



Electronic structure of FeWO₄ and CoWO₄ tungstates: First-principles FP-LAPW calculations and X-ray spectroscopy studies

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ABSTRACT

Total and partial densities of states of the constituent atoms of iron tungstate, FeWO₄, and cobalt tungstate, CoWO₄, have been calculated using the first-principles self-consistent full potential linearized augmented plane wave (FP-LAPW) method. The results obtained reveal that the O 2p-like states are the dominant contributors into the valence band of the tungstates under consideration, whilst the bottom of the conduction band of FeWO₄ and CoWO₄ is dominated by contributions of the empty Fe 3d- and Co 3d-like states, respectively. The FP-LAPW data indicate that the O 2p-like states contribute mainly into the top of the valence band, with also significant contributions throughout the whole valence-band region, of FeWO₄ and CoWO₄ compounds. Other significant contributors into the valence-band region are the Fe 3d- and W 5d-like states in FeWO₄ and the Co 3d- and W 5d-like states in CoWO₄. All the above d-like states contribute throughout the whole valence-band region of the tungstates under consideration, however maximum contributions of the W 5d-like states occur in the lower, whilst the Fe (Co) 3d-like states in the upper portions of the valence band, respectively. To verify the above FP-LAPW data, the X-ray emission bands representing the energy distributions of mainly the valence O p-, Fe (Co) d-, Fe (Co) p- and W d-like states were measured and compared on a common energy scale with the X-ray photoelectron valence-band spectrum of the corresponding tungstate. The experimental data were found to be in good agreement with the theoretical FP-LAPW results for the electronic structure of FeWO₄ and CoWO₄ compounds.

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1. Introduction

Iron tungstate, FeWO₄, and cobalt tungstate, CoWO₄, belong to a fascinating family of wolframite-type materials which have highly potential and technological applications in many areas such as scintillation detectors, optical fibers, humidity sensors, photoanodes, phase-change optical recording devices, laser hosts, catalysts, pigments, etc. [1–7]. Additionally, wolframite-type tungstates are considered to be novel and commercially important materials due to their several encouraging properties, mainly high values of thermal stability, refractive indexes and X-ray absorption coefficients [8,9]. In particular, among wolframite-type tungstates, FeWO₄ and CoWO₄ have been intensively studied. FeWO₄ and CoWO₄ tungstates are well-known p-type semiconductors [10–12]. From experimental measurements [10,13], the energy band gap, E_g , equals 2.8 and 2.0 eV for CoWO₄ and FeWO₄, respectively. Estimations by Lacomba-Perales et al. [14] based on correlations between the ionic radius of the A²⁺ cation in a number of AWO₄ tungstates

reveal values of $E_g = 2.43$ eV for CoWO₄ and $E_g = 2.35$ eV for FeWO₄. Iron and cobalt tungstates were studied in Refs. [15–18] to explore potential applications of these materials in magnetic fields. As it has been established by Weitzel [15], the magnetic unit cell ($2a, b, c$) of CoWO₄ is twice of the chemical unit (a, b, c) and identical with that of FeWO₄. Additionally, the magnetic properties of CoWO₄ are proved to be symmetric with respect to three orthogonal twofold axes x , y , and z : the ‘magnetic’ axes x and z are inclined to the vectors a and c of the crystal unit cell at an angle of 40° in the ac -plane, whilst the magnetic axis y lies along the crystal (true) two-fold axis b [16].

FeWO₄ and CoWO₄ tungstates are isostructural compounds crystallizing in a monoclinic structure belonging to the $P2_1/a$ space group, with unit cell parameters $a = 4.753$ Å, $b = 5.720$ Å, $c = 4.968$ Å, $\beta = 90.1^\circ$ for FeWO₄ [19] and $a = 4.670$ Å, $b = 5.687$ Å, $c = 4.951$ Å, $\beta = 90.0^\circ$ for CoWO₄ [20]. The findings by the authors [19,20] are consistent with those derived by other investigators [21–25], as data listed in Table 1 reveal. In the structure of FeWO₄ and CoWO₄ tungstates, with two formula per unit cell, every metal atom is surrounded by six oxygen atoms: zigzag chains of oxygen octahedra coordinating the metal ions are aligned along the c axis [10]. Iron(cobalt), tungsten and oxygen atoms occupy the 2f, 2e and 4g sites, respectively. As an example, Fig. 1 shows the crystal struc-

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Table 1
Lattice parameters of iron and cobalt tungstates as determined by different authors (monoclinic structure, space group $P2_1/a$).

Tungstate	Lattice parameters				Reference
	a (Å)	b (Å)	c (Å)	β (°)	
FeWO ₄	4.753	5.720	4.968	90.1	[19]
CoWO ₄	4.670	5.687	4.951	90.0	[20]
CoWO ₄	4.667	5.681	4.947	90.0	[21]
CoWO ₄	4.666	5.680	4.948	90.0	[22]
FeWO ₄	4.7289	5.707	4.9630	90.091	[23]
CoWO ₄	4.9478	5.6827	4.6694	90.0	[24]
FeWO ₄	4.753	5.720	4.968	90.8	[25]

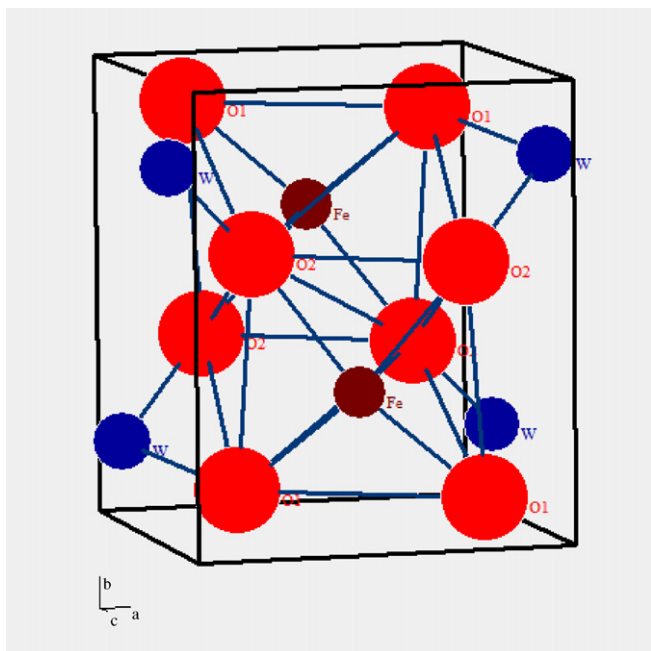


Fig. 1. Crystal structure of iron tungstate, FeWO₄: Fe, small brown balls; W, middle blue balls; O, large red balls. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

ture of FeWO₄. The existence of two non-equivalent positions for oxygen atoms (labelled as O1 and O2; Fig. 1) is characteristic of the structure of FeWO₄ and CoWO₄ tungstates. There are two tungsten atoms and one iron(cobalt) atom in the nearest arrangement of the O1 atoms, whilst one tungsten atom and two iron(cobalt) atoms are among the nearest neighbours of the O2 atoms [19,20].

Because technological applications of FeWO₄ and CoWO₄ tungstates are dependent significantly on their quality, different techniques are widely applied for obtaining these compounds in the form of either bulk single crystals (e.g., the flux method [10,13], chemical vapour transport [21]) or polycrystalline materials (e.g., a standard ceramic route [26], the co-precipitation method following by sintering at 500 °C for the formation of a monophasic compound [27]). With the development of nanotechnology, nanostructured transition metal tungstates have attracted much

Table 2
Positions of the constituent atoms of FeWO₄ and CoWO₄ used in the present FP-LAPW calculations.

Atom	Position of atoms in FeWO ₄ (Ref. [19])			Position of atoms in CoWO ₄ (Ref. [20])		
	x	y	z	x	y	z
Fe(Co)	0.5	0.6785	0.25	0.5	0.6712	0.25
W	0	0.1808	0.25	0	0.1773	0.25
O1	0.2167	0.1017	0.5833	0.2176	0.1080	0.9321
O2	0.2583	0.3900	0.0900	0.2540	0.3757	0.3939

more attention as compared with bulk materials [28,29]. Therefore, CoWO₄ nanoparticles were successfully synthesized at a low temperature of 270 °C by a molten salt method [29], by spraying the solution containing CoCl₂·6H₂O and Na₂WO₄·2H₂O on glass slides at 250–450 °C [7]. Using the same reaction reagents, Zhen et al. [24] have derived single-crystalline CoWO₄ nanorods with average diameter of 20 nm and lengths of 100–300 nm using the hydrothermal method, whilst the flower-like hollow cobalt tungstate nanostructures, which consist of CoWO₄ nanorods, have been synthesized by alcohol-thermal process at 180 °C employing a simple reaction between CoCl₂ and freshly prepared H₂WO₄ in a single alcohol system without any surfactants [30]. Hu et al. [31] have obtained FeWO₄ ferberite flowers using mixed FeCl₃ and WCl₆ at different ratios in a simple solvo-thermal process adopting cyclohexanol as the solvent. Iron and cobalt tungstate nanostructures, with average sizes of nanoparticles of about 150 and 70 nm in the case of FeWO₄ and CoWO₄, respectively, have been synthesized very recently in Ref. [32] employing the hydrothermal method and using sodium tungstate (Na₂WO₄·2H₂O), ferrous ammonium sulfate [(NH₄)₂Fe(SO₄)₂·6H₂O] and cobalt chloride (CoCl₂·6H₂O) solutions as precursors.

In a previous article [32], we have reported results of experimental studies of FeWO₄ and CoWO₄ tungstates employing X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES), and X-ray absorption spectroscopy (XAS) methods. The experimental results [32] indicate that the W 5d- and O 2p-like states contribute throughout the whole valence-band region of the FeWO₄ and CoWO₄ tungstates, however maximum contributions of the O 2p-like states occur in the upper, whilst the W 5d-like states in the lower portions of the valence band, respectively. Nevertheless, to the best of our knowledge, no theoretical band structure calculations have been made so far for FeWO₄ and CoWO₄. Therefore, in the present article we intend calculating the energy distribution of electronic states of different symmetries of the constituent atoms of iron and cobalt tungstates. With this aim, we have employed possibilities of the full potential linearized augmented plane wave (FP-LAPW) method as incorporated in the WIEN97 code [33] in order to study total density of states (DOS) and partial densities of states of FeWO₄ and CoWO₄ tungstates. Additionally, some new XES results concerning the energy distribution of the valence states of iron and cobalt in the tungstates under consideration will be reported in the present article.

2. Computational details

Calculations of the electronic structure of FeWO₄ and CoWO₄ tungstates have been carried out using the first-principles self-consistent FP-LAPW method with the WIEN97 code [33]. In the present FP-LAPW calculations, lattice parameters $a=4.753$ Å, $b=5.720$ Å, $c=4.968$ Å, $\beta=90.1^\circ$ for FeWO₄ and $a=4.670$ Å, $b=5.687$ Å, $c=4.951$ Å, $\beta=90.0^\circ$ for CoWO₄ as well as positions of the constituent atoms of the tungstates under study (Table 2) have been chosen in accordance with the crystallography data determined for the compounds in Refs. [19,20]. For calculations of the exchange-correlation potential, the generalized gradient approximation (GGA) by Perdew et al. [34] has been used. The *muffin-tin*

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