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Ab initio investigation of surface phonons on the (0 0 1) surface of ZrC

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ABSTRACT

We presented an *ab initio* pseudopotential study within the generalized gradient density functional approximation of the structural and electronic properties of the ZrC(0 0 1) surface. The calculated structural parameters for the ZrC(0 0 1) surface accord very well with previous experimental findings. The ZrC(0 0 1) surface is metallic, because at least one surface state crosses the Fermi level in the gap region of the projected electronic spectrum. Using our atomic and electronic structures, surface phonon dispersion curves are calculated by employing a linear response approach on the density functional perturbation theory. The calculated phonon spectrum compares very well with the experimental data. The atomic displacement patterns of the zone-center and zone-edge phonon modes are presented and analyzed for the ZrC(0 0 1) surface, carefully. Using this analyzation, energy locations and polarization characteristics of Love, Wallis, Lucas, and Fuchs–Kliewer modes have been determined.

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1. Introduction

Transition metal carbides are of large interest because of their amazing physical and chemical properties, which come from the mixing of covalent, ionic, and metal bonding [1]. Thus, they show unique combination of the properties displayed by covalent solids, ionic crystals, and transition metals. One such compound, ZrC, possesses high temperature oxidation resistance, high strength, high hardness, good thermal conductivity and toughness. Moreover, the mixture of zirconium carbide and tantalum carbide is an important cermet material. Thus, several experimental works have been carried out on the structural, electronic and vibrational properties of ZrC [2–5]. On the theoretical side, these properties of ZrC have been investigated using the density functional theory within the local density approximation [6–8] and generalized gradient approximation [7,9–13]. In addition to the bulk properties of the transition metal carbides, their surface properties should be studied because of their use as catalytic materials for the hydrogenation of benzene, ethylene, and carbon monoxide, decomposition of methanol. It is therefore of great interest to investigate the structural properties of ZrC(0 0 1) surface. On the experimental side, the atomic geometry of this surface has been obtained by using low-energy electron diffraction (LEED) technique [14]. This experimental study indicates the primitive (1×1) structure but a marked rippling relaxation of the surface layer. The first-principles molecular dynamics method (FPMD) [15] has been used to obtain the structural and electronic properties of ZrC(0 0 1). Vines et al. [9] have presented the structural and electronic properties of this surface using the generalized gradient approximation of the density functional scheme.

In addition to the structural and electronic properties of ZrC (0 0 1), phonon properties of this surface must be studied because surface vibrations are involved in may processes on surfaces at ambient as well as elevated temperatures, such as surface diffusion, phase transitions on clean and adsorbate-covered surfaces, and desorption processes. Phonon modes on this surface have been measured by the electron energy loss spectroscopy (EELS) [16]. The screened shell model [16] was used to calculate phonon dispersion curves for the ZrC(0 0 1) surface. However, surface atomic relaxation was not considered in this theoretical work [16]. Recently, we have investigated the vibrational properties of the (0 0 1) surfaces of TiC, HfC, NbC and TaC using the *ab initio* pseudopotential method [17–19]. The calculated results for all these surfaces accord very well with experimental data. The success of our calculations can be linked to a more rigorous treatment of the surface force constants and effective charges in the *ab initio* calculations. To best of our knowledge, the *ab initio* pseudopotential method has not been applied to calculate the phonon spectra and density of states for the ZrC(0 0 1) surface.

The goal of this work is to investigate structural, electronic, and phonon properties of the ZrC(0 0 1) surface by employing the plane-wave pseudopotential method, density functional theory, and a linear response technique. We provide a comparison of our calculated structural parameters with the results obtained from LEED study [14] and previous *ab initio* calculations [9]. The surface electronic states on this surface are identified by comparing the

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surface electronic and projected bulk electronic spectrum. The agreement between our experimental phonon spectra [16] is satisfactory. Finally, we have presented the energy locations and polarization characteristic of several interesting phonon modes such as Love, Wallis, Lucas and Fuchs–Kliewer [19].

2. Methods

Our calculations are made using the plane-wave pseudopotential approach within the framework of the density functional theory [20]. Electronic exchange and correlation energies are taken into account within the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof method [21]. To describe the electron–ion interaction we have used the Vanderbilt ultrasoft pseudopotentials [22]. The electronic wave functions are expanded in plane waves up to a maximal cutoff energy of 60 Ry. Self-consistent solutions to the Kohn–Sham equations were obtained by employing a set of sixty special **k** points. In our calculations, once the lattice parameter was determined, a model for the (0 0 1) surface has been constructed using a slab model approach. In this approach one uses a unit cell which is repeated periodically in two dimensions while it has a finite extent in the third one. In order to use the plane-wave basis set which is periodic in nature the corresponding slab is repeated in the third direction with slab separated by a sufficiently wide vacuum region. Our supercell was considered to contain 26 atoms located in a slab of 13 atomic layers and a vacuum region along the surface normal equivalent of five atomic layers. For the **k**-point sampling, twenty-eight special points have been used in the irreducible part of the surface Brillouin zone. The equilibrium positions of atoms in the unit cell are calculated by minimizing the total energy with the help of the Hellmann–Feynman forces, starting the atomic relaxation from the ideal positions derived from the symmetry of the bulk. Each atom is allowed to move with exception of the central-layer atoms. The equilibrium positions are determined with numerical uncertainty of less than 0.01 Å when all forces are smaller than 0.1 mRy/au.

Surface phonons on the ZrC(0 0 1) surface have been studied by means of the density-functional perturbation theory of Baroni et al. [23]. Within this approach, second derivatives of the total energy were calculated to obtain dynamical matrix. The response of the electrons is calculated iteratively, until self-consistency is achieved between the variation in the charge density and the screened perturbing potential. We have calculated six dynamical matrices corresponding to a $4\times4\times1$ **q**-point mesh within irreducible segment of the surface Brillouin zone. Then, two dimensional

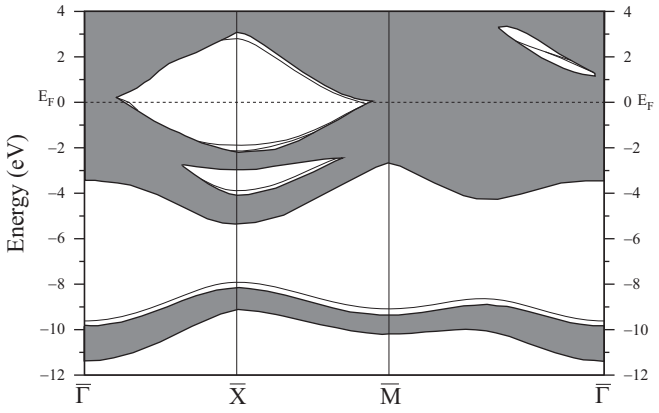

Fig. 2. The electronic states on the ZrC(0 0 1)(1 × 1) surface. Projected bulk spectrum is shown as hatched regions.

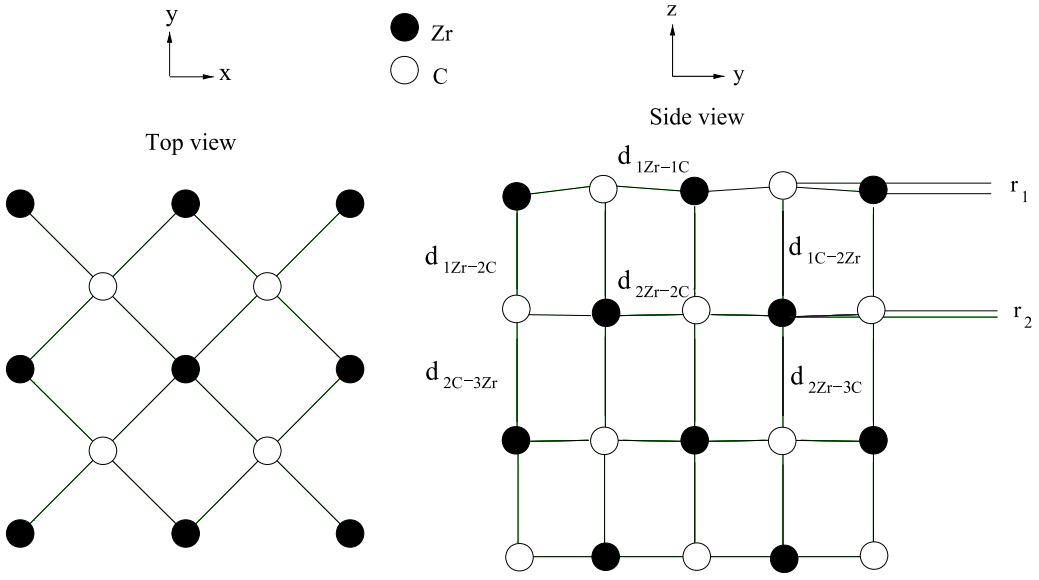

Fig. 1. Schematic illustration of relaxed side and top views of the ZrC(0 0 1)(1 × 1) surface. *r* and *d* values indicate the vertical buckling of top two layers and the bond lengths, respectively.

Table 1
Vertical buckling of top two layers (r_1 and r_2) and the calculated bond lengths (d_{Zr-C}), compared with previous experimental and theoretical results. Units: Å.

Source	r_1	r_2	d_{1Zr-1C}	d_{2Zr-2C}	d_{1Zr-2C}	d_{1C-2Zr}	d_{2Zr-3C}	d_{2C-3Zr}
This work	0.081	0.042	2.356	2.355	2.243	2.365	2.323	2.382
LEED [14]	0.13 ± 0.07	0.11 ± 0.07	–	–	2.20	2.43	2.28	2.39
ab initio [9]	0.09	0.05	–	–	2.26	2.39	2.34	2.40

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