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# Cu-site disorder in $CuAl_2O_4$ as studied by XPS spectroscopy

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The copper aluminate ($CuAl_2O_4$) find a various applications in modern techniques [1-3]. Therefore much attention is paid to fundamental properties that are determined primarily by its crystal structure of $CuAl_2O_4$. In $CuAl_2O_4$ spinel the $Cu^{2+}$-ions must be located in the center of A-tetrahedral sites and non-magnetic $Al^{3+}$ ions are in the center of octahedral B-sites. In this case, the $Cu^{2+}$ $d$-states split into $t_2$ and $e$ states. The degeneracy of $t_{2g}$-states can be removed due to spin-orbit coupling (SOC) or Jahn–Teller distortion, which lowers the $T_d$ symmetry of the crystal field. As a rule, the experimental results show that the crystal structure of $CuAl_2O_4$ at atmospheric pressure is cubic without any signs of tetragonal distortion [2].

However, possible stabilization of the cubic phase inevitable leads to formation of the spin-orbit entangled $J_{\rm eff} = 1/2$ state and strong exchange anisotropy, which may result in the spin-liquid ground state [4, 5]. This hypothesis was used in particular to explain absence of the long-range magnetic order in $CuAl_2O_4$ even at very low temperature [5]. Alternative explanation is based on presence of intrinsic disorder between tetra and octa sites, which prevents onset of antiferromagnetism.

It is no coincidence that in some early works it was assumed that about 30 % of $Cu^{2+}$ ions occupy octahedral positions [2, 3]. In this connection, of particular interest is the use of local spectral methods sensitive to the nearest surrounding of the exciting atoms. In the present paper we applied the of X-ray photoelectron spectroscopy (XPS) which is an element- and a site-selective probe.

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$CuAl_2O_4$ was prepared from a stoichiometric mixture of $Al_2O_3$ (99.9 %) and CuO (99.9 %). The mixture was pressed into a pellet and annealed on Pt foil at 1193 K for 84 h and at 1293 K for 38 h in air with several intermediate grindings. PHI 5000 VersaProbe spectrometer were used for XPS measurements. X-ray spot size was 200 $\mu$m and Al K$\alpha$ (1486 eV) was used. The calculations of $CuAl_2O_4$ were carried out using the Vienna ab initio simulation package [6].

Figure 1 displays XPS Cu $2p$ (a) and Auger Cu LMM (b) spectra of $CuAl_2O_4$. The XPS Cu $2p_{3/2}$ spectrum has two peak structure ($Cu_1$ and $Cu_2$) and is shifted to high-energy side with respect to that of Cu and $Cu_2O$. Another feature of bivalent copper in $CuAl_2O_4$ is the presence of a CT (charge transfer) satellite S at the same binding energy as in CuO arising from multiplet splitting effects due to the interaction between the Cu $2p$ core hole and the $3d^9$ electronic configuration [7]. The Auger Cu LMM spectra also provide the evidence that the main oxidation state of copper is 2+ [8]. It is generally believed that $CuAl_2O_4$ at atmospheric pressure is in the cubic phase without any signs of tetragonal distortion [5]. The spin-orbit coupling can be responsible for suppression of the Jahn–Teller distortions and absence of corresponding splitting in the Cu-$t_2$ states [9]. However, the local symmetry breaking induced by Jahn–Teller distortions cannot be completely ruled out, since for this the spin-orbit coupling constant $\lambda$ must exceed some critical value [10].

The energy difference of $Cu_1$ and $Cu_2$ peaks in XPS Cu $2p$ spectra is found around 1.2 eV, which is much larger than possible splitting due to both the spin-orbit coupling or the crystal-field splitting because of the Jahn–Teller distortions. In fact this energy difference

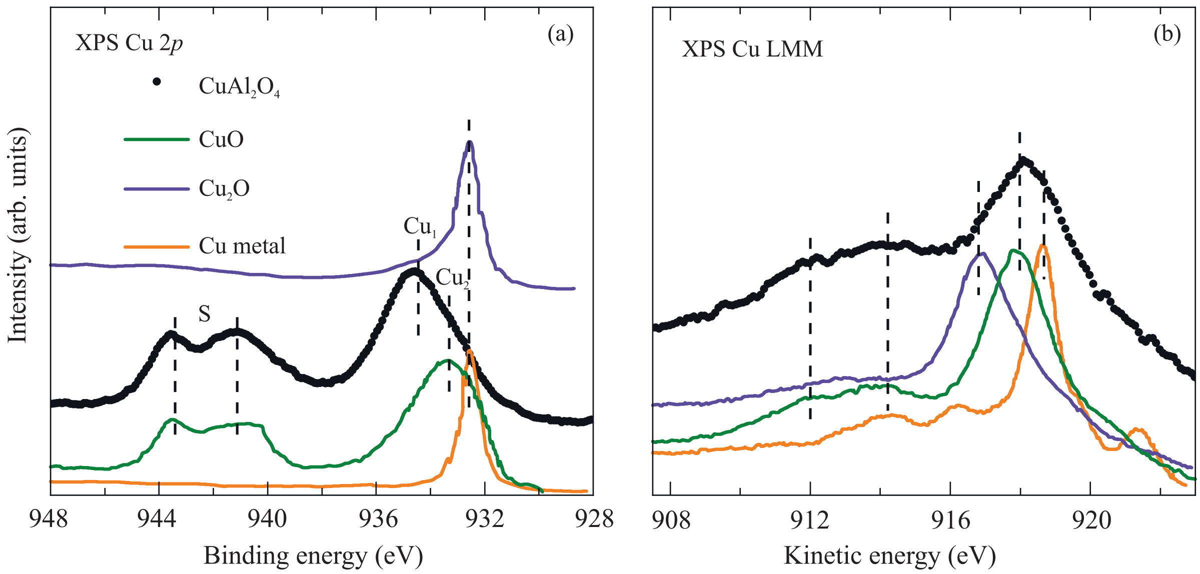


Fig. 1. (Color online) XPS Cu 2$p$ (a) and Auger Cu LMM (b) spectra of $CuAl_2O_4$. The reference spectra are taken from [7, 8]

is comparable with value fixed in splitting of Cu L XAS spectra [11] and the ratio of their intensities suggests that the $Cu_1$ and $Cu_2$ peaks correspond to the contributions of tetra- and octa-sites, respectively and estimates degree of disorder in 30 %. Therefore, we can conclude that the independent site-selective and element-selective X-ray measurements confirm a finite site-disorder in $CuAl_2O_4$.

The comparison of the obtained calculations results shows that taking into account the spin-orbit interaction does not lead to significant changes in the distribution of the total density of occupied states.

In conclusion, our results show the presence of a substantial Cu-Al disorder by the XPS measurements. This disorder may affect formation of an antiferromagnetic order and development of static Jahn–Teller distortions.

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