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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 $P2/c$; IT No. 13; $Z = 2$) yielded lattice parameters of $a = 6.93$, $b = 8.16$ and $c = 6.35$ Å ($\alpha = \gamma = 90°$, $\beta = 107.6°$; $V = 342.0$ Å^3), 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 1 The lattice parameters of bulk monoclinic $ZrCl_4$ calculated in the zero-temperature limit.

$ZrCl_4$ (P2/c)	DFT-PBE (this work)	XRD [20]	DFT-D3 (this work)
a (Å)	6.39	6.361 ± 0.004	6.38
b (Å)	8.16	7.407 ± 0.004	7.49
c (Å)	6.35	6.256 ± 0.004	6.25

β (°)	107.6	109.3 ± 0.04	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.

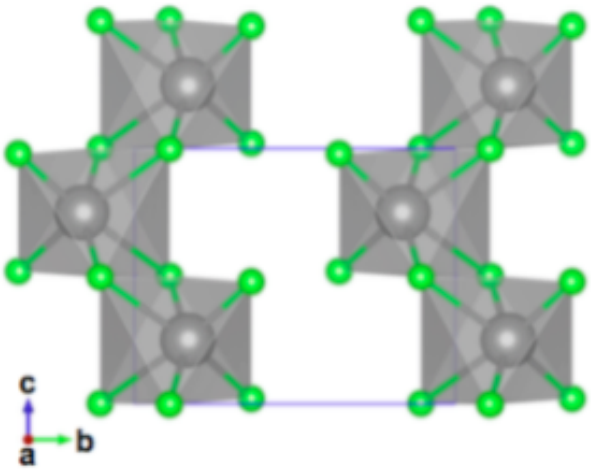

Figure 1 Crystal structure of bulk $ZrCl_4$ (space group P2/c; IT No. 13; Z = 2) optimized with DFT-D3(zero). The unit cell is represented by solid blue lines. Color legend: Cl, green; Zr, grey.

The computed bond distances between Zr centers (2*e* Wyckoff positions) and apical and bridge Cl ligands (4*g* Wyckoff positions) are dZr−Cl_{apical} = 2.33 Å and dZr−Cl_{bridge} = 2.50, 2.69 Å. These bond distances compare well with the XRD values of dZr−Cl_{apical} = 2.307 Å and dZr−Cl_{bridge} = 2.497, 2.656 Å [20]. The calculated (measured) Zr − Zr distance is 3.99 Å (3.962 Å), and the bond angles ∠Cl_{apical}ZrCl_{apical} and ∠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 ± 1 K, a monoclinic to cubic phase transformation around ≈ 538 K was discussed in previous studies [3]. Therefore, the present calculations for monoclinic $ZrCl_4$(cr) are limited to temperatures below ≈ 550 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 $K0$ and K' 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 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 K in this study are C_P^0=107.3 J/mol K^{-1} and S_P^0 = 162.1 J mol^{-1} K^{-1}.

In Summary, DFT-D3(zero) calculations were conducted to investigate the lattice dynamics and themo-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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