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Ab initio study of electronic, magnetic and optical properties of $CuWO_4$ tungstate

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ABSTRACT

Ab initio calculations based on the density-functional theory have been employed to study the electronic and magnetic properties of copper tungstate $CuWO_4$, as well as its optical characteristics in the ultraviolet region, up to 40 eV. The electronic structure around the band gap is dominated by the O *p*- and the Cu *d*-states and it is quite different from the recent spin-restricted calculations of the same compound. The most stable antiferromagnetic state and the values of magnetic moments at Cu sites and O(3) oxygen atomic sites (closest to Cu^{2+} ions in zigzag antiferromagnetic chains) are in agreement with experiments. The gap is found to be indirect with the acceptable value only after use of the LDA + *U* rotationally invariant self-consistent full potential linearized augmented plane wave (FP LAPW) approach. The optical spectra are analyzed, compared, and interpreted in terms of calculated band structures. It is shown that absorption process involves significant energy flow from the O ions to the Cu ions.

1. Introduction

For decades metal tungstates and molybdates AWO_4, or $AMoO_4$ ($A = Ca, Cd, Ba, Zn, Mn, Fe, Co, Ni, Cu$) have received great attention, firstly as promising scintillation materials for many applications in science and technology such as: compact muon solenoid (CMS) calorimeter in high-energy physics experiments at LHC, searches for extremely rare events (non-baryonic dark matter double-beta decay and radioactive decay of very long-living isotopes), for use in the positron emission tomography (PET) for the medical diagnosis of various diseases, and even for the production of positive electrodes of lithium rechargeable batteries [1–3]. The structural, optical and luminescence properties of metal tungstates were of the primary concern, and many workers have carried out experimental measurements and detailed electronic structure calculations within the framework of density functional theory (DFT) with the estimation of optical dielectric function and reflectivity for these materials (see for instance recent work by Fujita et al. [4] and references cited therein).

When metal tungstates contain 3*d* transition metals, pronounced electronic correlation effects produce interesting electronic and magnetic properties of the respective layered materials. Thus, $MnWO_4$ is a prototypical magnetoelectric multiferroics, in which the spiral spin – 1/2 structure and the ferroelectric polarization simultaneously appear (cf. Ref. [5]). The spin Heisenberg antiferromagnet $CuWO_4$, which is the subject of our present investigations, has been extensively studied both experimentally and theoretically [6–11]. This compound exhibit the low-dimensional magnetism since susceptibility profile displays a broad maximum at temperatures around 90 K, far above the Neel temperature of $T_N \sim 24$ K [7]. Copper tungstate $CuWO_4$ has lightly coupled zigzag chains of Cu^{2+} ions that are responsible for the observed low dimensional magnetic properties. Four decades ago the powder neutron diffraction study showed that $CuWO_4$ experienced phase transition to long-range antiferromagnetic (AF) state at low temperatures, and its magnetic unit cell is doubled along the *a*-axis [7]. The three-dimensional (3D) AF ordering temperature of $CuWO_4$ was found to be 23.0(2) K in the single-crystal neutron diffraction study from the temperature dependence of the magnetic (1/200) reflection [8].

Spin exchange interactions of $CuWO_4$ were thoroughly investigated starting from Doumerc et al. [9], who explained the temperature behavior of the magnetic susceptibility on the basis of spin – 1/2 1D AF alternating chain. Ten years latter Forsyth et al. [8] suggested that alternating chains are the CuO_4 zigzag chains running in the *c*-axis direction weakly coupled in the *b*-axis direction. Then Lake et al. [10], Ehrenberg et al. [12] and Koo and Whangbo [11] showed that AF alternating chains are not the CuO_4 zigzag chains in the *c*-direction but run along [210] direction and discussed the magnetic structure and low-lying excited states of copper tungstate in distorted wolframite-type structure. The low symmetry of this compound led to several models of magnetic ordering and to a large number of independent superexchange intrachain and super-superexchange interchain interaction parameters [10,11].

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The first-principles electronic structure of metal tungstates, has been calculated by the full potential linearized augmented plane wave (FP LAPW) method [13,15], the discrete variational X_α method [4,16] and the pseudopotential CASTEP code [17,18].

To the best of our knowledge, the unique theoretical band structure calculations made so far for the $CuWO_4$ were published only recently [15]. In spite of the well-known fact that $CuWO_4$ has a number of features in common with low-dimensional spin-1/2 antiferromagnets, the authors of Ref. [15] did only spin-restricted calculations and reported: "a rather good agreement of the experimental and theoretical data concerning the electronic properties of $CuWO_4$", the conclusion which we shall contest in the present work. The X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) methods were employed to investigate experimentally the electronic structure of copper tungstate (Khyzhun et al. [15] gave relatively complete survey of the experimental investigations). Let us additionally mention recent work of Ruiz-Fuertes et al. [19], who carried out the optical-absorption study at ambient pressure in order to get an estimation of the band gap. They have established the indirect gap of 2.3 eV and negative pressure coefficient for the $CuWO_4$ in their high-pressure optical studies up to 25 GPa.

In order to amend and correct recent spin-restricted band structure results for the copper tungstate [15] we have carried out detailed electronic structure calculations of this compound within the framework of local spin-density-functional theory. In addition to the determination of the most stable magnetic state and the distribution of one electron eigenstates, we have also estimated the anisotropic optical dielectric tensor and electron energy loss function for the $CuWO_4$ compound. In Section 2 the details of the crystal structure and the calculational methods are given. Density-functional theory results are presented in Section 3 and compared with recent spin-restricted electronic structure calculations [15]. The calculated optical properties are presented in Section 4 and discussed with reference to the recent X-ray emission results [15] and earlier results for the cadmium tungstate ($CdWO_4$) and cadmium molybdate (CdMoO4) obtained by Abraham et al. [14]. A brief summary and conclusions are given in Section 5.

2. Details of the calculation

The structure of copper tungstate $CuWO_4$ is presented in Fig. 1. The primitive cell contains two formula units with characteristic corner-linked CuO_6 and WO_6 octahedra. The Jahn–Teller effect of the Cu^{2+} cation causes a pseudo-tetragonal elongation of the CuO_6 octahedra. In the figure, it can be seen that although $CuWO_4$ is triclinic, its structure is topologically related to that of monoclinic wolframite (P 2/c) [8]. The WO_6 octahedra are slightly distorted as in the wolframite with W–O distances ranging from 1.8 to 2.2 Å. Nevertheless, the Jahn–Teller effect of Cu^{2+}, which reduces the degeneracy of 3*d* orbitals, is sufficient to cause a lowering of the monoclinic $P2/c$ symmetry to the triclinic $P\bar{1}$ symmetry. Therefore, the CuO_6 octahedra have a pseudo-tetragonally elongated geometry with four planar Cu–O distances close to 2 Å and two axial Cu–O distances around 2.4 Å [19,20]. The experimental crystal structure parameters and atomic positions in fractional coordinates (x,y,z) used in the present calculations are listed in Table 1 [20], while the basis function consists of the atomic orbitals of Cu, W and O as listed in Table 2.

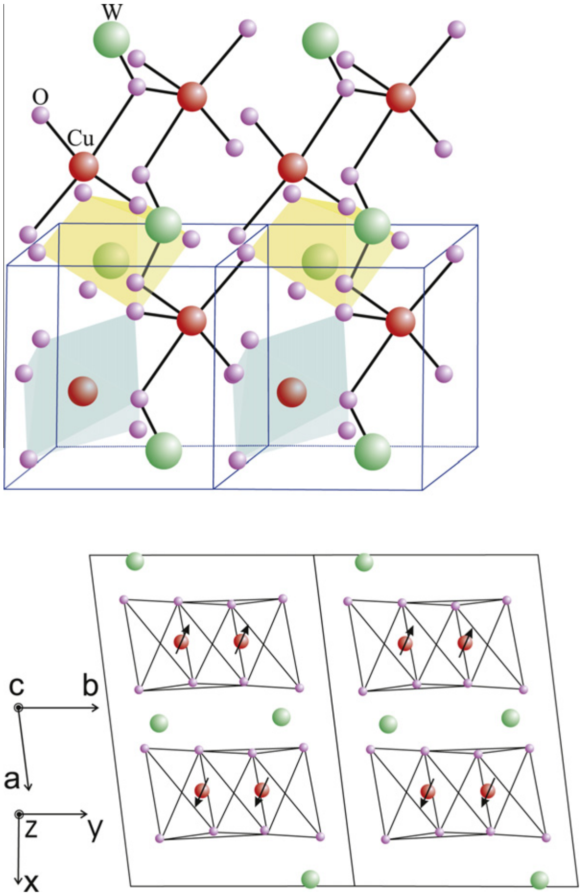

Fig. 1. The crystal structure of $CuWO_4$ with copper and tungsten octahedra shown together with its structure and antiferromagnetic order viewed along the *c*-axis.

Table 1
Atomic positions in fractional coordinates and muffin-tin radii used for the LAPW calculations of $CuWO_4$ [8]. In the leftmost column the crystal structure parameters are given for the triclinic unit cell with the $P\bar{1}$ space group.

	Atom	*x*	*y*	*z*	R_{MT} (bohr)
$a = 4.694$ Å	Cu	0.49537	0.65942	0.24524	1.95
$b = 5.830$ Å	W	0.02146	0.17353	0.25405	1.76
$c = 4.877$ Å	O(1)	0.25042	0.35475	0.42520	1.56
$\alpha = 91.64°$	O(2)	0.21551	0.88077	0.42901	1.56
$\beta = 92.41°$	O(3)	0.73511	0.38077	0.09822	1.56
$\gamma = 82.91°$	O(4)	0.78214	0.90774	0.05459	1.56

Table 2
Atomic orbitals used in the present LAPW calculations of the electronic structure of $CuWO_4$.

Atom	Core electrons	Semi-core electrons	Valence electrons	Semi-core and valence electrons
^{29}Cu	$1s^22s^22p^63s^2$	$3p^6$	$3d^{10}4s^1$	17
^{74}W	$1s^22s^22p^63s^23p^63d^{10}$ $4s^24p^64d^{10}$	$5s^25p^64f^{14}$	$5d^46s^2$	28
^{8}O × 4	$1s^2 \times 4$	$2s^2 \times 4$	$2p^4 \times 4$	6 × 4
Total	66	36	33	69

The fundamental properties of $CuWO_4$, in particular the electronic band structure, have been poorly investigated. Our primary goal here is to present a comprehensive study of the electronic structure, the most stable magnetic ordering and optical properties of copper tungstate. With this goal in mind, we have employed possibilities of the FP LAPW method as incorporated in the WIEN2k code [21]. In this method, the crystal potential, electronic wave functions and charge density are expanded in spherical harmonics inside the non-overlapping muffin-tin (MT) spheres of radii $R_{MT}(i)$ centered at each nuclear position, and in plane waves in the