

## CONDENSED-MATTER SPECTROSCOPY

# Local Surrounding of Vanadium Atoms in $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$ : X-Ray Absorption Spectroscopy Analysis<sup>1</sup>

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**Abstract**—In the present work local surrounding of vanadium atoms in layered copper-chromium disulfides  $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$  is investigated using high-resolution X-ray absorption spectroscopy above vanadium K-edge. Based on experimental and theoretically simulated spectra comparison it is shown that vanadium atoms replace chromium ones even at high concentrations of vanadium and that they are in 3+ oxidation state.

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## INTRODUCTION

Inorganic compounds with quasi-two-dimensional structure are of fundamental and practical interest nowadays. High temperature superconductors based on copper oxides and thermoelectric materials based on  $\text{Na}_x\text{CoO}_2$  or  $\text{Ca-Co-O}$  are examples of such materials. Another example is a superionic conductor at high temperatures copper chromium disulfide  $\text{CuCrS}_2$  [1]. Figure 1 shows  $\text{CuCrS}_2$  crystal fragment, in which  $\text{CrS}_2$  layers are separated by copper atoms.  $\text{CrS}_2$  layers are connected with weak Van-der-Waals forces. Copper ions in Van-der-Waals gap are weakly connected to sulfur atoms and occupy octahedral and tetrahedral positions. [1]. Phase transition temperature may be lowered by doing of  $\text{CuCrS}_2$  with vanadium. Due to its electrical properties  $\text{CuCrS}_2$  is possible to be applied in thermoelectric devices [2, 3]. When being doped with vanadium  $x = 0.2$   $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$  changes its state from ordered antiferromagnetic to spin-glass state [4]. Copper chromium disulfides were studied previously by electronic paramagnetic resonance [5], infrared spectroscopy, Raman spectroscopy [6], X-ray and neutron diffraction [7], X-ray photoelectron spectroscopy and X-ray emission spectroscopy [8–10]. X-ray absorption near-edge structure spectroscopy (XANES-spectroscopy) is sensitive to local surrounding of the absorbing atom and its oxidation state [11]. Previously XANES investigations were done only for samples with low concentration of vanadium ( $x = 0, 0.15, 0.20$ ) [12]. In the present work, XANES studies were carried out for  $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$  samples with  $x$  up to  $x = 0.40$ .

## METHODS

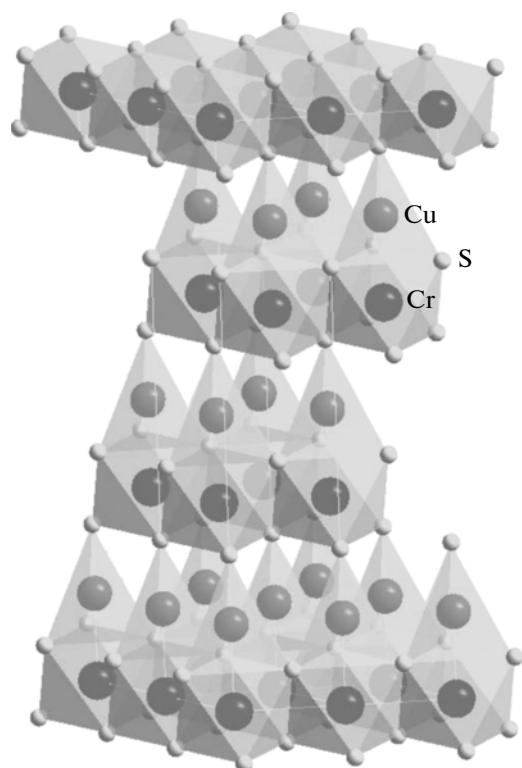
Geometry optimization of  $\text{CuCrS}_2$  structure in the presence of vanadium was carried out within the bounds of Density Functional Theory in plane wave approximation implemented in Wien2k code [13]. Exchange-correlation potential PBE96 was used, supercell size was  $2 \times 2 \times 1$ ; the amount of  $k$ -points was 150. The amount of plane waves is determined by the ratio:  $r_{\min}k_{\max} = 6$ , where  $R_{\min} = 1.86 \text{ \AA}$ —the radius of the smallest atom.

XANES spectra were calculated using self-consistent multiple scattering method realized in FEFF 8.4 code [14]. Hedin-Lundquist exchange-correlation potential was used. Full multiple scattering cluster radius was chosen to be equal  $10 \text{ \AA}$  after testing for convergence.  $4 \text{ \AA}$  cluster was used for the calculation of self-consistent potential.

## EXPERIMENT

Samples were synthesized using metal oxides of 99.99% purity. Products of thermal decomposition of  $\text{NH}_4\text{CNS}$  were used as sulfonators; argon of high purity was used as carrier gas. Oxides were placed into quartz tube; the air in this tube was displaced by argon and products of  $\text{NH}_4\text{CNS}$  decomposition. After that the mixture was heated up to  $800\text{--}1000^\circ\text{C}$ . The completeness of sulfiding was controlled by weighting of the samples and by analysis using DRON-3 diffractometer. Overall synthesis duration was 50 hours. The samples synthesized are fine-disperced powders (average grain size is about  $5 \mu\text{m}$ ) [5, 6, 8–10, 12].

<sup>1</sup> The article was translated by the authors.

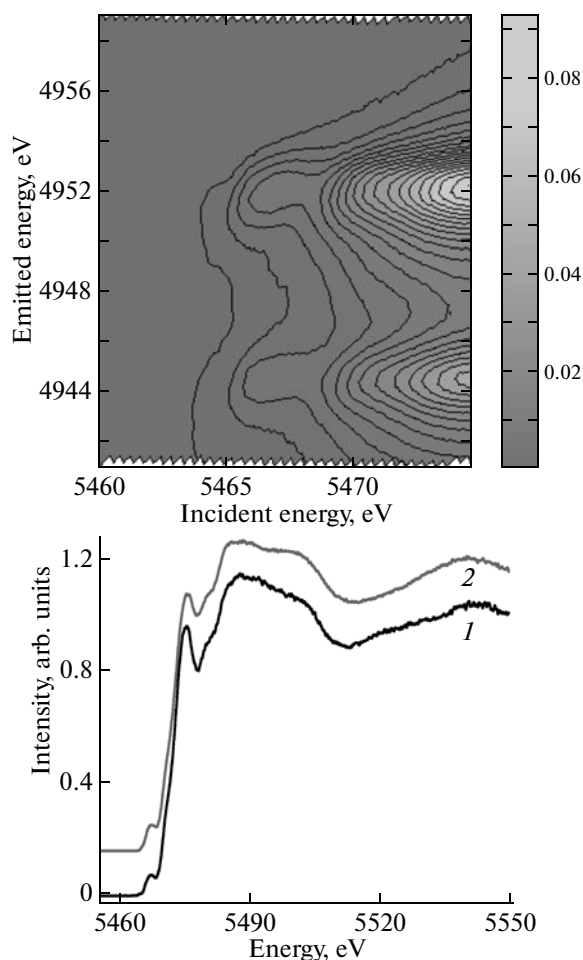


**Fig. 1.** Fragment of  $\text{CuCrS}_2$  crystal lattice which consists of chromium, sulfur and copper layers. Chromium atoms (grey colored) are in the centers of octahedrons, copper atoms (brown colored) are in the centers of octahedrons; sulfur atoms (yellow colored) are in vertexes of octahedrons.

Polycrystalline oxides  $\text{V}_2\text{O}_5$ ,  $\text{VO}_2$ , and  $\text{V}_2\text{O}_3$  were used as reference samples. Vanadium K-edge XANES spectra were measured at ID26 station of European Synchrotron Radiation Facility (Grenoble, France). For selecting of radiation of necessary excitation energy double Si(311) monochromator was used. Two curved mirrors were used for focusing. High resolution XANES spectra were obtained using X-ray fluorescence spectrometer. Avalanche photodiode was used as a detector of X-rays [15]. Sample, analyzing crystals and photodiode formed the Rowland circle. Five spherically curved Ge(311) crystals were used as analyzing crystals. Vanadium K-edge XANES spectra were measured by registration of  $\text{V}(K\alpha)$  fluorescence peak intensity (4952 eV) when changing the energy of exciting radiation near V K-edge. Energy resolution was 0.7 eV.

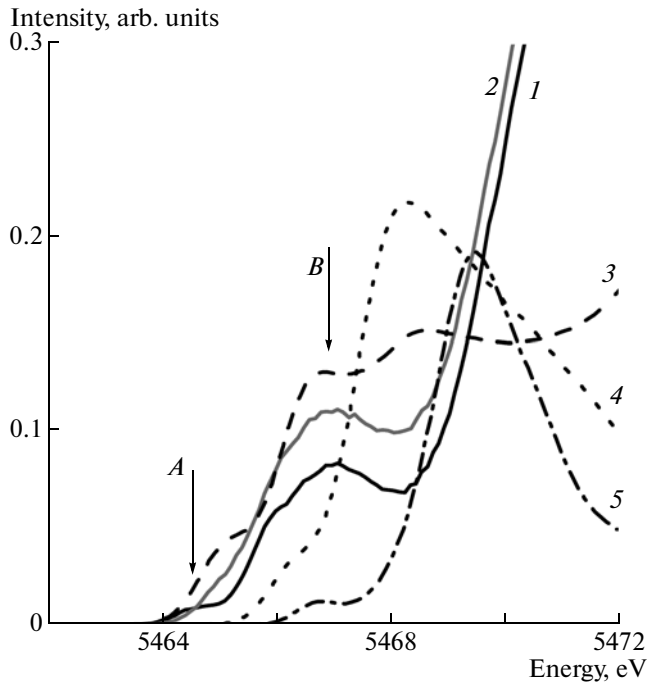
## RESULTS AND DISCUSSION

Figure 2 shows a typical example of  $K\alpha$  resonance emission spectra. Different shades of grey represent different intensity of scattered radiation as a function of exciting radiation energy and fluorescence radiation energy. Peaks corresponding to  $\text{V}(K\alpha_1)$  and  $\text{V}(K\alpha_2)$  can



**Fig. 2.** Resonance emission spectrum for  $\text{CuCr}_{0.95}\text{V}_{0.05}\text{S}_2$  near  $\text{V}K\alpha_{1,2}$ , presented as a 2-dimensional picture. Lines show different fluorescence intensity. Below are XANES spectra for the samples with  $x = 0.05$  and  $x = 0.4$ .

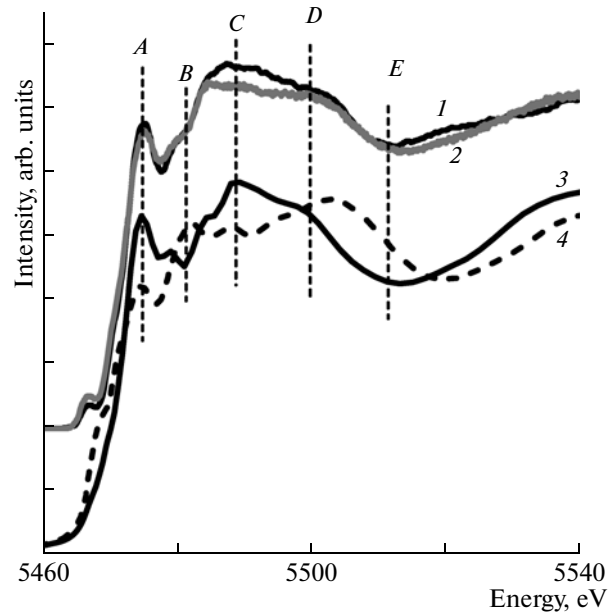
be seen. These peaks have an intensive fluorescence at the excitation energies above vanadium absorption edge energy (5465 eV). XANES spectrum will be described by the fluorescence intensity dependence on exciting radiation energy that corresponds to horizontal cross-section at 4953 eV [16]. Using of intense exciting radiation in a narrow range ( $\sim 0.7$  eV), which is significantly less than the natural width of vanadium  $1s$  state (1.01 eV), is a significant feature of such a method of XANES spectra registration [17, 18]. So this method allows reducing of line broadening of XANES spectra, which is especially important for the investigation of pre-edge peaks. XANES for  $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$  samples at  $x = 0.05$  and  $x = 0.40$  are also shown on Fig. 2. It can be seen that XANES spectra are identical for both samples. However, there are some differences in pre-edge range. These differences allow making a conclusion about the oxidation state of vanadium ions [19]. Pre-edge peak analysis gives the most reliable information about the oxidation state



**Fig. 3.** Experimentally measured K-XANES spectra in pre-edge range for  $\text{CuCr}_{0.95}\text{V}_{0.05}\text{S}_2$  (black line) and  $\text{CuCr}_{0.60}\text{V}_{0.40}\text{S}_2$  (grey line). For comparison pre-edge features of vanadium oxides ( $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$ , and  $\text{V}_2\text{O}_5$ ) are shown.

and the symmetry of vanadium atom because vanadium K-edge XANES spectra often have an intensive pre-edge peak which makes the elucidating of oxidation state using white line position extremely difficult [19]. Figure 3 shows the comparison of pre-edge features of vanadium K-edges for tri-, tetra-, and pentavalent vanadium oxides and  $\text{CuV}_{0.05}\text{Cr}_{0.95}\text{S}_2$  and  $\text{CuV}_{0.40}\text{Cr}_{0.60}\text{S}_2$  samples. Pre-edge structure shifts to higher energies as the oxidation number increases. For the compounds under investigation pre-edge peaks are close to those of  $\text{V}_2\text{O}_3$ , which may indicate that the vanadium oxidation number in the samples under study is 3+. It should be noted that chromium in  $\text{CuCrS}_2$  is in the same oxidation state.

Pre-edge peak *B* (5467 eV) intensity is increasing when the concentration of vanadium increases, but the small peak *A* (5464.5 eV) disappears in spectra for samples with high concentration of vanadium. Their energy position does not change when the concentration of vanadium changes. It can be seen that oxidation state of vanadium does not change when the concentration of vanadium is growing. However, the increase in the peak *B* intensity when increasing the concentration of vanadium indicates that new free states near Fermi level appear. It is advisable to analyze sulfur X-ray absorption spectra, which are informative



**Fig. 4.** Experimentally measured and theoretically simulated K-XANES spectra for doped copper chromium disulfides. At the top: experimentally measured K-XANES spectra for  $\text{CuCr}_{0.95}\text{V}_{0.05}\text{S}_2$  (black line) and  $\text{CuCr}_{0.60}\text{V}_{0.40}\text{S}_2$  (grey line). At the bottom: theoretically simulated XANES spectra for the replacement of chromium atoms 3 and for the insertion of vanadium atoms into the interstitial site 4.

for the investigation of electronic structure of sulfides [20, 21].

Figure 4 shows wide-ranged XANES spectra. Little difference is seen in the spectra for samples with different concentration of vanadium. To describe the position of vanadium atoms two models were considered: replacing of chromium atom and insertion of vanadium atom into interstitial site. Analysis of theoretical spectra for these two models shows that the replacement model gives a good agreement with the experimental data. Changes in interatomic distances after geometry optimization did not exceed 0.02 Å for this model. These lattice distortions are in agreement with X-ray diffraction experiments. Changes in vanadium concentration up to  $x = 0.4$  almost does not change theoretically simulated XANES spectrum for both models.

So, the most probable defect is the chromium atoms replacement by vanadium cations.

## CONCLUSION

In the present work high-resolution XANES spectra above V K-edge for  $\text{CuV}_{0.05}\text{Cr}_{0.95}\text{S}_2$ ,  $\text{CuV}_{0.40}\text{Cr}_{0.60}\text{S}_2$  samples and vanadium oxides were measured using X-ray fluorescence spectrometer. It is shown that vanadium atoms replace chromium ones in both samples.

Pre-edge range of XANES spectra analysis shows that vanadium is in oxidation state 3+. There are no significant changes in atomic structure near vanadium ions. Slight differences in XANES spectra of  $\text{CuV}_{0.40}\text{Cr}_{0.60}\text{S}_2$  in comparison to  $\text{CuV}_{0.05}\text{Cr}_{0.95}\text{S}_2$  can be explained by the appearance of new free states near Fermi level.

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