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Ab initio study of structural and electronic properties of copper and nickel tungstate

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ABSTRACT

Calculating accurate band gaps of semiconducting and insulating materials is one of the major challenges currently facing density functional theory (DFT) calculations. The atomic and electronic structure of antiferromagnetic $NiWO_4$ and $CuWO_4$ is studied in the plane wave based program VASP using pure, as well as hybrid forms of the exchange-correlation (xc) functional. It is shown that the atomic structure and the electronic density of states (DOS) of these two systems can be described as accurately with non-hybrid functionals as with more computationally expensive hybrid functionals. $NiWO_4$ cell dimensions with less than 0.6% mean relative error can be achieved using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) form of the xc functional. Lattice parameters comparable to those found with hybrid functionals for $CuWO_4$ can be obtained with the PBE+U correction method. The PBE+U correction can also be applied to the $CuWO_4$ system to produce the experimental band gap. The modified Becke-Johnson (mBJ) meta-GGA gives band gaps close to experimental ranges for both the $NiWO_4$ and $CuWO_4$ systems.

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1. Introduction

Transition metal tungstates (AWO_4) are a part of a larger group of scheelite and wolframite structures that exhibit unique properties which are useful in many different technological areas such as laser host material, optical fibers, scintillation detectors, among others [1,2]. Nickel tungstate ($NiWO_4$) and copper tungstate ($CuWO_4$) have recently found use as photocatalysts in various technologies such as photoanodes in water splitting devices [3–5] and photovoltaic electrochemical cells (PVEC's) [6–8], environmental decontamination [9], and electrochromic devices [10–13].

The band gap is important to the functionality of these materials and measuring it accurately is an ongoing venture. The band gap has been measured for $CuWO_4$ in powder, crystal, and thin film form using various techniques. The results have been shown to vary from 1.78 eV [9] up to 2.79 eV [2], but the general agreement now is that the value is close to 2.3 eV [4,5,8,14–19]. The $NiWO_4$ band gap measured via optical absorption spectra is 3.5 eV [10,20]. Therefore, the substitution of Ni for Cu leads to vastly different electronic properties, opening up the possibility to tune the band gap of these materials.

It is well known that density functional theory (DFT) calculations underestimate the electronic band gap. Hybrid forms of the exchange-correlation (xc) functional, which include mixing of Hartree-Fock (HF) exact exchange, are often able to improve the band gap. However, this comes at a cost since hybrid functionals generally require significantly more computing power than non-hybrid functionals. Both hybrid and non-hybrid functionals have previously been used to improve band gap calculations in these two materials. To the best of the authors' knowledge, no single non-hybrid xc functional has been shown to replicate the experimental band gap in both $NiWO_4$ and $CuWO_4$.

In the literature, there are several computational results for the band gap of $CuWO_4$ [17–19,21,22]. Khyzhun et al. [21] and Atuchin et al. [22] both computed band gaps of 1.9 eV using the full potential linearized augmented plane wave (FP-LAPW) method with the Perdew-Burke-Ernzerhof (PBE) [23] generalized gradient approximation (GGA). This is unusually high for the xc functional used. Lalić et al. [18] used the same approach, though calculated a band gap of 0.54 eV. Lalić also used the PBE+4 (Cu) correction and the modified Becke-Johnson (mBJ) [24] meta-GGA (mGGA) with this system and found band gaps of 1.5 eV [18] and 2.09 eV [19], respectively. Using linear combination of atomic orbitals (LCAO), Kuzmin et al. [17] also calculated 0.54 eV with PBE, in agreement with Lalić's result. In the same work Kuzmin also performed various hybrid functional calculations. The PBE0-13% hybrid functional agreed best with experiment giving a band gap of 2.32 eV.

To the best of the authors' knowledge there are only two computational studies reporting the band gap of $NiWO_4$. The first was

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reported by Kuzmin et al. [25] using the LCAO method with the PBE0-13% hybrid functional, which produced a band gap of 3.7 eV. The second was performed by Doudin et al. [26] using the PBE+6 (Ni,W) approach producing a band gap of 3.0 eV.

The hybrid functional PBE0-13% (LCAO) has been shown to produce accurate band gaps for both $NiWO_4$ and $CuWO_4$. However, if one were to study doping effects, e.g. $Cu_xNi_{1-x}WO_4$, a supercell would be required, rendering the use of hybrid functionals computationally prohibitive. The purpose of this work is to determine how introducing different hybrid functionals will affect the band gap and density of states of $NiWO_4$ and $CuWO_4$, and how non-hybrid corrections can be used to produce similar results. Various functionals are studied under the same framework to determine which functionals produce accurate atomic structure and electronic structure for the two systems. The rest of this article is organized as follows. Section 2 discusses computational methods employed in this work, Section 3.1 presents the results for $NiWO_4$ and Section 3.2 the results for $CuWO_4$, followed by conclusions in Section 4. Information for all optimized structures and band gaps calculated in this work is provided in the Supplementary Material found in Appendix A.

2. Computational details

The electronic and structural properties of $NiWO_4$ and $CuWO_4$ were studied using the plane wave based Vienna Ab-initio Simulation Package (VASP) code [27]. The PBE-GGA was used for the form of the xc functional. The ion-electron interactions were approximated with projector augmented wave (PAW) potentials [28]. Non-spherical contributions from gradient corrections inside the PAW spheres were included in calculations. A kinetic energy cutoff of 700 eV was used in the expansion of the Kohn-Sham single particle wave functions in a plane wave basis set. The two systems were optimized using the conjugate gradient algorithm so that the ground state configuration was reached when net forces on all ions were below 0.01 eV/Å. The density of states (DOS) were calculated using the tetrahedron method with Blöchl corrections with a $3 \times 5 \times 5$ Monkhorst-Pack [29] k-point grid for hybrid functionals and $11 \times 21 \times 21$ for PBE, PBE+U, and mBJ.

The $NiWO_4$ primitive cell has a wolframite structure with P2/c symmetry and is made up of hexagonally closed packed oxygen atoms with octahedral sites centered around the cations (see Fig. 1). The $CuWO_4$ primitive cell is a distorted wolframite-type structure with $P\bar{1}$ symmetry (triclinic). The Jahn-Teller effect of the Cu^{2+} cation causes an elongation of the CuO_6 octahedra which leads to the lower symmetry $P\bar{1}$ instead of the P2/c symmetry [18]. $NiWO_4$ and $CuWO_4$ undergo transitions to long range antiferromagnetic order below their Néel temperatures of $T_N \sim 67$ K and $T_N \sim 24$ K, respectively [30]. Note that the calculations performed do not take into account the effects of temperature. These two compounds share similar magnetic cells and are constructed by doubling their unit cells along the a-axis [30–32]. Energies were calculated for different magnetic configurations of $NiWO_4$ and $CuWO_4$. For both systems the most stable magnetic configuration was antiferromagnetic with alternating spin in layers of metal cations along the a-axis, in agreement with experiment. The magnetic cells are shown in Fig. 1 [33] and are the structures that were optimized with the self-consistent field method prior to DOS calculations.

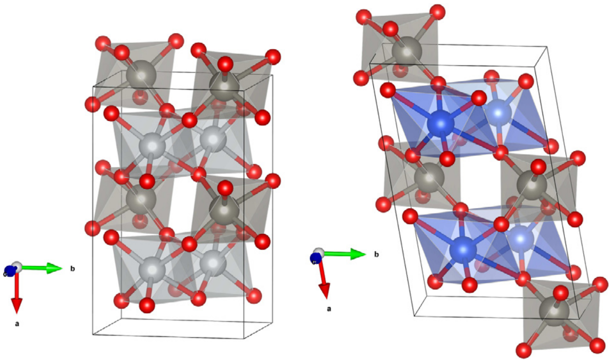

Fig. 1. Magnetic cells of $NiWO_4$ (left) and $CuWO_4$ (right), Ni: light grey, W: dark grey, O: red, Cu: blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The hybrid functionals PBE0 [34], HSE03 [35], and HSE06 [36] were employed with 13% and 25% mixing of HF exact exchange with PBE exchange. Two non-hybrid approaches: the simplified rotationally invariant approach to DFT+U proposed by Dudarev et al. [37] and the mBJ-mGGA were also utilized. The parameter U adds on-site Coulomb interactions to select atomic orbitals. In this work U is added to the d-states of the 3d transition metal (A = Ni,Cu) and in some cases also to tungsten. It will be noted as (A) when applied only to the 3d transition metal and (A,W) when U is applied to tungsten as well. The parameter U will be used to refer to U_{eff} which is defined as $U - J$. The mBJ-mGGA has been shown to give accurate band gaps for strongly correlated 3d transition-metal oxides which applies to the two systems being studied [38]. Since the mBJ potential cannot be expressed as the derivative of a functional, forces cannot be calculated; therefore, structure optimizations were not done with this form of the xc functional [38]. Instead, the structure was first optimized using PBE and then mBJ was used for the DOS calculations. A similar procedure was done with the hybrid functionals since computation is very expensive. Finally, for consistency, DOS calculations using the PBE+U method were performed on structures optimized with PBE, while the effects of U on the cell geometry were explored separately.

3. Results and discussion

3.1. Nickel tungstate

3.1.1. Cell structure

The structure parameters of $NiWO_4$ determined by neutron powder diffraction [39] at room temperature are shown in Table 1. Structure optimizations were done with PBE and PBE+U (Ni) and some representative results are shown in Table 1. In all calculations, the lattice vectors were slightly overestimated. Relaxations with the PBE-GGA gave the best agreement with neutron powder diffraction experiments with a mean relative error of 0.57%. This is only slightly higher than the PBE0-13% (LCAO) relaxation done by Kuzmin et al. who used the CRYSTAL06 code [25]. Increasing U tends to increase the length of a and b, worsening the structure's agreement with experiment. This trend appears to reverse at higher U (see Table A.1). Different optimization methods did not have a significant effect on the standard deviation of the bond lengths of NiO_6 and WO_6. There is a higher distortion of the WO_6 octahedra than that of the NiO_6 octahedra due to the second-order Jahn-Teller effect [40], which is apparent in all the $NiWO_4$ optimized structures.

3.1.2. Electronic structure

The band gap and features of the total electronic DOS are shown in Fig. 2. The spin up component is shown, which is nearly identical to the spin down component. Similar features appear in the occupied bands for all calculations except for PBE which has a small gap located near -0.8 eV. The conduction band in the PBE plot consists of a narrow band which begins at 1.0 eV and a wide band which

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