ELECTRONIC STRUCTURE OF COPPER IN HIGH-TEMPERATURE SUPERCONDUCTING CERAMICS

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It is supposed that the superconducting properties of CuO based ceramics are determined by the character of the Cu—O—Cu bond. Therefore the interest in investigations of the electronic structure of copper in ceramics as well as in CuO and Cu_2O is evident. At the same time there is a number of conflicting opinions in literature about the copper electronic structure in HTS-ceramics. Thus, according to the data in different works, copper in HTS have configurations: d^{10} and d^9, only d^9, d^{10} and d^8, d^8 and d^9.

The X-ray K- and L-lines shift method, developed in LNPI, combined with theoretical calculations in limits of the Hartree-Fock type methods has been applied successfully in the study of the heavy elements ($40<z<92$) electronic structure in their compounds /1/.

The calculation determines the binding energies in the best way for innermost electrons, for which $z_{eff.}$ must be close to z. The outermost electrons screened by the atom electrons from the nuclei field ($z_{eff.}=1$) must also be well described. Therefore for Cu ($z=29$) the applicability of HF-models is most validated for chemical shifts of the $K_{\alpha 1}$-line and K-edge.

The investigated HTS-ceramics ($La_{1.8}Sr_{0.2}CuO_4$, $La_{1.8}Ba_{0.2}CuO_4$, $YBa_2Cu_3O_{6+\delta}$) were practically monophase and their crystalline and physical parameters have corresponded to the literary ones.

For the determination of the copper electronic structure in HTS-ceramics as well as in CuCl, $CuCl_2$, Cu_2O and CuO the shifts of the copper $K_{\alpha 1}$ X-ray line and K-edge were measured with reference to metallic copper in the same procedure, /1/. The K-edge energy was determined as the first maximum in the first derivative absorption curve /2/. In accordance with the R. L. Barinsky and V. I. Nefedov data /3/ the copper K-edge position was connected with the $1s\rightarrow 4p$ electronic transition. The experimental shifts of the copper $K_{\alpha 1}$ X-ray line (ΔE_α) and K-edge (ΔE_e) as well as their theoretical analogs for one 3d- and 4s-electron: $\Delta E^s_{\alpha,e}$ and $\Delta E^d_{\alpha,e}$ are given in Table 1.

Table 1

Shifts of copper $K_{\alpha 1}$-line (ΔE_α) and K-edge (ΔE_e)

	Sample	ΔE_α, meV	ΔE_e, meV
1	Cu_2O	105±5	1085±189
2	CuCl	164±5	2980±429
3	CuO	94±3	3972±627
4	$CuCl_2$	98±6	6633±441
5	$YBa_2Cu_3O_{6+\delta}$ — tetra	52±5	7076±1439
6	$YBa_2Cu_3O_{6+\delta}$ — ortho	47±5	9216±1261
7	$La_{1.8}Ba_{0.2}CuO_4$	79±7	10918±1358
8	$La_{1.8}Sr_{0.2}CuO_4$	61±7	11111+947
9	Calc. DF(r) for 4s	215	3600
10	Calc. DF(r) for 3d	—395	9515

The combined consideration of the experimental and theoretical shifts of the copper $K_{\alpha 1}$ X-ray line and K-absorption edge assuming their additivity ($\Delta E_{\alpha,e}=\Delta n_s \Delta E_{\alpha,e}+\Delta n_d \Delta E_{\alpha,e}$) enable to determine the effective numbers of the copper s- and d-bound electrons or the 4s- and 3d-orbitals population, i. e. the copper electronic structure in the compound. The best results are obtained when using theoretical shifts for one 4s- and 3d-electron calculated in the limits of the Dirac-Fock method with full relaxation. In this case the solutions (the 3d- and 4s-orbitals population) practically always lie in the physical range ($0\leqslant n_s\leqslant 1$, $n_d\leqslant 10$) and agree well with the Pauling ionicity data for Cu_2O, CuCl, CuO and $CuCl_2$. The results of the determination of the 3d-, 4s-orbitals population in the investigated com-

Table 2

Copper 4s- and 3d-orbital populations

	Sample		3d-orbital	4s-orbital
1	Cu_2O		10.04±0.01	0.59±0.03
		*	10.00	0.54±0.07
2	CuCl		9.98±0.03	0.21±0.P5
3	CuO		9.85±0.04	0.29±0.07
4	$CuCl_2$		9.69±0.03	−0.02±0.05
		*	9.70±0.02	0.00
5	$YBaCu_3O_{6+\delta}$ — tetra		9.62±0.09	0.05±0.16
		*	9.59±0.01	0.00
6	$YBa_2Cu_3O_{6+\Delta}$ — ortho		9.48±0.08	−0.18±0.15
		*	9.57±0.02	0.00
7	$La_{1.8}Ba_{0.2}CuO_4$		9.41±0.08	−0.46±0.16
		*	9.65±0.05	0.00
8	$La_{1.8}Sr_{0.2}CuO_4$		9.37±0.06	−0.43±0.11
	*	*	9.60±0.07	0.00

pounds are given in Table 2 (by stars are marked the solutions obtained under conditions: $0 \leqslant n_s \leqslant 1$, $n_d \leqslant 10$):

1. The chemical bond in Cu_2O and CuCl is realized only owing to the copper 4s-electrons. The 4s-electrons are not removed fully to a ligand but are localized partially on copper. In CuO and $CuCl_2$ the 3d-electrons participate in the chemical bond too, but their participation degree is small, i. e. the 3d-orbital population is high: $n_d \geqslant 9.7$.

2. In metal-oxide ceramics: $YBa_2Cu_3O_{6+\delta}$ (in the tetragonal and orthorombic phase) and $La_{1.8}(Ba,Sr)_{0.2}CuO_4$ the copper 4s-electron is drawn off fully to a ligand (oxygen) and the 3d-orbital populations are equal or slightly smaller than in $CuCl_2$ ($n_d \approx 9.4—9.7$). The copper electronic structure in ceramics is close to $3d^{9.4—9.7}4s^0$.

3. The total charge on the copper atoms increases in the Cu_2O—CuCl—CuO—$CuCl_2$ row in the range $q \approx 0.5—1.3$. There is a general tendency for th Cu—O bond: the charge on the copper atoms increases with the growth of the copper formal valence. In all metal-oxide ceramics the charges on the copper atoms are practically equal ($q \approx 1.4$) and are greater than in CuO and, evidently, in $CuCl_2$.

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