



(This is a sample cover image for this issue. The actual cover is not yet available at this time.)

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at SciVerse ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsciElectronic structure and optical properties of CuWO_4 : An ab initio studyM.V. Lalić^{a,*}, Z.S. Popović^b, F.R. Vukajlović^b^a Universidade Federal de Sergipe, Departamento de Física, P.O. Box 353, 49100-000 São Cristóvão, SE, Brazil^b "Vinča" Institute of Nuclear Sciences, University of Belgrade, 11001 Belgrade, Serbia

ARTICLE INFO

Article history:

Received 12 March 2012

Received in revised form 26 April 2012

Accepted 18 May 2012

Keywords:

Copper tungstate CuWO_4

Electronic structure

Spin-unrestricted

Band-structure calculations

Improved band gap

Optical properties

ABSTRACT

Electronic structure and optical properties of copper tungstate CuWO_4 were investigated using density functional theory with improved version of exchange potential suggested recently by Tran and Blaha (2009) [7] (TB-mBJ). The calculated band gap value is found to be in excellent agreement with the recent experimental results. The values of the magnetic moments at the Cu sites and O (3) oxygen atomic sites (closest to the Cu^{2+} ions in antiferromagnetic chains) are in good agreement with experiments also. The principal characteristic of the calculated electronic structure is significant rearrangement of the Cu 3d states near the valence band top as compared to our earlier PBE and PBE + *U* calculations of the same compound. This fact causes the different optical response of the CuWO_4 as well, which is analyzed and interpreted in terms of calculated electronic structure. A comparison of the calculated properties with available experimental data indicates that the TB-mBJ approach provides a better description of the electronic and optical properties of the CuWO_4 compound than the standard PBE and PBE + *U* approaches.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Long-lasting interest for metal tungstates and molybdates AWO_4 , or AMoO_4 ($A = \text{Ca, Cd, Ba, Zn, Mn, Fe, Co, Ni, Cu}$) comes from their scintillation properties which have provided applications in many fields of science and technology [1,2]. Therefore, for the metal tungstates the structural, optical and luminescence properties were of the primary concern (see for instance our previous work [3] and references cited therein). When metal tungstates contain 3d transition metals, electronic correlations produce unusual magnetic properties in respective layered materials. Thus, MnWO_4 is a typical magnetoelectric multiferroic, where spiral spin structure and ferroelectric polarization simultaneously appear [4], while the low symmetry Heisenberg antiferromagnet copper tungstate CuWO_4 led to several models of magnetic ordering and to a large number of independent superexchange intrachain and super-superexchange interchain interaction parameters [5,6]. We recently performed the first spin-unrestricted density functional theory (DFT) calculations of the electronic and magnetic properties of copper tungstate CuWO_4 , as well as its optical characteristics in the ultraviolet region up to 40 eV [3]. It is well known that for materials with the pronounced electronic correlations a DFT approach produces unsatisfactory band gap and often put cationic *d* bands inappropriately as compared to experiments. As a consequence, their interactions with the anion *p* valence bands are artificially

enlarged and these bands are falsifiable shifted extremely close to the conduction bands. The band gap problem was lately successfully tackled through the DFT calculations with use of a modified Becke-Johnson (mBJ) exchange potential as proposed by Tran and Blaha [7]. Several groups have used the new mBJ potential and got improved results for electronic properties for a wide range of different materials (for the recent estimation of merits and weaknesses of mBJ approach cf. [8]). In the present paper we have completed our previous investigations of electronic structure and optical properties of CuWO_4 [3], now on the basis of TB-mBJ exchange potential [7]. The mBJ calculations, when compared with our previous results, seem to lead to noticeably better agreement with known experimental facts.

2. Details of the calculation

The present calculations were performed in the framework of the full potential linearized augmented plane wave (FP LAPW) method using the WIEN2k code [9]. The crystal structure of copper tungstate CuWO_4 (taken from the experiment), the convergence of the basis set in real and reciprocal space, muffin-tin atomic radii and the self consistency criteria are the same as in our previous work [3]. Additionally, in the present work we took into account the spin-orbit coupling for heavy W atoms via second variational procedure, using scalar-relativistic eigenfunctions of the Kohn–Sham Hamiltonian as a basis. Further, we used the Tran–Blaha recipe, when applying a modified version of Becke and Johnson exchange potential [10] for the calculation of band

* Corresponding author. Tel.: +55 79 2105 6809; fax: +55 79 2105 6807.

E-mail address: mlalic@ufs.br (M.V. Lalić).

gaps and other electronic properties, as explained in the recent work of Koller et al. [8]. On the basis of calculated electronic structure (i.e. knowing the Kohn–Sham orbitals) of the CuWO_4 we computed the $\text{Im}(\epsilon_{\alpha\beta})$ up to incident radiation energy of $\hbar\omega = 40$ eV. The real part of dielectric tensor is then determined using Kramers–Kronig relation. Both, the real and imaginary parts of $\epsilon_{\alpha\beta}$ were calculated on a mesh of 112 $\mathbf{k}$ -points in the irreducible wedge of the first Brillouin zone, exactly as in the case of calculation of electronic structure. In the course of a presentation, for comparison purposes with our previous spin-unrestricted results [3], we shall use the abbreviations ‘PBE’ and ‘PBE + U ’. The first abbreviation denotes our previous FP LAPW results obtained by use of standard generalized gradient approximation (GGA) for the exchange–correlation as parametrized by Perdew et al. [11]. The second abbreviation denotes spin-polarized calculations with the Hubbard type Coulomb correction added (in the framework of so-called LDA + U method of Anisimov et al. [12]). This method cured, at least partially, the deficiencies of local density and local spin density approximation (LDA and LSDA) in treating Mott–Hubbard or charge transfer insulators.

2.1. Electronic structure

Fig. 1 shows the calculated density of electronic states (DOS) for the CuWO_4 in relatively large energy interval around the Fermi level.

The band marked as number 1 contains oxygen $2s^2$ -states (32 electrons). The broad band numbered as 2 is a mixture of oxygen $2p^4$ -states (64 electrons), Cu $4s^23d^8$ -states (40 electrons), W $5d^46s^2$ -states (24 electrons); (totally 128 electrons). The band number 3 contains the Cu $3d$ -states hybridized with some O $2p$ -states (4 electrons). The band number 4 contains empty Cu $3d$ -states (4 electrons, 2 for spin up and 2 for spin down), hybridized with some amount of neighboring O $2p$ -states. The band number 5 is composed of empty W $5d$ -states (24 electrons), hybridized with some amount of neighboring O $2p$ -states, while the band number 6 is a mixture of O's $2p$ -, Cu $4p$ - and W $6p$ -states. It should be noticed that elementary cell of the CuWO_4 contains four formula units. Thus, each of the four Cu sites contributes one d -electron into the band 3, and there is a place for another one within the empty band 4.

In the most recent experimental study of electronic and optical properties of the CuWO_4 [13] the authors deduce a scheme that shows the arrangement of the CuWO_4 principal bands (O $2p$, Cu $3d$, W $5d$) around the Fermi level. They conclude that the top of the valence band is composed of the O $2p$ - and the Cu $3d$ -states (with the dominance of the latter), while the conduction band bottom consists of the W $5d$ -states. None of the three types of calculations performed by our group (PBE and PBE + U in the Ref. [3], mBJ in the present work) succeeded to produce the W $5d$ -states

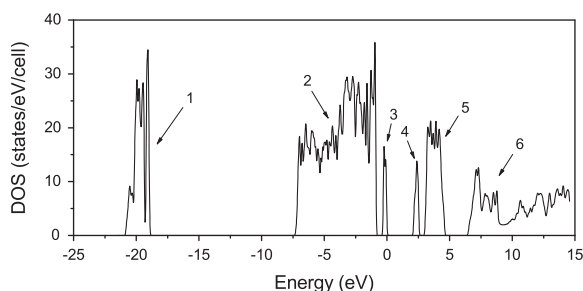


Fig. 1. CuWO_4 DOS calculated by the FP LAPW method with exchange–correlation effects simulated by modified Becke–Johnson potential [7]. Fermi level is positioned at zero eV.

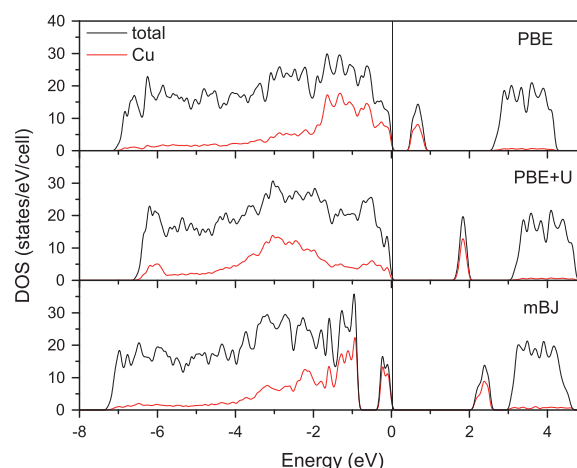


Fig. 2. The CuWO_4 electron density of states in the vicinity of the Fermi level, as calculated by the FP LAPW method using three types of exchange–correlation potentials: PBE (top), PBE + U (middle) and mBJ (bottom). The Cu d -states are presented by red curves. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

at the conduction band bottom: instead an empty Cu $3d$ -band would appear there. The theoretical band gap is therefore caused by splitting between the occupied and unoccupied Cu d -states. Since the transitions between them are forbidden that might cause the difficulties in experimental observation of the narrow empty Cu d -band below the wide W $5d$ -band. Relative positions of the occupied Cu $3d$ - and O $2p$ -states within the valence band are shown in the Fig. 2, which compares the electronic structure from the present calculations with the electronic structure calculated in the Ref. [3]. The occupied $5d$ -states of the W are widely scattered in the low-energy region of the valence band for all three types of calculations.

The Fig. 2 clearly exhibits the influence of different kinds of exchange–correlation potentials on rearrangement of the Cu $3d$ -states, and the latter can be checked to experimental data [13].

1. According to PBE calculations [3] the occupied Cu d -states are positioned mainly between -2 and 0 eV, at the very top of the valence band. This fact is in accordance with the recent experimental data [13]. On the other hand, the empty Cu d -states are within a narrow band centered at approximately 0.8 eV, making the band gap of solely 0.54 eV in strong disagreement with the experimental measurements [13,14].
2. The PBE + U calculations partially cure the band gap problem. The on-site effective Coulomb repulsion ($U_{\text{eff}} = 4$ eV), which we used in previous work [3], separates the centers of the occupied and empty d -states of Cu, leading to the gap value of 1.5 eV in better agreement with the experiment [13,14]. However, the occupied Cu d -states, are concentrated between -2 and -4 eV, and the very top of the valence band is mostly of the O $2p$ character. This fact does not agree with experimental data [13].
3. Finally, the present mBJ calculations seem to lead to the best agreement with known experimental facts. Obviously the Cu $3d$ -states dominate the very top of the valence band, while at the same time the calculated gap is very close to the experimental one.

Considering magnetic moments on the Cu and neighboring oxygens O (3), the mBJ results are similar to the values from the PBE and PBE + U calculations, while the gap size is in much better agreement with the experiment (see Table 1).

Table 1

Band gap sizes and the Cu and O (3) magnetic moments, as calculated by FP LAPW method with different exchange–correlation potentials, and compared with experimental data.

	PBE [3]	PBE + U [3]	mBJ	Expts.
μ_{Cu} [μ_B]	0.58	0.74	0.84	0.67 [15]
$\mu_{\text{O}(3)}$ [μ_B]	0.10	0.07	0.07	0.06 [15]
Gap size [eV]	0.54	1.50	2.09	2.0–2.3 [13,14]

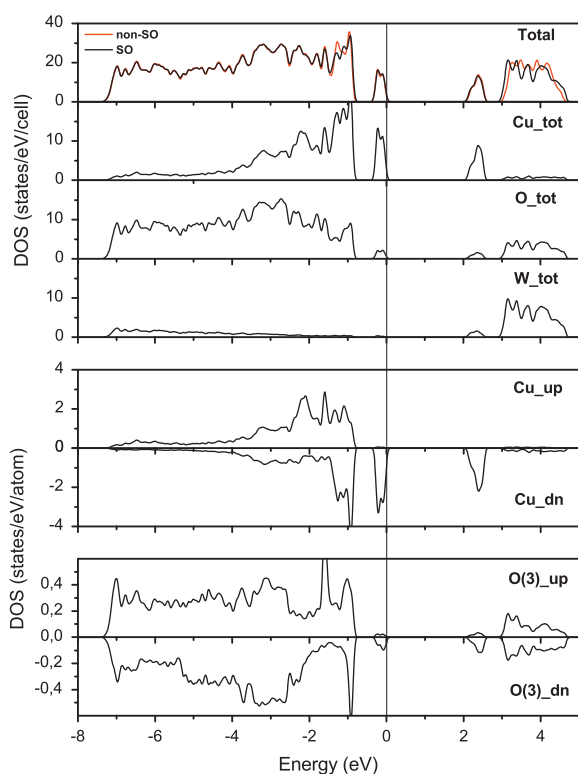


Fig. 3. The total and the partial DOS for CuWO_4 compound, resulting from the FP LAPW calculations with the spin-orbit coupling included and with the mBJ exchange–correlation potential. The graph on the top shows also the DOS resulting from calculations without spin-orbit coupling (red curve), for the reason of comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The details of the CuWO_4 electronic structure resulting from the mBJ calculations are presented in the Fig. 3. For easier comparison this figure has the same format as the figures of electronic structures from the PBE and PBE + U calculations [3]. The 4 graphs on the top of this figure present the PDOS contribution for each atomic specie in the unit cell, while the bottom graphs show the PDOS for one particular Cu atom (the one whose total spin is “up”) and its nearest O atom (labeled as the O(3)) to whom some amount of the magnetic moment is transferred.

The graph at the top of the Fig. 3 clearly shows that the spin-orbit coupling does not play important role for the CuWO_4 , at least not in the energy interval around the Fermi level. The position, width and form of the empty W p-states are practically unchanged in comparison with the calculations which did not take into account spin-orbit coupling on the W atoms. Further, the Fig. 3 shows that mBJ calculations produce significantly different band structure comparing to the PBE and PBE + U calculations [3]. The main difference arises from different energy arrangement of the Cu d-states. The copper ion is surrounded by oxygen octahedron which splits the Cu 3d energy levels onto t_{2g} and e_g states. With

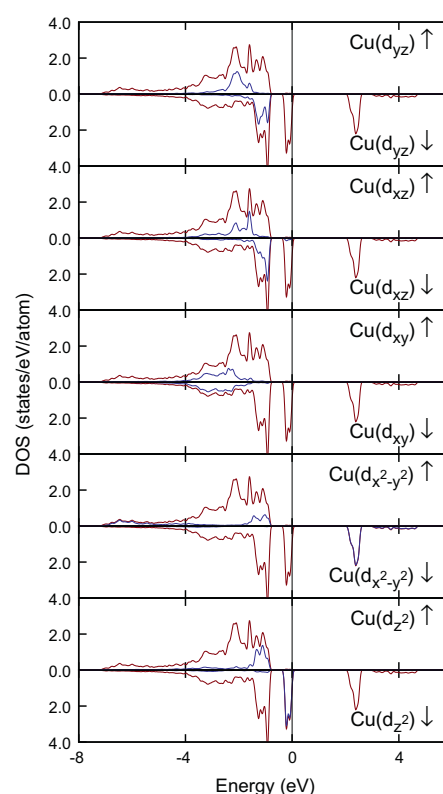


Fig. 4. Orbital decomposition of the Cu 3d-states in the CuWO_4 compound (blue curves). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a suitable choice of local coordinate system for Cu ion, having orthogonal axes pointing approximately towards neighboring oxygen atoms, t_{2g} and e_g states should be properly separated. The octahedron deformation is causing the further splitting of the Cu d-states. The mBJ calculations pronouncedly exhibit the splitting of these states, which was not the case with the PBE and PBE + U calculations. For the local coordinate system of the Cu atom (shown at the top part of the Fig. 5) we have nicely separated e_g and t_{2g} d-states and observed splitting between occupied d_{z^2} and unoccupied $d_{x^2-y^2}$ states in the spin down channel, as could be seen in the Fig. 4.

The splitting of the e_g states occurs because the oxygen octahedron around the Cu is irregular and elongated along the z' -axis. Since the oxygens near the local $x'y'$ plane are closer to the Cu than the oxygens along the z' -axis, the Cu $d_{x^2-y^2}$ states have their lobes more strongly overlapped with the O p-states than the d_{z^2} states. As a consequence, the d_{z^2} states decrease in energy forming the very top of the valence band, while the $d_{x^2-y^2}$ increase in energy, forming the very bottom of the conduction band. This situation is schematically presented in the Fig. 5.

2.2. Optical properties

The Fig. 6 shows the calculated imaginary part of dielectric function of the CuWO_4 compound along the different crystal directions (x, y, z directions are approximately parallel to the crystalline a, b and c directions respectively).

This figure shows anisotropic optical properties of the CuWO_4 . Optical absorption curves are interpreted in terms of electronic structure presented in the Fig. 1. Red curves represent absorption caused by electronic transitions from the occupied band 3 to the empty bands 4, 5 and 6. Since the CuWO_4 unit cell has the center of inversion, the Cu d–d transitions are improbable. Thus, the main

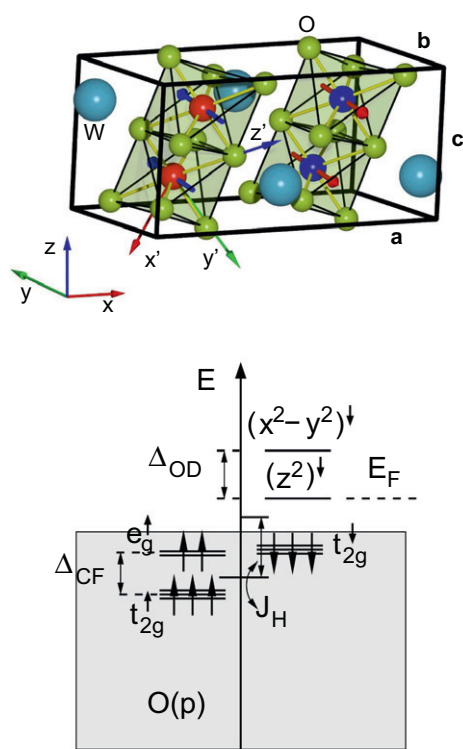


Fig. 5. The crystal structure of antiferromagnetic CuWO_4 with copper octahedra shown together with the schematic representation for energy bands obtained by TB-mBJ method. Shaded region stands for broad populated O-2p bands. The Cu-3d states are represented with lines. Around each Cu ion there is approximately an octahedron of oxygen atoms leading to a crystal field splitting (CF) between t_{2g} and e_g states. Octahedron deformation (OD) introduces further splitting between occupied d_{z^2} (below E_F) and unoccupied $d_{x^2-y^2}$ (above E_F) states in the spin down channel. On a top of that there is also a spin splitting (J_H).

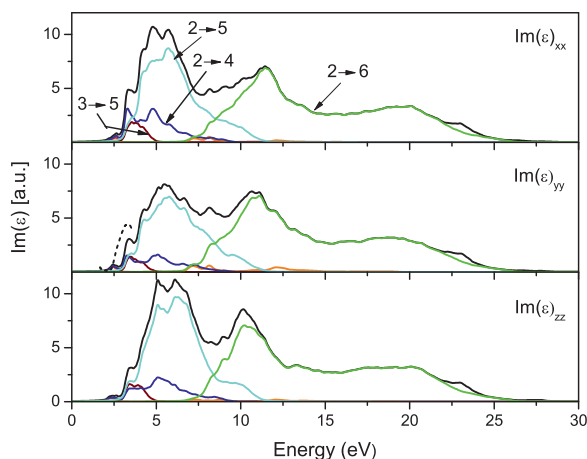


Fig. 6. Imaginary part of dielectric tensor of the CuWO_4 compound calculated along the three different crystal directions. It is directly proportional to the corresponding optical absorption of light polarized along these directions. For comparison, the experimental curve extracted from the Ref. [13], is shown in the middle graph (dashed line). The intensity of this curve is chosen arbitrarily. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

contribution comes from the transitions from the band 3 to the band 5 (electron transfer from the Cu to the O's that are the neighbors of both the Cu and the W). Blue curves represent light absorption caused by an electron transfer from the broad band 2 to the empty bands 4 and 5 (transitions from O's to the Cu within the CuO_6 octahedron, and transitions from O's to the W within the

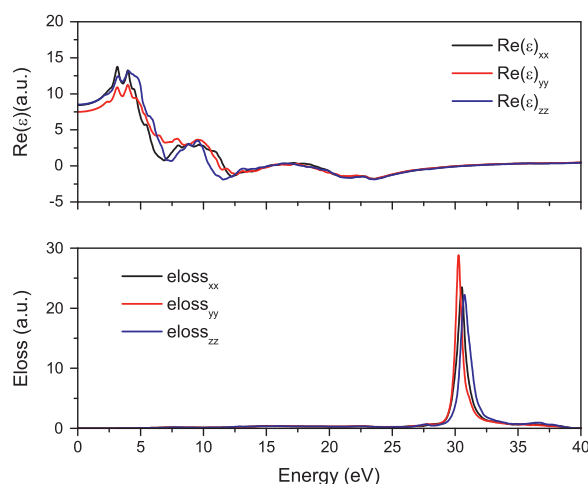


Fig. 7. Real part of dielectric tensor (upper graph) and electron energy loss function (lower graph) of the CuWO_4 compound, in arbitrary units. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

WO_6 octahedron respectively). Finally, the green curve represents the absorption caused by electronic transitions from the band 2 to the high energy conduction band number 5. In summary, it could be said that the first broad peak in CuWO_4 absorption spectrum is dominated by an electronic transfer from neighboring O's to the Cu and especially to the W atoms, while the first two shoulders of this peak are influenced by electron transfer from the occupied Cu d_{z^2} states to the empty Cu $d_{x^2-y^2}$ states (first shoulder, very small intensity) and to the empty p-states of neighboring O's (second shoulder).

Unfortunately, there are just a few published experimental papers that discuss the CuWO_4 absorption spectrum, and all of them study this spectrum only to maximum 3.5–4.0 eV [13,16,17]. As it can be seen from the Fig. 6, the pure material just starts to absorb photons at these energies, and it is very difficult to make more complete comparison with the theory. As an illustration we show the most recent experimental absorption curve of the CuWO_4 , extracted from the Ref. [13], in the middle graph of the Fig. 6. As the authors of the Ref. [13] did not specify how the light was polarized, the comparison of this curve with the $\text{Im}(\epsilon)_{yy}$ is only provisory. It seems that the position of the peak of the experimental curve coincides well with the position of the second shoulder of the theoretical curve, especially for the $\text{Im}(\epsilon)_{xx}$ and $\text{Im}(\epsilon)_{yy}$. However, in order to be completely sure of that, it is necessary to know how the absorption curve behaves for higher photon energies (i.e. whether it continues to decrease or starts to increase). Also, it seems that the first shoulder of the theoretical curve, which includes the Cu–Cu and the Cu–O electron transitions, was not recorded experimentally. Nevertheless, it is observed in the Ref. [16] at somewhat lower energies (between 1.0 and 1.5 eV) and attributed to the Cu–Cu electronic transitions influenced by the Jahn–Teller distortion of the CuO_6 octahedron. Finally, it is quite possible to confirm that the threshold of the calculated mBJ absorption spectrum agrees well with the threshold of the experimental spectrum. The above discussion offers indications that the mBJ calculations correctly describe the optical absorption spectrum of the CuWO_4 (at least in its near ultraviolet region), being more successful than the previous PBE or PBE + U calculations. However, further optical experiments in near and far ultraviolet region are necessary in order to completely reveal the electronic structure details and finally valorise the accuracy of various types of exchange–correlation terms in Kohn–Sham Hamiltonian. With a motivation to offer more theoretical predictions for such desired experiments, we show in Fig. 7 the calculated real part of dielectric tensor and electron energy loss spectrum (EELS) of the CuWO_4 along the three crystal

directions. Both $\text{Re}(\epsilon)$ and EELS resulted from the mBJ calculations present significant differences in comparison with the previous PBE and PBE + U calculations [3]. The electronic part of static dielectric constant, defined as $\text{Re}(\epsilon)$ at zero energy, has the following values: $\text{Re}(\epsilon)_{xx}(0) = 8.435$ (PBE: 13.059; PBE + U : 7.114), $\text{Re}(\epsilon)_{yy}(0) = 7.500$ (PBE: 9.243; PBE + U : 6.018), $\text{Re}(\epsilon)_{zz}(0) = 8.516$ (PBE: 9.614; PBE + U : 6.858). The prominent peak in the EELS, identified as the energy of plasmon oscillation (collective excitations of the electronic charge density in the material) is centered at the energy of approximately 31 eV, contrary to approximately 26 eV as calculated by the PBE and PBE + U [3].

3. Conclusions and summary

The merits of recent Tran–Blaha approach, which uses the modified Becke–Johnson exchange potential when calculating electronic structures, have been estimated for the case of complex scintillating antiferromagnetic tungstate compound CuWO_4 with the special emphasis to its optical properties. The calculated mBJ electronic structure and optical spectra seem to lead to the better agreement with the known experimental facts. The Tran–Blaha mBJ approach opens a gap almost in a perfect agreement with experiments [13,14] and also gives appropriate values for magnetic moments at Cu and O (3) sites. Additionally, it changes the character of electronic states near the valence band top. Namely, fully separated narrow band mostly of the Cu d_{z^2} + O p character were obtained there. The spectral redistribution of copper 3d states is the most important difference compared to earlier investigations of the same compound in the framework of PBE and PBE + U approaches [3]. This spectral redistribution of Cu d electronic states produces definite changes in the optical properties of CuWO_4 , which seems to lead to the better agreement with known experimental facts. The results presented here are also important in connection with the new findings [13] about the proclivity of tungstate CuWO_4 to act as a promising photo-catalyst for water splitting. The detailed knowledge of electronic dispersion close to the energy gap region, i.e., near the valence band maximum edge, around the bottom of the conduction band and the exact

composition of the conduction band, is of a crucial importance for these catalytic processes [13]. In order to completely reveal the electronic structure details and finally judge the accuracy of various types of exchange–correlation functionals further optical experiments in near and far ultraviolet region would be very welcomed.

Acknowledgments

This work has been supported by the Serbian Ministry of Education and Science under Grant No. 171033. M.V. Lalić gratefully acknowledges the CNPq (Brazilian funding agency) for financial support.

References

- [1] M. Kobayashi, Y. Usuki, M. Ishii, M. Itoh, M. Nikl, Nucl. Instrum. Meth. Phys. Res. A 540 (2005) 381–394.
- [2] V.B. Mikhailik, H. Kraus, J. Phys. D: Appl. Phys. 39 (2006) 1181–1191.
- [3] M.V. Lalić, Z.S. Popović, F.R. Vukajlović, Comput. Mater. Sci. 50 (2011) 1179–1186.
- [4] Kouji Taniguchi, Mitsuru Saito, Taka-hisa Arima, Phys. Rev. B 81 (2010) 064406–064411.
- [5] B. Lake, D.A. Tennant, R.A. Cowley, J.D. Axe, C.K. Chen, J. Phys.: Condens. Matter 8 (1996) 8613–8634.
- [6] Hyun-Joo Koo, Myung-Hwan Whangbo, Inorg. Chem. 40 (2001) 2161–2169.
- [7] F. Tran, P. Blaha, Phys. Rev. Lett. 102 (2009) 226401–226404.
- [8] D. Koller, F. Tran, P. Blaha, Phys. Rev. B 83 (2011) 195134–195143.
- [9] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Techn. Universitat Wien, Austria, 2001. ISBN 3-9501031-1-2.
- [10] A.D. Becke, E.R. Johnson, J. Chem. Phys. 124 (2006) 221101–221104.
- [11] J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [12] V.I. Anisimov, F. Aryasetiawan, A.I. Lichtenstein, J. Phys.: Condens. Matter 9 (1997) 767–808.
- [13] J.E. Yourey, B.M. Bartlett, J. Mater. Chem. 21 (2011) 7651–7660.
- [14] J. Ruiz-Fuertes, D. Errandonea, A. Segura, F.J. Manjón, Zh. Zhu, C.Y. Tu, High Pressure Res. 28 (4) (2008) 565–570.
- [15] J.B. Forsyth, C. Wilkinson, A.I. Zvyagin, J. Phys.: Condens. Matter 3 (1991) 8433–8440.
- [16] J. Ruiz-Fuertes, M.N. Sanz-Ortiz, J. Gonzalez, F. Rodriguez, A. Segura, D. Errandonea, J. Phys.: Conf. Ser. 215 (2010) 012048–012052.
- [17] S.K. Arora, T. Mathew, N.M. Batra, J. Phys. Chem. Solids 50 (1989) 665–668.