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Ab initio study of electronic, magnetic and optical properties of CuWO₄ 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 Cu²⁺ 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.

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1. Introduction

For decades metal tungstates and molybdates AWO₄, or AMoO₄ (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 3d transition metals, pronounced electronic correlation effects produce interesting electronic and magnetic properties of the respective layered materials. Thus, MnWO₄ 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 CuWO₄, 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 CuWO₄ has lightly coupled zigzag chains of Cu²⁺ ions that are responsible for the observed low dimensional magnetic properties. Four decades ago the powder neutron diffraction study showed that CuWO₄ 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 CuWO₄ 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 CuWO₄ 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 CuO₄ 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 CuO₄ 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 CuWO₄ were published only recently [15]. In spite of the well-known fact that CuWO₄ 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 CuWO₄", 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 CuWO₄ 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 CuWO₄ compound. In Section 2 the details of the crystal structure and the calculational methods are given. Densityfunctional 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 (CdWO₄) 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 CuWO₄ is presented in Fig. 1. The primitive cell contains two formula units with characteristic corner-linked CuO₆ and WO₆ octahedra. The Jahn-Teller effect of the Cu²⁺ cation causes a pseudo-tetragonal elongation of the CuO₆ octahedra. In the figure, it can be seen that although CuWO₄ is triclinic, its structure is topologically related to that of monoclinic wolframite (P 2/c) [8]. The WO₆ 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 Cu²⁺, which reduces the degeneracy of 3d orbitals, is sufficient to cause a lowering of the monoclinic P2/c symmetry to the triclinic $P\overline{1}$ symmetry. Therefore, the CuO₆ 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.

The fundamental properties of CuWO₄, 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





Fig. 1. The crystal structure of CuWO₄ 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 CuWO₄ [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	у	Ζ	R_{MT} (bohr)
<i>a</i> = 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	0(1)	0.25042	0.35475	0.42520	1.56
$\alpha = 91.64^{\circ}$	O(2)	0.21551	0.88077	0.42901	1.56
$\beta = 92.41^{\circ}$	0(3)	0.73511	0.38077	0.09822	1.56
$\gamma = 82.91^{\circ}$	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 CuWO₄.

Atom	Core electrons	Semi-core electrons	Valence electrons	Semi-core and valence electrons
²⁹ Cu ⁷⁴ W	1s ² 2s ² 2p ⁶ 3s ² 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ² 4p ⁶ 4d ¹⁰	3p ⁶ 5s ² 5p ⁶ 4f ¹⁴	3d ¹⁰ 4s ¹ 5d ⁴ 6s ²	17 28
$^8 O imes 4$ Total	$1s^2 \times 4$ 66	$\begin{array}{c} 2s^2 \times 4 \\ 36 \end{array}$	$\begin{array}{c} 2p^4 \times 4 \\ 33 \end{array}$	6 × 4 69

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 $R_{\rm MT}(i)$ centered at each nuclear position, and in plane waves in the

interstitial region between the atomic spheres. For the exchangecorrelation potential we have used the generalized-gradient approximation (GGA) as parameterised by Perdew et al. [22]. The tetrahedron method with a mesh of 112 irreducible **k**-points was used for the Brillouin-zone integrations. The convergence of the basis set is controlled by the *RK*_{MAX} parameter for which we take 7.0, while the reciprocal space truncation was controlled by parameter *G*_{MAX} for which we used 12 bohr⁻¹.

For the self-consistency cycle we used two convergence criteria: $\Delta E_{tot} \leq 10^{-5}$ Ry and $\Delta \rho \leq 10^{-5}$ eV/bohr³, both of which should be satisfied for the last two iterations. In order to examine the magnetic properties of the copper tungstate and to estimate the effects of spin polarization on the calculated properties, our calculations were carried out for the non-magnetic and magnetic variants. In the latter case the ferromagnetic (F) and three AF orderings were assumed. The schematic representation of the most stable AF solution for this compound is given in Fig. 1. Besides standard local-spin-density-calculations (LSDA) we also performed spin-polarized calculations with the Hubbard type Coulomb correction added (in the framework of so-called LDA + *U* method of Anisimov et al. [23]). This method cured, at least partly, the deficiencies of LDA and LSDA in treating Mott–Hubbard or charge transfer insulators.

Finally, the optical characteristics of CuWO₄ were analyzed in terms of its complex dielectric tensor $\varepsilon_{\alpha\beta}$, whose imaginary part Im($\varepsilon_{\alpha\beta}$) is directly proportional to the optical-absorption spectrum of the compound. The Im($\varepsilon_{\alpha\beta}$) is computed within the frame of random phase approximation, in the limit of linear optics and neglecting electron polarization effects, using the following formula [24]:

$$\mathbf{Im}[\varepsilon_{\alpha\beta}(\omega)] = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{if} \int_{\mathsf{BZ}} \frac{2d\mathbf{k}}{(2\pi)^3} \times \langle \varphi_{i\mathbf{k}} | p_{\alpha} | \varphi_{f\mathbf{k}} \rangle \\
\times \langle \varphi_{f\mathbf{k}} | p_{\beta} | \varphi_{i\mathbf{k}} \rangle \delta(E_f(\mathbf{k}) - E_i(\mathbf{k}) - h\omega) \tag{1}$$

for a vertical transition from a filled initial state of energy $E_i(\mathbf{k})$ to an empty final state of energy $E_f(\mathbf{k})$ with the same wave vector \mathbf{k} . ω is the frequency of the incident radiation, m the electron mass, \mathbf{p} the electron momentum operator, and α and β stand for the projections x, y, z of the incident light polarization.

On the basis of calculated electronic structure (i.e. knowing the Kohn–Sham (KS) orbitals) of the CuWO₄ we computed the Im($\varepsilon_{\alpha\beta}$) up to incident radiation energy of $\hbar\omega$ = 40 eV. The real part of dielectric tensor is then determined using Kramers–Kroning relation. Both real and imaginary parts of the $\varepsilon_{\alpha\beta}$ were calculated with a mesh of 112 **k**-points in the irreducible wedge of the first Brillouin zone, exactly as in the case of calculation of the electronic structure. All optical constants of the material (as reflectivity, refraction index, electron energy loss) could then be calculated by combining the real and imaginary part of dielectric tensor [25]. All graphs were produced with the Lorentzian broadening of 0.06 eV. The scissors operator, which shifts the conduction band bottom, was not applied.

3. Electronic structure results

3.1. Paramagnetic calculations

As a first step, we determined self-consistently paramagnetic electronic band structure of the copper tungstate $CuWO_4$ with the wolframite-type crystal structure. In Fig. 2a, the complete spin-restricted electronic structure of $CuWO_4$, calculated on the basis of FP LAPW method with GGA corrections included, is presented. This figure shows the energy bands around the Fermi level in the [-4,6] eV energy interval. Our results for the paramagnetic FP LAPW density of states (DOS) of CuWO₄ are given in Fig. 2b.

Unexpectedly, the band structure results we obtained appeared inconsistent with the recent results reported in Ref. [15]. Contrary to the experiments [19,26], we got the metallic solution, while the authors of Ref. [15] obtained the solution with 'too good' energy gap of E_g = 1.9 eV, using the same band structure method (as we did) with similar convergency parameters [21,22]. We have no explanation for such a discrepancy. Additionally we performed paramagnetic calculations of CuWO₄ on the basis of very robust linear muffin-tin orbital method in the atomic sphere approximation (LMTO ASA) with GGA corrections included (we have used the ASA version of Savrasov's LMTO code [27]), and obtained practically the same density of states as with FP LAPW method (cf. top box in Fig. 2b). It is a well-known fact that conventional band structure calculations incorrectly give a metallic ground state for 3d transition metal monoxides MnO, FeO, CoO and NiO and various copper oxide compounds with some kind of layered structure (the most notable examples are high- T_c cuprates). The physics of this may be different and number of extensions of density-functional theory were suggested, which, in different manners, led to insulating ground states for these compounds (for more details see the work of Mazin and Anisimov [28]). It has been always much more disturbing to have, incorrectly, a metallic behavior in the local density approximation (LDA) calculation than just to have an incorrect gap. It is usually desirable to obtain a gap at the level of density functional calculation, no matter how small it is, in order to be able to define the physical correction (Mott-Hubbard, charge transfer, self-interaction correction, etc.) in an unambiguous fashion. Since the work of Oguchi et al. [29], the most convenient way has been to try to open a gap with some kind of magnetic ordering.

3.2. Spin polarized FP LAPW calculations

The spin-restricted band structure calculations produced incorrect metallic solution of the wolframite structure of CuWO₄. The band structure depicted in Fig. 2a indicates the instability of the nesting with twofold periodicity along *a*-axis (Γ B-direction). Bearing in mind earlier experimental findings about Neel order and short-range magnetic fluctuations in weakly coupled zigzag dimerized chains running in the [2, -1, 0] direction (cf. Ref. [10]), it is very desirable and natural to check the stability of several possible magnetic orderings in the CuWO₄ in the framework of FP LAPW band structure method. To the best of our knowledge this is the first attempt to do the spin-polarized LDA calculations of this compound. Three-dimensional magnetic effects are always present to some extent if non-magnetic ions separate the copper chains. Relying on these facts and experimental findings for the copper tungstate CuWO₄ compound [7-10], we did standard local spin density approximation (LSDA) calculations for a $2 \times 1 \times 1$ supercell, for the ferromagnetic (F) and AF orderings (we are further presenting the results only for the most stable antiferromagnetic ordering schematically depicted in Fig. 1, which is in accordance with the accepted fact that the copper chains occupy alternating planes perpendicular to the c^* -axis weakly coupled both within the planes and between the planes [10]). For this compound we found that the AF ordering (Fig. 1) is energetically more favorable compared to the ferromagnetic and paramagnetic state. Energy gains are: $\Delta E(1) = E(F) - E(AF) = 0.029 \text{ eV/Cu}$ atom and $\Delta E(2) =$ E(Paramagnetic) - E(AF) = 0.118 eV/Cu atom.

LSDA electronic bands along several Brillouin-zone (BZ) directions and the total and partial density of states (DOS) for AF ordering in the wolframite CuWO₄ are given in Fig. 3a and b. Less stable ferromagnetic state gives rather small energy gap of $E_g \sim 0.1$ eV, while the AF ordering produce finite band gap of $E_g \sim 0.54$ eV.

This AF band gap value could be assumed as a manifestation of the well-known failure of LSDA to account properly for the electronic correlations in the CuWO₄. Recent measurements of M.V. Lalić et al./Computational Materials Science 50 (2011) 1179-1186



Fig. 2. The band structure (a) and total density of states (b) of paramagnetic CuWO₄ (for more details see the text).



Fig. 3. Plots of the energy bands (a) and the total DOS and the partial DOS (b) calculated for CuWO₄ by standard LSDA FP LAPW method.

Ruiz-Fuertes et al. [19] have given the indirect band gap energy of CuWO₄ (2.3 eV). The situation is much better with the values of magnetic moments at Cu sites. We are getting the μ_{Cu} = 0.58 bohr magnetons (μ_B) at copper sites. We also found the magnetic moments of $\mu_{O(3)} = 0.1 \ \mu_B$ on the O(3) sites (oxygen atoms closest to Cu^{2+} ions in zigzag AF chains). These results are in agreement with the neutron diffraction experiments of Forsyth et al. [8], where: μ_{Cu} = 0.67 μ_B , and $\mu_{O(3)}$ = 0.06 μ_B were obtained. In the energy region presented in Fig. 3b the main contribution to the atomic DOS curves comes from the Cu 3d-, W 5d- and O 2p-like states. As can be ascertained from that figure, the W 5d- and Cu 3d-like states contribute approximately equally into the bottom of the valence band, while the O 2p-like states contribute substantially throughout the whole valence band region of the CuWO₄. Significant contribution of the Cu 3d-like states is evident in the upper part of the valence band also. It is readily seen, from Fig. 3(b), that the bottom of the conduction band is composed mainly of the Cu 3d- and O 2p-like states. Contrary to the results of Ref. [15] the contribution of W 5d-like states is quite insignificant here. Hybridized W 5d- and O 2p-like states are principal contributors to the higher

sub-band of the unoccupied conduction band of the copper tungstate under study (the center of this band is shifted almost 3 eV compared to the center of the lowest conduction band).

3.3. LDA + U calculations

The electronic structure of wolframite CuWO₄ was also studied by means of the LDA + *U* approach, for the most stable AF ordering obtained in spin-polarized FP LAPW calculations. Unlike the LSDA, where the most stable AF ordering from Fig. 1 for the *P*2/*c* crystal structure produced a very small band gap and acceptable values for magnetic moments at Cu and O(3) sites, the LDA + *U* method produced an insulating solution with pronounced energy-gap value of ~1.5 eV and magnetic moments at copper and its closest oxygen site $\mu_{Cu} = 0.74 \,\mu_B$ and $\mu_{O(3)} = 0.068 \,\mu_B$ respectively. These results were obtained for effective Coulomb correlation parameter $U_{eff} = 4 \,\text{eV}$ (effective Coulomb correlation parameter as incorporated in WIEN2k code) [30]. Both the band gap value and magnetic moments are improved in LDA + *U* calculations as compared with experimental values obtained in Refs. [19,26] and [8], respectively. Let us note that in practical calculations, the Coulomb correlation parameter U is often considered as a free parameter to achieve the proper agreement with of calculated and measured properties of the investigated systems [31]. We have chosen the U value somewhere in between the theoretical [32] and experimental [33] estimates for copper and several copper compounds.

The complete presentation of the LDA + U electronic structure and DOS results for the title compound was given in Fig. 4a and b. The calculated band gap for CuWO₄ in Fig. 4a is indirect. The bottom of the conduction band (CB) is at the B point of the first Brillouin zone (BZ) and the top of the valence band is at a point along Γ G close to the middle of this symmetry direction. The direct gap at Γ is ~1.43 eV (less than 5% difference compared to the true indirect gap). In this manner, the difference between the direct and indirect band gaps is so small that for all practical purposes the CuWO₄ can be considered as a direct band gap insulator. It is interesting to remark that our results for ordinary LSDA calculations produced two bands with almost no dispersion (the top valence and the lowest conduction band) along Γ B (cf. Fig. 3a).

Bands along the BZ symmetry lines and total DOS curves in Figs. 3 and 4 look very similar to one another. But, more careful inspection reveals that the details of the dispersion of the group of lowest conduction and the topmost valence band states are pretty different for the LSDA and LDA + U calculations. The Hubbard type correlations included in the framework of the LDA + U method have modified significantly the Cu *d* states, and have increased the magnetic moment on the Cu sites and the insulating gap value, as compared to the LSDA results. Other features characteristic for the inclusion of Coulomb correlation such as: spectral weight redistribution between transition metal Cu 3*d* and O 2*p* bands, enhancement of the oxygen contribution to the top of the valence band, mainly Cu 3*d* character of unoccupied bands indicating a charge transfer character of the gap, come into sight also for the wolframite CuWO₄.

Closer inspection of Figs. 3a and 4a reveals that the spin-polarized bands of CuWO₄ around the Fermi level, with their small dispersion, are extremely similar to the respective bands of the quasione-dimensional transition metal compound α' – NaV₂O₅ and to the bands of the first inorganic spin-Peierls chain AF compound Cu-GeO₃ (for more details we refer the reader to [34]). This fact suggests clearly the spin – 1/2 1D AF alternating chain structure of the title compound.

4. Optical properties

We calculated a complex second-order dielectric tensor of an anisotropic CuWO₄ crystal, describing the linear response of an electronic system to an applied external electric field in *x*, *y* and *z*-direction. The imaginary part of the dielectric tensor directly relates to the band structure of a material and is computed on the basis of single particle orbital and energy approximated by the spin-polarized solutions of the KS equations. On the basis of the calculated band structure for the CuWO₄ we computed the Im($\varepsilon_{\alpha\beta}$) for this compound utilizing the formula (1) and the Re($\varepsilon_{\alpha\beta}$) of the dielectric tensor by the Kramers–Kroning relation. These and other optical constants are presented for LSDA AF and LDA + *U* AF solutions of KS equations.

Optical analysis for the CuWO₄ in AF phase was performed on the basis of both spin-polarized and LDA + U electronic structure in the energy interval (-1-2 Ry). The density of states, for these cases, are depicted in Fig. 5 and show the respective band structures of CuWO₄, which we utilize for optics calculation. LDA + U calculations were reproduced with the U_{eff} = 4 eV for Cu d-states.

Fig. 6 shows imaginary part of dielectric tensor of the $CuWO_4$ along the three Cartesian directions (*x*, *y*, *z*).

For both type of calculations it is seen that the CuWO₄ absorption spectrum consists of three distinct parts: (1) a pronounced peak centered around 1.0 eV (2.0 eV) for LSDA (LDA + *U*) calculations, (2) the broad peak centered near 4.0 eV (5.0 eV), and (3) the almost flat absorption band at energies greater than 6.0 eV (6.5 eV). The spectrum is anisotropic, i.e. its intensity depends on polarization of the incident radiation. This property is especially pronounced for the first two peaks of the absorption spectrum. The major difference between LSDA and LDA + *U* spectra reflects in the position and the form of the first absorption peak. Such strong optical anisotropy of the CuWO₄ is due to low crystal symmetry and the peculiarities in the crystal structure, namely the existence of the bridge-oxygen ions connecting neighboring CuO₆ and WO₆ complexes.

Let us note here that, since the x, y and z-axes make small angles with a, b and c crystal axes, the values of the optical constants for the crystallographic a, b and c-axes are approximately the same as those of the x, y and z-axes. The interpretation of the absorption spectrum in terms of calculated band structure is shown in Fig. 7.



Fig. 4. Plots of the energy bands (a) and the total DOS and the partial DOS (b) calculated for the CuWO₄ by LDA + U FP LAPW calculations with U_{eff} = 4 eV.



Fig. 5. Total LSDA AF DOS (spin up + spin down) of the CuWO₄ compound in the vicinity of the Fermi level (at 0 eV). LDA + *U* results are presented in the lower graph (Band nomenclature is the following: Band number 1: oxygen $2s^2$ -states (32 electrons); Band number 2: mixture of oxygen $2p^4$ -states (64 electrons), Cu $4s^23d^9$ -states (44 electrons), W $5d^46s^2$ -states (24 electrons); (totally 132 electrons); Cu 3d-states are concentrated mainly in the higher energy part of this band, between -2 and 0 eV; Band number 3: empty Cu 3d-states (4 states, 2 for spin up and 2 for spin down). These states are hybridized with some amount of neighboring O *p*-states; and Band number 5: mixture of the O's 2p-, Cu 4p- and W 6p-states.)



Fig. 6. The components of the imaginary part of the dielectric tensor of $CuWO_4$, in arbitrary units. They are directly proportional to the absorption intensity of the incident light polarized along the *x*, *y* and *z*-directions respectively. The LDA + *U* calculations are presented in the upper graph.

The first peak in absorption spectrum originates from electronic transitions from the occupied band of highest energy (numbered as 2 in Fig. 5) to the conduction band of lowest energy (numbered as 3 in Fig. 5). As the band 3 is mostly composed of the Cu *d*-states, these transitions should involve electron transfer between (1) the occupied and unoccupied Cu *d*-states, and (2) between the occupied *p*-states of neighboring oxygens and unoccupied Cu *d*-states. The first possibility must be rejected since the CuWO₄ unit cell possesses the center of inversion, and consequently the Cu *d*-*d* transitions are dipole forbidden. Thus, the origin of the first peak is attributed to the electron transitions from the 2*p*-states of O's, which are nearest neighbors of the Cu, to the empty 3*d*-states of Cu, involving charge and energy transfer from O's to the Cu muffin-tin spheres. The different position and the form of this absorption peak, as resulted from different treat-

ments of the Cu *d*-states, can be explained by the fact that the LDA + U pushes the Cu empty *d*-states away from the valence band top and significantly changes the form of the populated O's *p*-states (Figs. 3b and 4b).

The second peak in absorption spectrum is dominated by electronic transitions from the occupied band of highest energy (bands number 2 in Fig. 5) to the conduction Band numbered as 4 inFig. 5, which contains predominantly the W empty d-states. Since the W d-d transitions are forbidden, the second peak is formed by electron transitions between the populated p-states of O's, which are nearest neighbors of the W, and unpopulated W d-states. As neither the W d-states nor its neighboring O's *p*-states are affected by the LDA + U treatment, this absorption peak is very similar for both kinds of calculations (Figs. 6 and 7). Finally, the higher energy flat part of absorption spectrum originates from the electron transfer from the occupied band of highest energy to the high-energy conduction band (bands number 5 in Fig. 5), which consists of the mixture of the states from all constituents. Electronic transitions from populated O's s-states (bands number 1 in Fig. 5) contribute very little to the overall absorption spectrum in both LSDA and LDA + U calculations.

Fig. 8 shows the components of calculated real part of CuWO₄ dielectric tensor. It demonstrates large optical anisotropy of the material. The electronic part of static dielectric constant, defined as Re($\varepsilon_{\alpha\beta}$) at zero energy, has very different values for three orthogonal direction (*x*,*y*,*z*) of light polarization: 13.059, 9.243 and 9.614 respectively for non-LDA + *U*, and 7.114, 6.018 and 6.858 for LDA + *U* calculations.

The calculated dielectric tensor components $\varepsilon_{\alpha\alpha}$, shown in Figs. 6–8 indicate that dominant transitions occur within approximately 10 eV above the band gap. These results for the dielectric tensor are quite similar to respective results for cadmium tungstate (CdWO₄) and cadmium molybdate (CdMOO₄) obtained by Abraham et al. [14] (although shifted several eV to the left, since we are working without ad hoc scissors operator correction for the band gap). Closer inspection reveals that the *d*-like states of Cu and W are differently arranged, above the band gap, compared to Cd and W(Mo) states with flat absorption band at energies greater than 6 eV. This result looks acceptable bearing in mind mentioned *d*-like states redistribution and the magnetism of the investigated compound.

In the case of energy loss function (Fig. 9) it is observed a less anisotropic behavior. This function is proportional to the energy loss probability for a fast electron moving across a medium. The most prominent peak in the spectrum is identified as the energy of plasmon oscillation, signaling the collective excitations of the electronic charge density in the material. For the CuWO₄ this energy is found to be approximately 26 eV, along the three orthogonal directions within the crystal.

Emission characteristics of the CuWO₄, obtained experimentally (cf. Fig. 5 in Ref. [15]), could be easily explained on the basis of our band structure results. Looking at the DOS curves of copper tungstate in Figs. 3b and 4b, we can infer that the main contributions of W 5d- and O 2p-like states are observed at the bottom and near the top of the valence band of copper tungstate, respectively, with contributions of these states throughout whole valence band of the compound. Top of the valence band of CuWO₄ is dominated by the contributions of the Cu 3*d*-like states, again in accordance with Khyzhun et al. experimental X-ray emission results [15]. The big difference between theirs and our theoretical calculations occurs in the region of the conduction band. We got gapped solution in spin-polarized FP LAPW calculations with the Cu 3d-like states in the lower part of the conduction band, while their solution has a large band gap of 1.9 eV already for the spin-restricted calculations. Although this gap value is in M.V. Lalić et al./Computational Materials Science 50 (2011) 1179-1186



Fig. 7. The components of imaginary part of dielectric tensor of the CuWO₄ as a function of incident radiation energy. They are interpreted in terms of calculated band structure shown in Fig. 5, where the band nomenclature 1–5 is defined. The LDA + U calculations are presented on the right graph.



Fig. 8. Components of the real part of dielectric tensor of the CuWO₄ compound. The LDA + U calculations are presented in the upper graph.

good agreement with the measured values of $E_{g} = 2.3$ [19] and E_{g} = 2.06 eV [35], we believe that their paramagnetic solution is not correct. The dominant contribution in the lower portion of the conduction band in our FP LAPW calculations comes from Cu 3d-like states (cf. Figs. 3b and 4b), while Khyzhun et al.s [15] obtained W 5d-like states in this region. These authors did not use the existing possibility of Wien computer code to calculate optical constants from their band structure results. The main difference of our calculated band structure comes from the position and width of Cu 3d-like bands. The Cu 3d-like states distribute not only in the valence band but also in the conduction band (in the immediate neighborhood of valence band top). Such the redistribution is crucial for the explanation of magnetic properties and the most stable state of this compound. An extra Cu 3d-like band appears in our spin-unrestricted calculations between the top of the valence band and the W 5d-like band centered at approximately 3.7 eV above the top of the valence band (both for AF LSDA and for AF LDA + U).



Fig. 9. Electron energy loss function of the CuWO₄ compound. LDA + *U* calculations are presented in the upper graph.

5. Summary and conclusions

The present first-principles LSDA and LDA + U calculations of CuWO₄ performed by means of FP LAPW method are the first spin-unrestricted calculations of this compound. We got the paramagnetic electronic energy bands of CuWO₄ that are completely different from the earlier results obtained for the same compound in the framework of the same FP LAPW band calculational method [15]. We have no explanation for this disagreement.

Despite that fact we were able to get the following results in agreement with the experiments:

- The most stable solution we obtained is the antiferromagnetic solution schematically represented in Fig. 1.
- Relatively small band gap of $E_g \sim 0.54$ eV was obtained in LSDA, while LDA + *U* method produced quite acceptable insulating solution with pronounced energy-gap value of ~1.5 eV (experiments are from 2. to 2.3 eV) [19,35].

M.V. Lalić et al./Computational Materials Science 50 (2011) 1179-1186

 We also got nice agreement with the experimental values of magnetic moments at Cu sites and O(3) oxygen atomic sites (closest to the Cu²⁺ ions in zigzag AF chains).

Additionally, we calculated a complex second-order dielectric tensor of CuWO₄ crystal, which gave the linear response of an electronic system to an applied external electric field in the x, y and zdirection, and presented the interpretation of the absorption spectrum in terms of calculated band structure. We also noticed some common features of our calculated optical properties of CuWO₄ crystal to the respective results for cadmium tungstate (CdWO₄) and cadmium molybdate (CdMoO₄) obtained earlier [14]. Detailed comparison of the present optical results with experiment will be possible only after the completion of single-crystal optical measurements. At the end we should say that the present first-principles FP LAPW calculations of CuWO₄ disclose that the O 2p-like states are the main contributors into the valence band of the compound. The new result is that the lower part of the conduction band is dominated by contributions of the Cu 3d-like states, while W 5*d*-like conduction states are centered about 3 eV above these copper like states. Additionally, the W 5d- and Cu 3d-like states contribute mainly at the bottom and at the top of the valence band of copper tungstate, respectively (cf. AF LSDA results in Fig. 3b), while significant portions of contributions of the O 2*p*-like states throughout the valence band region is characteristic of the electronic structure of CuWO₄. Noticeable spectral redistribution of Cu 3d-like states in LDA + U calculations is evident from Fig. 4b.

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1186