic phase, zinc blende (B3), has not been studied systematically. Since, fabrication of ZrC is still at an early stage and so far only rock salt-ZrC [9] is reported, ab-initio calculations for zinc blende ZrC would provide some insight and act as a possible guide for future experimental work on ZrC. Recently Korir et al. [6] have studied the structural properties of ZrC in RS phase and pointed out that RS-ZrC should be much more favorable in energy and should possess excellent mechanical and dynamical properties. In this study, we report on the first principles investigation of structural, mechanical and dynamical properties of zirconium carbide in zinc blende phase. To, fulfill the goal; we have used not only the static calculations but also the lattice dynamical calculations. The stability of the phase will be discussed in the light of both structural and dynamical properties. We find that the ZrC in zinc blende phase is stable structurally, mechanically and dynamically. As a result the frequency of all phonon modes in phonon dispersion curves is positive at ambient condition as in RS phase and unlike CsCl phase [4]. The paper is organized as follows: the method of the calculation is given in Section 2, followed by discussion of the

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simulation results on structural, electronic, mechanical and dynamical properties of ZB-ZrC in Section 3. Finally, the conclusion is present in Section 4.

2. Computational details

In the present study we have used implementation of plane wave density functional theory (DFT) in the Kohn–Sham framework using ABINIT simulation package [10–12]. The wave functions describe only the valence and the conduction electrons, while the core electrons are taken into account through pseudo-potentials. For the exchange correlation functional we have employed the generalized gradient application (GGA) functional developed by Perdew, Burke and Ernzerhof (PBE) [13] and local density application (LDA) functional developed by Teter Pade parameterization [12]. The electron–ion interaction is described through the use of Troullier–Martin type pseudo-potentials.

Before starting the work on ground state and linear response calculations [11,12], a set of convergence tests have been performed in order to choose correctly the mesh of k-points and the cutoff kinetic energy of plane waves. The kinetic energy cutoff for the plane wave basis is set to 60 Ha for both pseudo-potentials. The Brillion zone is sampled by $6 \times 6 \times 6$ and $4 \times 4 \times 4$ Monkhorst–Pack mesh [14] of k-points for GGA and LDA calculations respectively. The convergence test proves that the BZ sampling and the kinetic energy cutoff are sufficient to guarantee an excellent convergence. Phonon frequencies are subsequently obtained using the linear response approach based on the density functional perturbation theory (DFPT) [12]. The expression is obtained from the second derivatives of the total energy with respect to the phonon displacement of atoms or an external electric field.

3. Results and discussion

The total energies and pressures have been calculated as a function of the primitive cell volume for ZB-ZrC used to determine the structural, mechanical and other properties. The structure of zinc-blende phase of ZrC is optimized at the pressure of 0 GPa. Fig. 1 shows the total energy versus volume of the ZrC in zinc blende structure for two different pseudo-potential schemes. However, the total energy calculated for ZB, RS and CsCl phases suggests that the total energy of ZrC is minimum in RS phase, which suggests that the RS-ZrC is energetically more favorable. Table 1 lists the lattice constant and mechanical properties of ZB-ZrC. Table 1 also lists other theoretical data, available only for lattice constant and bulk modulus. The structural and mechanical properties of ZB structure of ZrC are scarce in literature [6–8]. Since there are no experimental or other theoretical data on other mechanical properties of ZB, we could not compare them. We believe that the values are consistent as they have been derived from lattice constant obtained from optimized structure. Further, the study through lattice constant is successful in predicting the dynamical stabilities along with the electronic properties for ZrC in zinc blende phase seen in what follows.

The cubic crystals have three independent elastic constants, called C_{11}, C_{12} and C_{44}, which have been calculated to investigate the mechanical stability of ZrC in the B3 crystal structure. For a cubic crystal, the bulk modulus is defined as $B = C_{11} + C_{12}/3$. Similarly, the relationship between C_{11} and C_{12}, called as tetragonal shear (C') constant where $C' = C_{11} - C_{12}/2$, can be obtained by applying the volume conserving tetragonal strains and can be written as

$$\varepsilon = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \frac{-\delta^2 - 2\delta}{(1+\delta)^2} \end{pmatrix} \tag{1}$$

where δ is the deformation parameter. The elastic constants of ZB-ZrC calculated using the density functional perturbation theory are presented in Table 1. The calculated elastic constants of ZrC in ZB phase satisfy the mechanical stability criteria for a (cubic) structure [15,16] at ambient conditions. They are

$$C_{11} + 2C_{12} > 0, \ \ C_{44} > 0, \ \ \text{and} \ \ C_{11} - C_{12} > 0 \tag{2}$$

i.e. bulk B, shear G and tetragonal shear moduli $C' = C_{11} - C_{12}/2$ are positive. The lower value of bulk modulus and elastic constants using GGA than those of LDA can be attributed to the underestimation of cohesive energy in the case of GGA. The bulk modulus for ZB-ZrC is lower than its counterpart for rock salt and CsCl phases [4]. This can be understood from the density of states near Fermi level and will be discussed later along with the electronic band structure and DOS. However, the agreement between present and other theoretical data on bulk modulus is better in the case of GGA than that of LDA. It is also noticed that the C_{11} is close to C_{12} while C_{44} is lower. This indicates that the velocity of a longitudinal wave in the [1 0 0] direction is much larger than the shear wave as C_{44} is almost half of C_{11}. The Zener anisotropy factor (A), Poisson's ratio (υ), Young's modulus (Y), shear modulus (C') and polycrystalline shear modulus (G) of zirconium carbide (ZrC) in zinc blende structure, which are useful elastic properties for any applications, particularly for its hardness, have also been investigated.

The calculated Zener anisotropic factor A, Poisson's ratio υ, Young's modulus Y, polycrystalline and tetragonal shears modulus

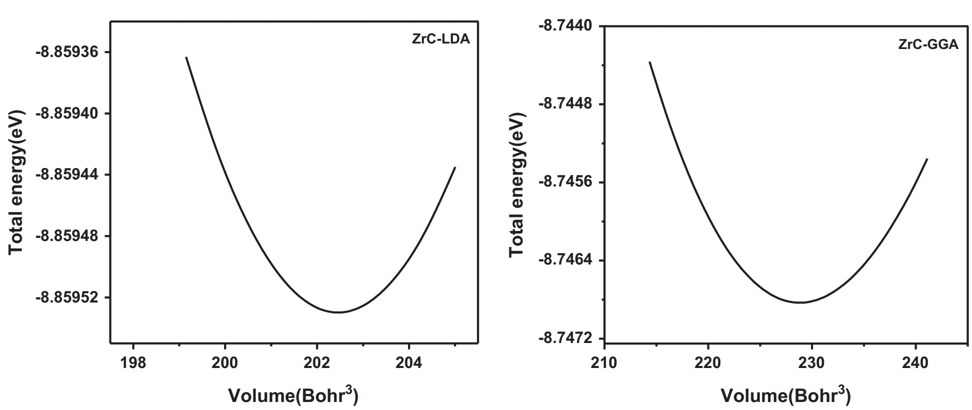

Fig. 1. Determines the equilibrium lattice constant from minima of ground state total energy for ZrC of ZB phase from GGA and LDA.