

# ELECTRONIC STRUCTURE OF $\text{K}_2\text{SO}_4:\text{Cu}^{2+}$ (3%) CRYSTALS

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## Introduction

Crystalline materials are widely used in modern industry as active and passive elements of optical, acousto-optical, opto-electronic and linear optical devices. The great interest is attracted to their anisotropic properties, which can not be obtained in isotropic media. The anisotropic effects find practical application and also are interesting from the fundamental point of view. An important task for researches is to modify materials in order to change their physicochemical properties in a way that will improve certain desired properties or make the materials more resistant to external factors. One of the ways to modify crystalline materials is the introduction of various impurities into structure in the process of their synthesis [1].

Perspective from the upper consideration are anisotropic dielectric crystals of  $\text{A}_2\text{BX}_4$  class. For these, interesting results are reported on a study of influence of impurities on the thermal, luminescence and optical properties, in particular in  $\text{LiNH}_4\text{SO}_4$  [2],  $\text{LiKSO}_4$  [3],  $\text{Li}_2\text{SO}_4$  [4],  $\text{LiNaSO}_4$  [4],  $\text{K}_2\text{SO}_4$  [5] crystals. Crystals of this group are characterized by a variety of structural transformations which provide possibilities for significant changes of their physical properties in particular under the influence of the external fields [6-8].

The work is devoted to the study of the influence of doping by transition metal  $\text{Cu}^{2+}$  ions on the crystal structure, band-energy structure of the  $\text{K}_2\text{SO}_4$  crystal as a representative of  $\text{A}_2\text{BX}_4$  group crystals. The work combines both the experimental results and theoretical ab initio calculations.

## Method of crystal growth and the experimental techniques

The PS crystals were obtained using slow-evaporation method at constant temperature from an aqueous solution. As initial reagents the  $\text{K}_2\text{SO}_4$  and copper

sulfate pentahydrate  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ , the mass of which was 3% of the total mass of dissolved salts were used. The crystals obtained during 25 days revealed good optical quality and had shape of elongated prism with dimensions about  $9 \times 8 \times 15$  mm.

The structure of crystals was investigated by X-ray powder diffraction using an automatic STOE STADI P diffractometer (manufacturer STOE & Cie GmbH, Germany) with linear position-precision detector (PSD) according to the modified Guinier geometry scheme. The main parameters were as follows: Cu  $K\alpha_1$ -radiation source; detector – concave Ge-monochromator (111) of a Johann type; scanning –  $2\theta/\omega$ ;  $2\theta$  angles interval  $10.000 \leq 2\theta \leq 110.305^\circ$   $2\theta$  with increments of  $0.015^\circ$   $2\theta$ ; detector step  $0.480^\circ$   $2\theta$ ;  $U = 40$  kV;  $I = 37$  mA.

XPS core-level and valence-band spectra of the  $\text{K}_2\text{SO}_4$ :  $\text{Cu}^{2+}$ (3%) and pure  $\text{K}_2\text{SO}_4$  crystals were measured using the UHV-Analysis-System (SPECS, Berlin, Germany). The XPS spectra were excited with Mg  $K\alpha$  X-ray source ( $E = 1253.6$  eV). The energy scale of the UHV-Analysis-System for the present XPS measurements was calibrated using metallic pure gold and copper samples following the technique [6]. Since the XPS technique is very sensitive to charging effects, the later were taken into account using the C 1s line as a reference: its binding energy was assumed to be equal to 284.6 eV as recommended for such kind of materials [7,8]. In addition, the XES O  $K\alpha$  band (transition  $\text{K} \rightarrow \text{L}_{\text{II,III}}$ ) representing energy distribution of O  $2p$  electronic states was derived with RSM-500 monochromatic spectrometer equipped with a reflecting mirror (radius of curvature of about 2 m) and a grating (radius of curvature of about 6 m, 600 grooves per mm).

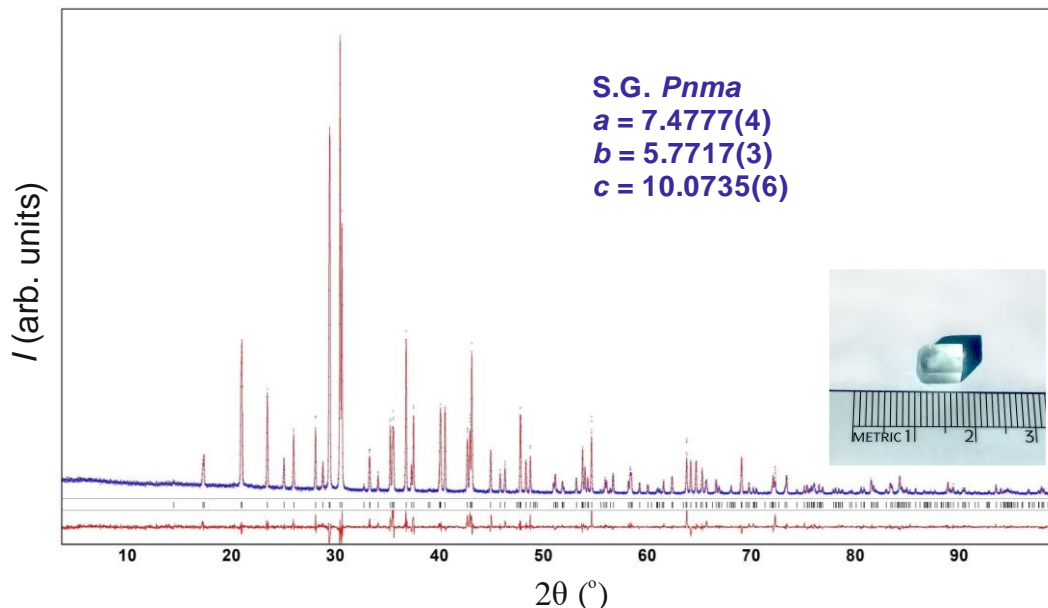
## Calculation technique

The calculations of the band-energy structure of PS:  $\text{Cu}^{2+}$  (3%) crystals were performed using the density functional theory (DFT). The exchange-correlation energy which describes the quantum effects in electron interaction was chosen in a form of a generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) parameterization. The chosen cut-off energy of plane waves was equal to  $E_{\text{cut-off}} = 360$  eV. The valence electrons used for the calculations had the following configuration: K  $3s^2 3p^6 4s^1$ ; S  $3s^2 3p^4$ ; O  $2s^2 2p^4$ ; and Cu  $3d^{10} 4s^1$ . Before the principal properties calculations the geometry optimization of the crystal structure was performed. The convergence parameters used during the structure optimization procedure were as follows: convergence of total energy  $5 \times 10^{-6}$  eV/atom, maximum force  $1 \times 10^{-2}$  eV/Å, maximum pressure  $3 \times 10^{-2}$  GPa and maximum displacement  $3 \times 10^{-4}$  Å.

## Crystalline structure of copper-doped potassium sulfate crystals

The X-ray phase analysis of the specimen revealed its single-phase character identified as the phase of the  $\text{K}_2\text{SO}_4$  compound (a mineral with own arcanite

structural type in  $\beta$ -modification, which is stable below  $\sim 840$  K up to room temperature).



**Fig. 1.** Experimental (blue points), theoretical (red solid line) and difference (red line below) diffraction patterns of the specimen  $\text{K}_2\text{SO}_4:\text{Cu}^{2+}$  (3 %), together with marks of the Bragg reflexes for phase of the refined composition of  $\text{K}_{1.84(1)}\text{Cu}_{0.08(1)}\text{SO}_4$ .

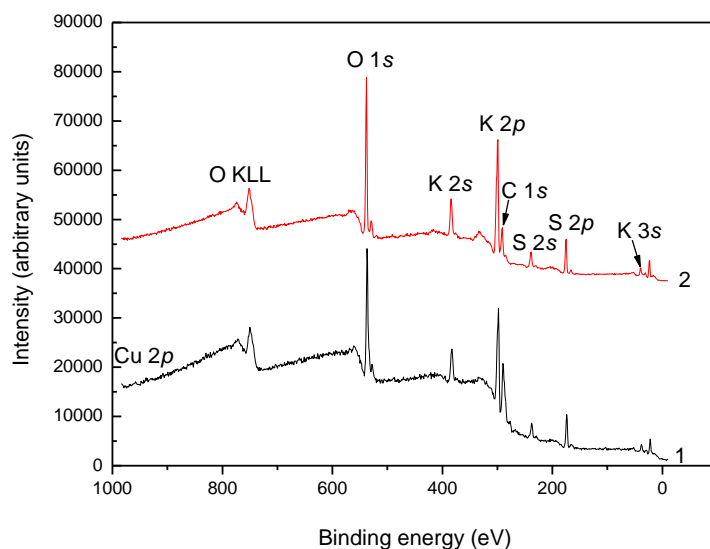
The refined composition of the phase is  $\text{K}_{1.84(1)}\text{Cu}_{0.08(1)}\text{SO}_4$ , space group *Pnma*,  $Z = 4$ , unit cell parameters:  $a = 7.4777(4)$ ,  $b = 5.7717(3)$ ,  $c = 10.0735(6)$  Å, the volume of the unit cell  $V = 434.76(7)$  Å<sup>3</sup>, the reliability factors of the crystal structure refinement  $R_I = 0.0754$ ,  $R_p = 0.1109$ ,  $R_{wp} = 0.1328$ ,  $R_{exp} = 0.0933$  (Table 1).

**Table 1.** Coordinates, isotropic displacement parameters of atoms  $B_{iso}$ , and position occupancy factors  $G$  in the structure of  $\text{K}_{1.84(1)}\text{Cu}_{0.08(1)}\text{SO}_4$  compound

Atom	Wyckoff position	$x$	$y$	$z$	$B_{iso}, \text{Å}^2$	$G$
K1	$4c$	0.1727(3)	1/4	0.4112(3)	1.45(8)	0.939(4)
K2	$4c$	0.4894(3)	1/4	0.7020(2)	0.90(7)	0.903(4)
S	$4c$	0.2308(3)	1/4	0.0804(3)	1.70(9)	1
O1	$4c$	0.0351(7)	1/4	0.0818(6)	2.1(2)	1
O2	$4c$	0.7927(9)	1/4	0.5626(6)	2.0(3)	1
O3	$8d$	0.3011(6)	0.0363(7)	0.1472(4)	1.7(2)	1
Cu	$8d$	0.110(7)	0.083(3)	0.257(5)	1.8(2)	0.040(2)

## XPS characterization of the $\text{K}_2\text{SO}_4$ : $\text{Cu}^{2+}$ (3%) and pure $\text{K}_2\text{SO}_4$ crystals

The survey XPS spectra of pristine surfaces of  $\text{K}_2\text{SO}_4$ :  $\text{Cu}^{2+}$ (3%) and pure  $\text{K}_2\text{SO}_4$  crystals are presented in Fig. 2. It is obvious that all the spectral features are well ascribed to the core-levels or Auger lines of the atoms composing the crystals under study. The exception is only carbon, which presence is detected via the C 1s line, and it is due to surface adsorbed hydrocarbon species as a result of exposure of the crystals to laboratory air. However, its content in the both crystals under study is minor as Fig. 2 presents.

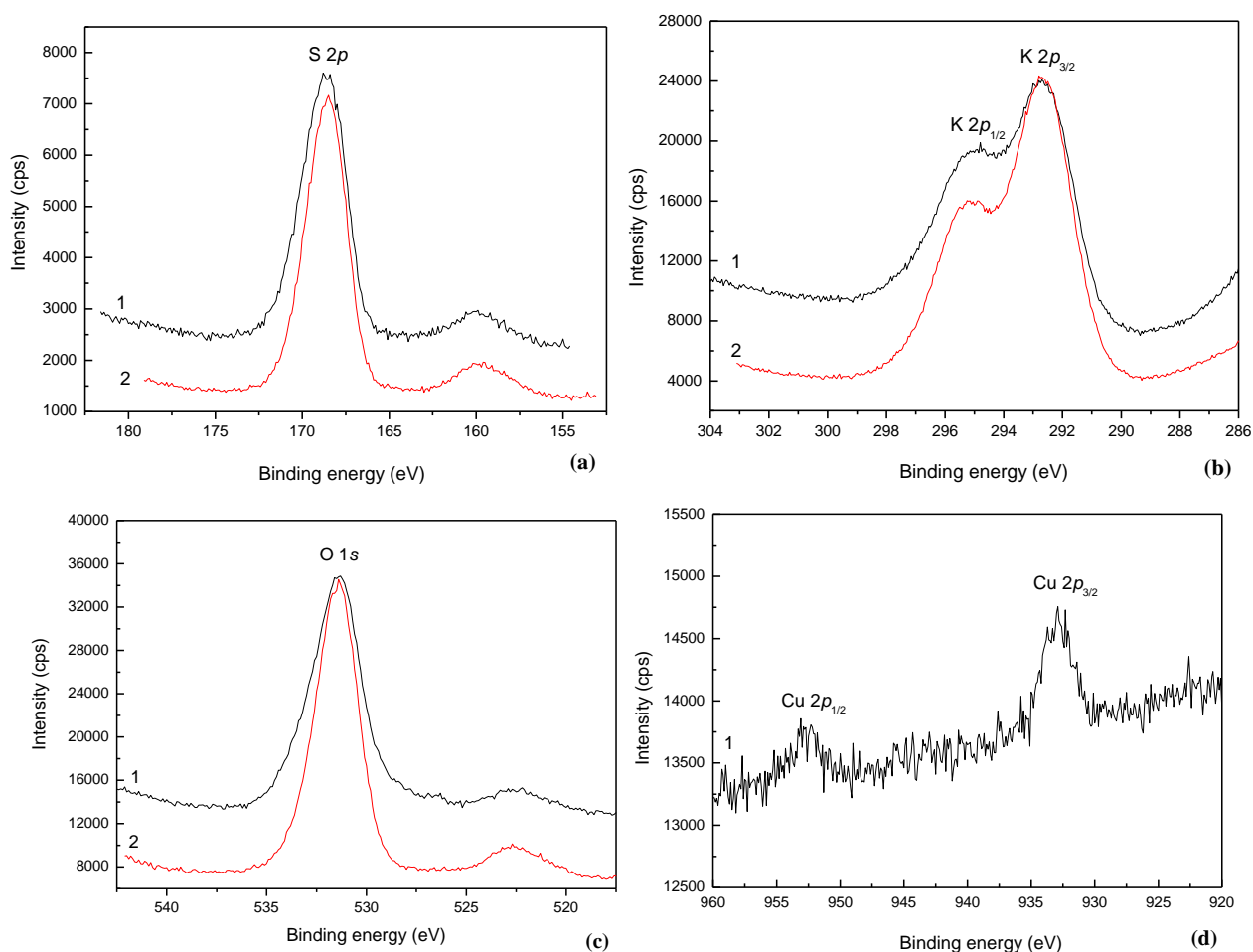


**Fig. 2.** Survey XPS spectra of pristine surfaces of (1)  $\text{K}_2\text{SO}_4$  crystal doped with 3% of copper and, for comparison, (2) pure  $\text{K}_2\text{SO}_4$ .

Detailed XPS core-level spectra of pristine surfaces of  $\text{K}_2\text{SO}_4$  crystal doped with 3% of copper and, for comparison, of pure  $\text{K}_2\text{SO}_4$  are presented in Fig. 3, while their binding energies are tabulated in Table 3. It is obvious that no significant changes in the binding energies (BEs) of core-level electrons associated with potassium, sulfur, and oxygen are detected when going from  $\text{K}_2\text{SO}_4$  to  $\text{K}_2\text{SO}_4$ :  $\text{Cu}^{2+}$ (3%). Probably, this fact is because of the small amount of copper additives in the case of the  $\text{K}_2\text{SO}_4$ :  $\text{Cu}^{2+}$ (3%) sample under consideration. In the sequence  $\text{K}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4$ :  $\text{Cu}^{2+}$ (3%) we do not detect any substantial changes in the shapes of the XPS core-level spectra (Fig. 3) as well as in the energy distribution of the valence electrons in the valence-band region (Fig. 4). As can be seen from Fig. 8, only a minor sub-band marked as ‘a’ looks to appear in the case of the  $\text{K}_2\text{SO}_4$ :  $\text{Cu}^{2+}$ (3%) sample in the near Fermi region. Its formation, as will be shown later by band-structure calculations, can be associated with contributions of Cu 3d states.

Comparison with literature data [9,10] indicates that charge state of sulfur atoms in  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ :  $\text{Cu}^{2+}$ (3%) is close to that in  $\text{NaSO}_4$  and  $\text{FeSO}_4$  ( $\text{BE}(\text{S } 2p) = 168.5 \text{ eV}$  [9]). Further, charge state of potassium in the compounds under study is

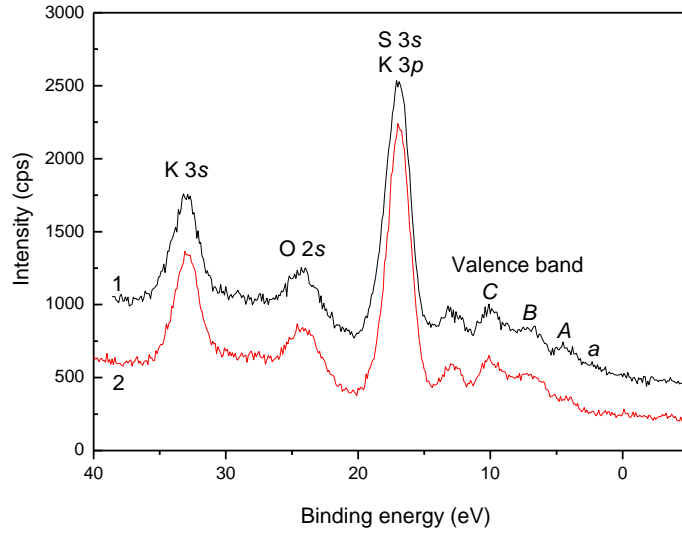
close to that in  $\text{KNO}_3$  ( $\text{BE}(\text{K } 2p_{3/2}) = 292.6\text{--}292.7 \text{ eV}$  [9,10]), while charge state of oxygen is similar to that in  $\text{KOH}$  ( $\text{BE}(\text{O } 1s) = 531.5 \text{ eV}$  [9]). Furthermore, binding energy of copper in  $\text{K}_2\text{SO}_4$ :  $\text{Cu}^{2+}(3\%)$  (Table 2) is close to that in  $\text{Cu}_2\text{O}$  [9].



**Fig. 3.** Detailed XPS core-level spectra of pristine surfaces of (1)  $\text{K}_2\text{SO}_4$  crystal doped with 3% of copper and, for comparison, (2) pure  $\text{K}_2\text{SO}_4$ : (a)  $\text{S } 2p$ , (b)  $\text{K } 2p$ , (c)  $\text{O } 1s$ , and (d)  $\text{Cu } 2p$ .

**Table 2.** Binding energy values ( $\pm 0.1 \text{ eV}$ ) of  $\text{K}_2\text{SO}_4$  crystal doped with 3% of copper and, for comparison, of pure  $\text{K}_2\text{SO}_4$

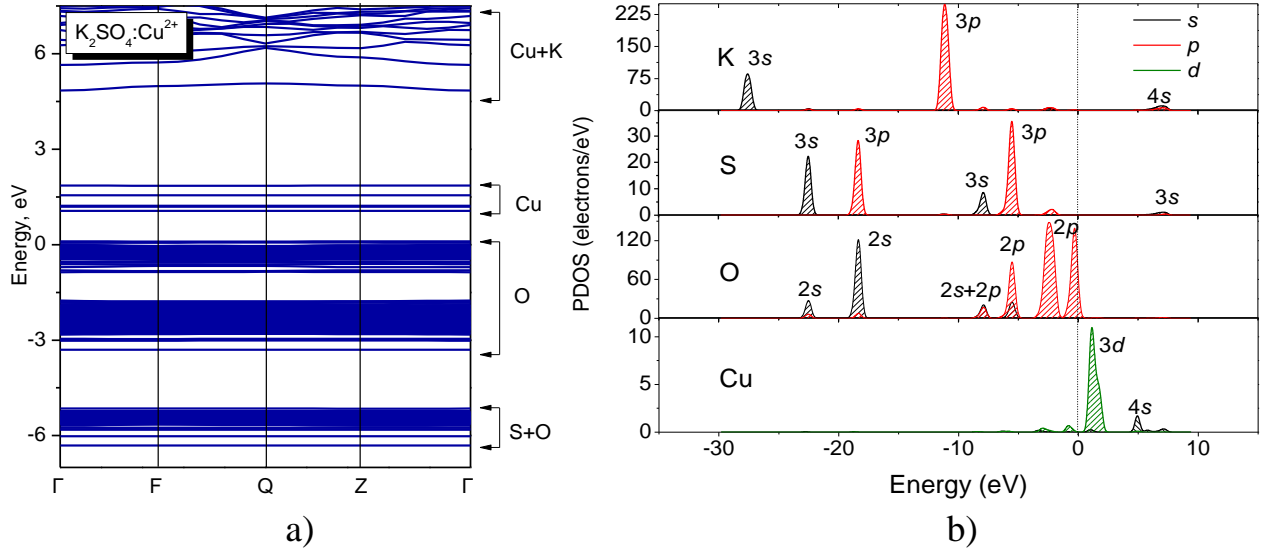
Core-level	$\text{K}_2\text{SO}_4$ : $\text{Cu}^{2+}(3\%)$	$\text{K}_2\text{SO}_4$
$\text{O } 2s$	24.3	24.3
$\text{K } 3s$	33.0	33.0
$\text{S } 2p$	168.7	168.6
$\text{K } 2p_{3/2}$	292.7	292.7
$\text{K } 2p_{1/2}$	295.0	295.1
$\text{O } 1s$	531.4	531.5
$\text{Cu } 2p_{3/2}$	932.9	—
$\text{Cu } 2p_{1/2}$	952.6	—



**Fig. 4.** XPS valence-band spectra of pristine surfaces of (1)  $\text{K}_2\text{SO}_4$  crystal doped with 3% of copper and, for comparison, (2) pure  $\text{K}_2\text{SO}_4$ .

### Band-energy structure of $\text{K}_2\text{SO}_4:\text{Cu}^{2+}$ crystals

The electronic structure of pure PS crystal is well studied by now. In particular, some articles are devoted to the calculation of the band structure using augmented spherical-wave (ASW) method [11] and DFT-PBE method [12]. The electronic band structure  $E(\mathbf{k})$  of doped  $\text{K}_2\text{SO}_4:\text{Cu}^{2+}$  is calculated in this work for the first time within DFT GGA-PBE method and built in special points and along high symmetry lines of BZ (Fig. 5). Obtained band structure is quite similar to the reported for pure crystal in [11] and [12]. The electronic states are generally very flat (possess low dispersion). The conduction band levels have a higher dispersion that indicates the lower effective mass of charge carriers and higher carriers' mobility. The valence band consist of few narrow subbands separated by the gaps. These subbands can provide additional electron transitions between them. Such transitions can be interesting for core-valence luminescence. The energy value to 0 eV corresponds to valence band maximum. The band gap is formed by the valence band maximum and conducting band minimum located at BZ center. The value of band gap is equal to 5.8 eV. Few electronic levels are localized in the band gap region. These levels correspond to the impurity electronic states of  $\text{Cu}^{2+}$  ions. Detailed analysis of fig. 5 reveal a narrow bundle of five energy levels corresponding to the copper  $d$ -electrons and located within the energy range of 1.06-1.8 eV. In the tetrahedral surrounding the electronic  $d$ -level splits into two  $e$  and  $t_2$  energy levels. The  $e$ -level is double degenerated, while  $t_2$  is triple degenerated energy level, which lay higher than  $e$ -level in the energy scale on about  $10Dq$ . Thus, the observed split of electronic  $d$  states into more than two sublevels appears due to removing of the degeneracy by a low-symmetry ligand field.

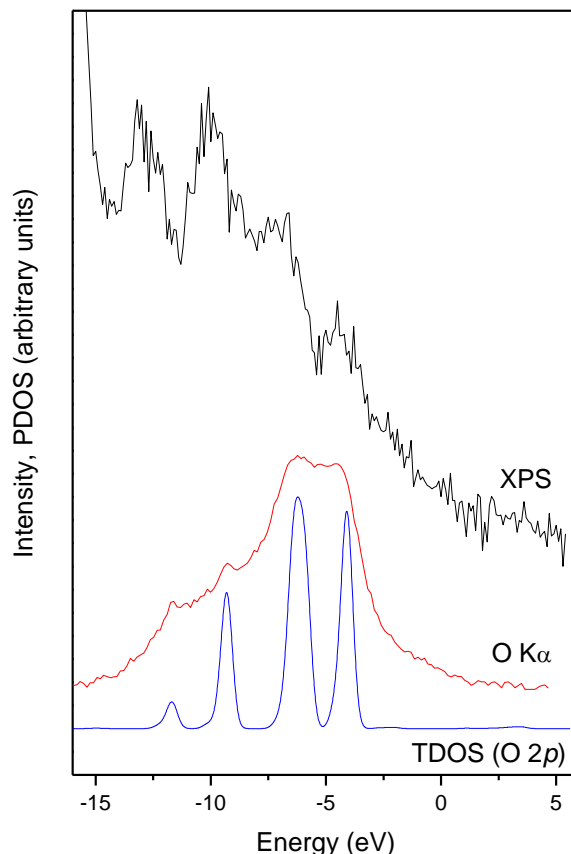


**Fig. 5.** The band structure (a) and partial density of states (b) of  $\text{K}_2\text{SO}_4:\text{Cu}^{2+}(3\%)$  crystals calculated using GGA functional.

Figure 5 shows the partial density of states constructed from individual contributions of atoms and allows to identify the origin of electronic levels. As can be seen from the figure, the top of the valence band, coincided with 0 eV, is composed by oxygen  $p$ -states, which are represented by electronic levels from 0 to  $-5$  eV. Lower levels from  $-6$  to  $-8$  eV are formed by the mixture of  $2p$   $3p$  and  $2s$   $3s$  states of oxygen and sulfur. Observed strong peak at  $-12$  eV corresponds to  $3p$  potassium atoms. Two peaks at  $-18.5$  eV and  $-22.5$  eV are formed by the  $2s$  states of oxygen hybridized with  $3p$  and  $3s$  states of sulfur respectively. At  $-28$  eV the single  $3s$  band of potassium is observed. The conduction band minimum originates from the  $3s$  and  $4s$  electrons of sulfur and potassium atoms. Near the bottom of conduction band the localized  $4s$  level of Cu is located. Additionally, the split  $3d$  levels of copper are located at 1.06-1.8 eV. The calculated band structure describes the general features of pure PS crystal reported in [11] and [12].

Regarding the band-structure calculations of  $\text{K}_2\text{SO}_4:\text{Cu}^{2+}(3\%)$  suggesting that O  $2p$  electronic states contribute mainly at the top of the valence band of this compound, they are supported experimentally when matching the XPS valence-band spectrum and X-ray emission O  $K\alpha$  band of the Cu-doped  $\text{K}_2\text{SO}_4$  crystal on a common energy scale with the curve of partial O  $2p$  density of states of this compound (Fig. 6). It is worth mentioning, that for good correspondence of the energy positions of the experimental and theoretical fine-structure features, the curve of partial O  $2p$  DOS was shifted away from the Fermi energy position by 3.8 eV as recommended to do in the case of comparison of the XPS and XES data with theoretical PDOS curves for semiconductors and insulators [13]. As can be seen from Fig. 12, the shape of XES O  $K\alpha$  bands is in reasonable agreement with the theoretical predictions regarding the energy positions of the fine-structure features and it is

apparent that the main contributions of O  $2p$  states in  $\text{K}_2\text{SO}_4: \text{Cu}^{2+}(3\%)$  are detected at the top of the valence band of this compound.



**Fig. 6.** The XPS valence-band spectrum and X-ray emission O  $K\alpha$  band of the Cu-doped  $\text{K}_2\text{SO}_4$  crystal matched on a common energy scale with the curve of partial O  $2p$  density of states of this compound.

## Conclusions

The crystal of potassium sulfate doped with copper (3%) was synthesized. Structural studies has shown that the crystalline structure of a  $\text{K}_2\text{SO}_4: \text{Cu}^{2+}$  (3%) crystal can be considered as a result of a multiple heterovalent substitution of  $2\text{K}^+$  by  $\text{Cu}^{2+}$  ions in the structure of potassium sulfate with the formation of a  $\text{K}_{1.84(1)}\text{Cu}_{0.08(1)}\text{SO}_4$  compound.

The calculated band-energy structure of  $\text{K}_2\text{SO}_4: \text{Cu}^{2+}(3\%)$  do not differ significantly from that of pure potassium sulfate. The main difference is found in the presence of split levels of Cu  $d$ -electrons in the band gap, the degeneration of which is reduced due to the action of the crystal field. Minor contributions of Cu states are observed at the top levels of valence band and bottom levels of conduction band. The top of the valence band of crystal is formed by oxygen  $p$ -states and the bottom of the conduction band is formed by  $s$ -states of potassium and  $s$ -states of copper. Regarding the band-structure calculations of  $\text{K}_2\text{SO}_4: \text{Cu}^{2+}(3\%)$  suggesting that O  $2p$  electronic states contribute mainly at the top of the valence band of this compound, they are supported experimentally when matching the XPS valence-band spectrum and X-ray



emission O K $\alpha$  band of the Cu-doped K<sub>2</sub>SO<sub>4</sub> crystal on a common energy scale with the curve of partial O 2*p* density of states of this compound.

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