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First-Principles LCAO Calculations on 5d Transition Metal Oxides: Electronic and Phonon Properties

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ABSTRACT

First-principles quantum chemistry calculations within the periodic linear combination of atomic orbitals (LCAO) formalism have been used to probe electronic and phonon properties of crystalline 5d transition metal oxides ReO_3 , ZnWO_4 and CaWO_4 . The obtained equilibrium crystal structure is in good agreement with known crystallographic data. Rhenium trioxide is correctly predicted to be a metal, whereas both tungstates—a wide gap insulating compounds. The phonon frequencies, calculated by the frozen phonon method, agree rather well with those obtained by infrared and Raman spectroscopies.

Keywords: Quantum chemistry, crystal structure, electronic structure, phonons, oxides

INTRODUCTION

The investigation of electronic and phonon properties of crystals is an actual problem for the experimental data interpretation and prediction of their properties. Recent developments in quantum chemistry (QC) open new possibilities to address this problem [1]. Traditionally QC approach is applied to the instantaneous atomic configuration and is oriented on the evaluation of compound electronic properties (atomic charges, band structure, DOS, etc) and geometry optimization. However, QC methods allow not only evaluating the phonon

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Figure 1. Crystal structure of cubic ReO₃, monoclinic wolframite ZnWO₄ and tetragonal scheelite CaWO₄. (See Color Plate I)

related properties but also the detailed interpretation of infra-red and Raman spectroscopic data.

In this work, we applied QC approach to probe electronic and phonon properties of crystalline 5d transition metal oxides ReO_3 , $ZnWO_4$ and $CaWO_4$ (Fig. 1). The difference in the electronic and atomic structure of these oxides makes them very attractive for demonstration of modern QC possibilities.

Rhenium trioxide ReO₃ is known as a "covalent metal", having unusually high electrical conductivity, which is close to that of copper or silver. It has cubic perovskite-type structure (space group Pm3m) with rhenium ions being at the centres of [ReO₆] regular octahedra connected by corners (Fig. 1a). The metallic conductivity is caused by the Re⁶⁺(5d¹) delocalized 5d-electron. Due to the strong covalent bonding between rhenium and oxygen atoms the [ReO₆] octahedra are rather rigid that makes ReO₃ a good candidate to be a negative thermal expansion compound [2].

Tungstates $A^{2+}WO_4$ ($A^{2+} = Zn^{2+}(3d^{10}4s^2)$ or $Ca^{2+}(4s^2)$) are wide-gap insulating materials, which crystal structure depends on the A^{2+} cation size. ZnWO₄ [3] has monoclinic wolframite-type structure (space group *P2/c*) composed of distorted [WO₆] and [ZnO₆] octahedra (Fig. 1b), whereas CaWO₄ [4] has tetragonal scheelite-type structure (space group *I*4₁/a) composed of [WO₄] tetrahedra and [CaO₈] polyhedra (Fig. 1c). These materials are important for such technological applications as scintillators, self-activated phosphors, laser hosts, etc.

In this work, the first-principles periodic linear combination of atomic orbitals (LCAO) calculations allowed us to determine the equilibrium structure, band gap, bulk modulus, electronic band structure and density of states (DOS), phonon dispersion curves across the first Brillouin zone as well as infrared and Raman frequencies. The obtained results are compared with available experimental data.

CALCULATION DETAILS

First-principles periodic LCAO calculations were performed using the CRYS-TAL06 code [5]. We used the Hay-Wadt (HW) effective small core potentials (ECP) and the corresponding atomic basis sets for metal atoms (Re,W,Zn,Ca), excluding diffuse Gaussian type orbitals. The all-electron basis set was used for oxygen atoms. Hybrid Hartree-Fock-DFT Hamiltonians (B3PW and PBE0) were used in the self-consistent field (SCF) calculations of rhenium trioxide and tungstates, respectively. The details of the geometry optimization and electronic structure calculations can be found in [6]. The values of calculated structural parameters are given in Table 1. The magnitudes Δ of the differences between theoretical and experimental values are given in Å for lattice parameters (*a*,*b*,*c*) and atoms fractional coordinates (*x*,*y*,*z*) or in degrees (°) for the angle β between *a* and *c* axes in ZnWO₄.

The ab initio calculations of phonon frequencies were performed by the *direct (frozen phonon) method* [7]. In the "frozen-phonon" approach [8] the phonon energy is determined as the difference in the energies of the distorted and equilibrium crystalline lattices for a particular atom displacement. The values of the phonon frequencies were calculated at the Brillouin zone center (BZC) in ZnWO₄ and CaWO₄, whereas these frequencies were obtained for several high-symmetry Brillouin zone points in ReO₃, performing calculations for the supercells consisting of 8 and 16 primitive cells. In ReO₃ the calculated for the symmetry points of BZ frequencies were interpolated over the symmetry directions using fropho code by A.Togo [9]. Fig. 2b demonstrates the convergence of the calculated phonon dispersion curves with the supercell size increasing.

RESULTS AND DISCUSSION

The values of the calculated and experimental equilibrium structure parameters are compared in Table 1. In the simple cubic ReO₃ only one lattice parameter (*a*) is required to describe the structure, and the agreement between its theoretical and experimental (at T = 2 K [2]) values is better than 0.01 Å. In more complicated tetragonal CaWO₄ the five parameters (*a*, *c*, *x*, *y*, *z*) are required to describe the structure: their values agree within about 0.04 Å with the experimental ones [3], obtained at room temperature (RT). Finally, the crystal lattice of monoclinic ZnWO₄ is determined by 12 structural parameters. Here the agreement between our theory and experiment at T = 12 K [4] is better then 0.01 Å for the lattice parameters, 0.2° for the cell angle and better than 0.07 Å for atomic positions within the unit cell. These results clearly demonstrate the capabilities of modern quantum chemistry in predicting the structure of crystalline materials: the accuracy of ab initio QC results approaches to the

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		ReO_3			$CaWO_4$			$\mathrm{ZnWO_4}$	
	LCAO B3PW	Exper. [2] $T = 2 K$	م (Å)	LCAO PBE0	Exper. [3] $T = RT$	م (Å)	LCAO PBE0	Exper. [4] T = 12 K	$\Delta (\mathrm{\AA,^{\circ}})$
a (Å)	3.7424	3.7477	0.0053	5.266	5.2429	0.023	4.684	4.6826	0.0014
b (Å)							5.709	5.7088	0.0002
c (Å)				11.41	11.3737	0.0363	4.930	4.9233	0.0073
(\circ) β							90.70	90.541	0.159
Zn(Ca) (y)							0.677	0.6812	0.023
W (y)							0.181	0.1814	0.000
O ₁ (x)				0.150	0.1507	0.0007	0.215	0.23	0.070
O ₁ (y)				0.009	0.0086	0.0004	0.895	0.8848	0.060
O ₁ (z)				0.210	0.2106	0.0006	0.437	0.43	0.037
O ₂ (x)							0.256	0.269	0.060
O ₂ (y)							0.375	0.3796	0.025
O ₂ (z)							0.402	0.406	0.018

Calculated and experimental values of structural parameters and their difference (Δ) for cubic ReO₃, monoclinic ZnWO₄ and tetragonal CaWO₄. Table 1



Figure 2. (a) Electronic band structure and density of states (DOS) for ReO_3 . (b) Phonon dispersion curves for ReO_3 calculated (LCAO, B3PW) by the frozen-phonon method for 8 and 16 supercells. (c) A comparison of experimental Raman spectrum from [20] and calculated total phonon density of states.

accuracy of experimental structural techniques as diffraction and x-ray absorption spectroscopy.

The electronic band structures for rhenium trioxide and tungstates are reported in Figures 2a and 3, respectively. Our calculation correctly predicts that ReO₃ is metallic: the Fermi level is located about 2.3 eV above the bottom of the conduction band, composed mostly of the Re 5d states. The upper part of the valence band in ReO₃ is mainly due to the O 2p states, mixed with the Re 5d states. The partially covalent character of the Re-O bonds is supported by atomic charges q(Re) = +2.70e and q(O) = -0.90e, obtained from the Mulliken population analysis.

Both CaWO₄ and ZnWO₄ are insulators having direct band gap E_g equal to 6.5 eV and 5.4 eV, respectively. These values are slightly larger than the experimental ones (5.2 eV in CaWO₄ [10]; 4.6 [11] and 4.9 [12] in ZnWO₄). For comparison, the band gap values of 4.09 eV [13] and 5.27 eV [14] were found for CaWO₄ by the linear augmented-plane-wave (LAPW) and the LCAO with B3LYP Hamiltonian methods, respectively, whereas the value of $E_g = 2.63$ eV was determined for ZnWO₄ from cluster-type DV-X α calculations [12].



Figure 3. Electronic band structure for (a) CaWO₄ and (b) ZnWO₄. The zero energy (E = 0 eV) corresponds to the top of the valence band.

The origin of valence and conduction bands in both tungstates is similar. The valence band is mostly composed of the O 2p states, mixed with W 5d states, whereas the conduction band is mainly due to W 5d states. In ZnWO₄ there is additionally a narrow band at about -9 eV below the Fermi level originating from the Zn 3d states. The knowledge of the bands origin allows one to correlate their widths with the values of interatomic distances. An increase of the widths of both conduction and valence bands from CaWO₄ to ZnWO₄ is caused by a decrease of the interatomic distances from *R*(W-W) = 3.867 Å and *R*(O-O) = 2.984 Å in CaWO₄ [3] to *R*(W-W) = 3.229 Å and *R*(O-O) = 2.451 Å in ZnWO₄ [4]. Finally, the atomic charges were obtained from Mulliken population analysis: q(Ca) = +1.75e, q(W) = +2.89e, q(O) = -1.16e in CaWO₄; q(Zn) = +1.54e, q(W) = +2.76e, q(O1) = -1.13e and q(O2) = -1.02e in ZnWO₄. The atomic charge values suggest a partially covalent W-O bonding.

The isotropic bulk modules B_0 were calculated by varying the lattice constant and fitting the dependence E(V) of a crystal total energy on its volume by a third-order Birch-Murnaghan equation of state. The obtained value for ReO₃ $B_0 = 278$ GPa is in agreement with the experimental one $B_0 = 210.8$ GPa [15] and other theoretical values from [16] evaluated using the full-potential linear muffin-tin orbital (FP-LMTO) $B_0 = 304$ GPa, Hartree-Fock (HF) B_0 = 282 GPa and HF+correlation $B_0 = 320$ GPa methods. The bulk modulus value $B_0 = 87$ GPa for CaWO₄ is also in good agreement with those found experimentally ($B_0 = 74$ GPa [17]) and obtained theoretically by ab initio



Figure 4. Experimental infrared (left column) and Raman (right column) spectra in polycrystalline CaWO₄ and ZnWO₄. The position of the LCAO calculated bands are shown by vertical lines. (See Color Plate II)

pseudopotential plane-wave (PW) theory ($B_0 = 72$ GPa [17], 74 GPa [18]). Finally, our bulk modulus $B_0 = 257$ GPa for ZnWO₄ overestimates the value $B_0 = 140$ GPa obtained theoretically in [19] by the PW theory. Unfortunately, no experimental value of B_0 is available for ZnWO₄ to the best of our knowledge.

Next we discuss the results of phonon calculations (Figures 2b,c and 4). The phonon dispersion curves for ReO₃ were calculated using hybrid Hartree-Fock-DFT Hamiltonian (B3PW) within the frozen-phonon scheme for 8 and 16 supercells to check the convergence. Here one expects 12 phonon modes. According to factor group analysis at the BZC (Γ -point), one T_{1u} mode is an acoustic mode, two T_{1u} modes are infrared (IR) active *odd* (u) optic modes, and one T_{2u} mode is a 'silent' mode. These modes are shown in Fig. 2b, including the LO-TO splitting. One should note that there is a gap of about 200 cm⁻¹ in the phonon density of states (PDOS) separating the upper three optical modes from the other ones.

The absence of *even* (g) modes Γ -point suggests that no Raman active modes are expected in perfect cubic ReO₃. However, the experimental Raman signal was observed in [20] from a single-crystal, polycrystalline powder and thin film ReO₃ and associated with the defect-induced Raman scattering. Due

to the metallic conductivity of ReO_3 the thickness of the sub-surface region probed by the laser is limited. In [20] it was estimated that the scattering occurs within the confined skin layer of 10–20 nm. According to the theory of Raman scattering in nanosystems [21], the phonon confinement should induce the Raman selection rule breaking causing the modes from the whole Brillouin zone contribute into the Raman signal. In Fig. 2c we compare calculated total PDOS and the Raman spectrum from [20]. The similarity between the shape of the PDOS and the experimental signal supports our interpretation within the framework of the phonon confinement model.

For tungstates CaWO₄ and ZnWO₄ the phonon calculations were limited to the BZC (Γ -point). At the Γ point a group theoretical analysis predicts 26 lattice modes for the tetragonal CaWO₄ [22]: $3A_g + 5A_u + 5B_g + 3B_u + 5E_g$ + $5E_u$ from which the 13 even (g) modes ($3A_g + 5B_g + 5E_g$) being Raman active, the 10 odd (u) modes ($5A_u + 5E_u$) being IR active and thee odd modes ($3B_u$) are silent. For the wolframite ZnWO₄ there are 36 lattice modes [23,24]: $8A_g + 10B_g + 8A_u + 10B_u$, with the 18 even (g) vibrations being Raman active modes, and 18 odd (u) vibrations being IR active. The calculated frequencies were indexed as infrared and Raman active modes, which are compared with experimental signals in Fig. 4. Note that the intensity of infrared active modes was also calculated. Both infrared and Raman phonon bands are qualitatively well reproduced, but the quantitative agreement is better for infrared signals. In Raman spectra the theory tends to overestimate the phonon frequencies, especially, at high energies. However, the largest observed difference is below 50 cm⁻¹.

CONCLUSIONS

In this work, we have used quantum chemistry (QC) approach to investigate electronic and phonon properties of crystalline 5d transition metal oxides ReO_3 , $ZnWO_4$ and $CaWO_4$. Both metal (ReO_3) and non-metal ($ZnWO_4$ and $CaWO_4$) oxides have been studied by ab initio calculations using pure DFT and hybrid exchange-correlation. In particular, the crystallographic structure has been predicted with the accuracy approaching to that of the experimental structural techniques as diffraction and x-ray absorption spectroscopy.

The phonon properties have been calculated by the *direct (frozen phonon) method* [7] not only at the Brillouin zone center but also at other symmetry points and along the BZ directions. The calculated frequencies have been compared with the results of infrared and Raman spectroscopies as well as of inelastic neutron and x-ray scattering experiments. Rather good accuracy of ab initio phonon frequencies calculations makes them suitable for the prediction of the crystal vibrational properties especially in situations when the experimental approach is difficult or impossible due to selection rules. Finally, the accuracy of present QC calculations makes them suitable for the use in a combination with the force-field approach to access the temperature dependent atomic structure, which can be employed for interpretation of the x-ray absorption spectroscopy results using recently developed scheme [25].

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