

Ab Initio Study of Zirconium(IV) Chloride

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INTRODUCTION

Zirconium halides are of crucial importance in numerous research fields and industrial applications such as unconventional catalysis [1], refining of Zr-containing ores by Kroll reduction [2], chemical vapor deposition (CVD) [3], or nuclear engineering [4-6]. For example, chlorination has been proposed for large-scale separation and selective recovery of Zr, as $ZrCl_4$, from U-Zr alloys or used nuclear fuel cladding [4, 5]. In addition, ZrX_4 (X=Br, Cl) is utilized in the preparation of CVD zirconium carbide layers of tristructural-isotropic (TRISO) nuclear fuel micro-particles [6]. Although an accurate knowledge of the properties of zirconium halides is key to optimizing process conditions for the aforementioned applications, recent and accurate thermomechanical information for Zr halides remains scarce [3]. In particular, for crystalline $ZrCl_4$ the low-temperature calorimetric measurements by Todd [7] and Efimov et al. [8], in the temperature ranges 52 – 296 K and 9 – 315 K, are still used as references [3]. In addition, no comprehensive computational studies of the thermomechanical properties of $ZrCl_4$ (cr) have been reported, to the best of our knowledge. Here, we report computational studies of the structural, lattice dynamics, and thermomechanical properties of bulk monoclinic $ZrCl_4$ using the zero-damping dispersion-corrected density functional theory [DFT-D3(zero)], the quasi-harmonic approximation (QHA).

Total-energy calculations were carried out using Grimme's dispersion-corrected DFT (DFT-D3)[9], as implemented in the Vienna *ab initio* simulation package (VASP) [10]. The exchange-correlation energy was computed using the generalized gradient approximation (GGA), with the parameterization of Perdew, Burke, and Ernzerhof (PBE) [11]. Previous first-principles studies demonstrated that standard functionals, such as PBE, correctly reproduce the structure-properties relationship of bulk zirconium and Zr alloys, as well as transition-metal chloride compounds [12-15].

The projector augmented wave (PAW) method [16,17] was utilized to model the interaction between valence electrons and ionic cores. PAW pseudopotentials were used to represent the remaining core electrons together with the nuclei. The Kohn-Sham (KS)

equations were solved using the blocked Davidson iterative matrix diagonalization scheme [18]. A plane-wave cutoff energy of 500 eV was chosen for the electronic wavefunctions, ensuring total-energy convergence to within 1 meV/atom. Partial occupancies of the wavefunctions were controlled using Gaussian smearing, with a Gaussian width of 0.1 eV. Simultaneous ionic and cell relaxations of $ZrCl_4$ were conducted, without symmetry constraints applied. The Hellmann-Feynman forces acting on atoms were calculated with a convergence tolerance set to 0.01 eV/Å. The Brillouin zone (BZ) was sampled using the Monkhorst-Pack k -point scheme [19] with a k -point mesh of $5 \times 5 \times 5$.

RESULTS

Initial structural optimization calculations with standard DFT-PBE for the bulk monoclinic $ZrCl_4$ unit cell (space group $P2_1/c$; IT No. 13; $Z = 2$) yielded lattice parameters of $a = 6.93$, $b = 8.16$ and $c = 6.35$ Å ($\alpha = \gamma = 90^\circ$, $\beta = 107.6^\circ$; $V = 342.0$ Å³), considerably larger than X-ray diffraction (XRD) measurements [20]. This stems from the lack of a correct description of cohesive van der Waals interactions resulting from dynamical correlations between fluctuating charge distributions in standard DFT. Therefore, Grimme's dispersion-corrected DFT (DFT-D3) was utilized in this study. Table 1 summarizes the calculated and experimental structural parameters.

Table I. The lattice parameters of bulk monoclinic $ZrCl_4$ calculated in the zero-temperature limit.

$ZrCl_4$ (P2/c)	DFT-PBE	XRD [20]	DFT-D3
a (Å)	6.39	6.361	6.38
b (Å)	8.16	7.407	7.49
c (Å)	6.35	6.256	6.25
β (°)	107.6	109.3	107.6
Volume(Å ³)	342	278.2	282.9

The lattice parameters of bulk monoclinic $ZrCl_4$ calculated in the zero-temperature limit are in excellent agreement with experimental values from XRD (X-ray diffraction) measurements [20] as shown in Table 1. The optimized $ZrCl_4$ unit-cell, featuring chains of edge-sharing coordination octahedra along the [001] direction, is depicted in Figure 1.

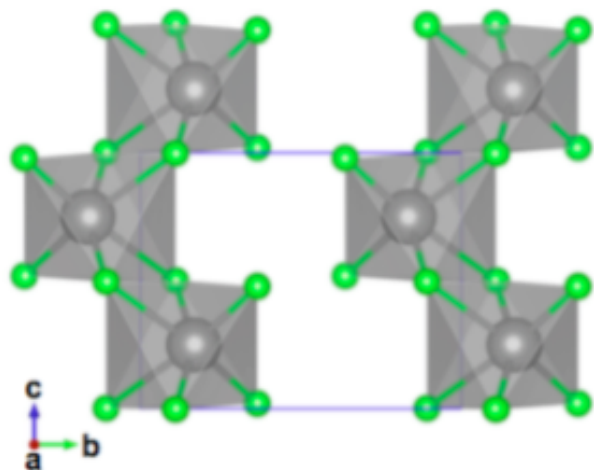


Fig. 1. Crystal structure of bulk $ZrCl_4$ (space group $P2_1/c$; IT No. 13; $Z = 2$) optimized with DFT-D3(zer). The unit cell is represented by solid blue lines. Color legend: Cl, green; Zr, grey.

The computed bond distances between Zr centers ($2e$ Wyckoff positions) and apical and bridge Cl ligands ($4g$ Wyckoff positions) are $d_{Zr-Cl_{apical}} = 2.33 \text{ \AA}$ and $d_{Zr-Cl_{bridge}} = 2.50, 2.69 \text{ \AA}$. These bond distances compare well with the XRD values of $d_{Zr-Cl_{apical}} = 2.307 \text{ \AA}$ and $d_{Zr-Cl_{bridge}} = 2.497, 2.656 \text{ \AA}$ [20]. The calculated (measured) Zr–Zr distance is 3.99 \AA (3.962 \AA), and the bond angles $\angle Cl_{apical}ZrCl_{apical}$ and $\angle Cl_{bridge}ZrCl_{bridge}$ are 100.9 and 79.6° (100.66 and 79.54°), respectively.

Phonon analysis was conducted using the finite-displacement method near equilibrium volume within the QHA in order to derive thermal properties of bulk $ZrCl_4$. A temperature effect was added to the calculated total energy $U(V)$ of the system through the phonon contribution. While the melting point of $ZrCl_4$ was reported as $710 \pm 1 \text{ K}$, a monoclinic to cubic phase transformation around $\approx 538 \text{ K}$ was discussed in previous studies [3]. Therefore, the present calculations for monoclinic $ZrCl_4(cr)$ are limited to temperatures below $\approx 550 \text{ K}$. The computed thermal evolutions of K_0 and K_0' using the Vinet equation of state [22]. The bulk modulus and its pressure derivative are predicted to vary from $K_0 = 8.7$ to 7.0 GPa and from $K_0' = 10.4$ to 8.9 GPa

between 0 and 550 K . Interestingly, both K_0 and K_0' do not decrease monotonically with temperature, but exhibit instead maxima in the vicinity of ≈ 20 and 80 K , respectively.

The isobaric molar heat capacity (C_p) and entropy (S) are calculated and compared with the available experimental data [27]. It is found that our calculated entropy, isochoric molar heat capacity, and isobaric molar heat capacity at standard pressure ($P = 1 \text{ bar}$) for bulk $ZrCl_4$ are in excellent agreement with low-temperature heat capacity measurements by Todd [7] and Efimov et al. [8]. The standard values calculated at $T = 298.15 \text{ K}$ in this study are $C_p^0 = 107.3 \text{ J/mol K}^{-1}$ and $S_p^0 = 162.1 \text{ J mol}^{-1} \text{ K}^{-1}$.

In Summary, DFT-D3(zer) calculations were conducted to investigate the lattice dynamics and thermo-mechanical properties of bulk monoclinic $ZrCl_4(cr)$. The isobaric molar heat capacity derived from phonon calculations within the quasi-harmonic approximation is in fair agreement with existing calorimetric data. New heat-capacity measurements for high-purity $ZrCl_4(cr)$ are desirable, especially above room temperature where calorimetric data are scarce.

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