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XPS STUDY OF "INFINITE CHAIN" Ca₂CuO₃ AND Ca_{0.5}Sr_{0.5}CuO₂ COMPOUNDS

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At K_{α} excited photoelectron spectra (X-ray photoelectron spectroscopy) of the O 1s, Cu 2p, Ca 2p, Sr 3d core levels were measured for "infinite chain" Ca₂CuO₃ and Ca_{0.5}Sr_{0.5}CuO₂ compounds. The analysis indicates that for Ca₂CuO₃ the surface electronic structure is strongly influenced by a humid atmosphere. The surface layer is formed predominantly by copper hydroxide. The minor features of Cu 2p and O 1s are characteristic of the bulk bonding states. The valences of the Cu, Ca, and Sr atoms are close to 2+. The core electron binding energies (\approx 934 eV peak) are due to the $2p_{3/2}3d^{10}L^1$ configuration of Cu(II) ions in the square planar coordination for both samples.

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The original interest in the experimental studies of Ca₂CuO₃ was associated with the special magnetic properties of this compound showing one-dimensional antiferromagnetic ordering at low temperatures [1]. The latter is a consequence of a particular structure of Ca₂CuO₃. It belongs to the "infinite chain" (IC) compounds of the R₂CuO₃-type (R = Ca or Sr). The crystal structure of (IC) is formed by infinite chains of Cu-O bonds along the \hat{b} -axis. In addition, no oxygen atom is located between Cu atoms neighbouring along the \hat{a} -axis, which differs from the Cu-O₂ plane structure of La₂CuO₄ [2]. The distance between Cu atoms along the \hat{c} axis is about three times as large as the distance along the \hat{a} and \hat{b} axes. In this respect, the local environment of Cu in (IC) compound is similar to the fourfold symmetry of the Cu(1) site in YBa₂Cu₃O₇. The lattice structure of Ca_{0.5}Sr_{0.5}CuO₂ can be derived from SrCuO₂ (in the ambient pressure phase). The low-pressure form of SrCuO₂ contains Cu-O double chains bundled by edge-sharing [3]. Therefore, the samples studied have a common structural unit of a planar CuO₄ square and may be considered a 1D analog of the hole-doped cuprates.

In this work, the electronic structure and the chemical stability of samples of Ca₂CuO₃ and Ca_{0.5}Sr_{0.5}CuO₂ were investigated by X-ray photoelectron spectroscopy (XPS). XPS experiments were carried out at 300 K using a surface science instrument XPS800-Kratos spectrometer with a monochromatized X-ray

TABLE

XPS of the Cu 2*p* and O 1*s* region at 300 K for studied samples. HTS — high-temperature superconductors, rel. int. = relative intensity.

| Sample | Region | BE (eV) | Rel. int. (%) | FWHM (eV) | Attributed to |
|--|---------------|---------|---------------|--------------------------------------|---|
| Ca ₂ CuO ₃ (orthorhombic structure <i>Immm</i>) | Cu 2 <i>p</i> | 933.9 | 85 | 2.8 | the main line represents a well-screened final state (Cu 2 <i>p</i> _{3/2} 3 <i>d</i> ¹⁰ <i>L</i> ¹) where <i>L</i> denotes the holes on the surrounding ligand. This is typical of the Cu ²⁺ state observed in HTS compounds by other workers; square planar |
| | | 936.0 | 40 | 3.5 | Cu-(OH) ⁻ group |
| | | 942.0 | 40 | | the satellite represents an un-screened (Cu 2 <i>p</i> _{3/2} 3 <i>d</i> ⁹) final state |
| | O 1 <i>s</i> | 528.9 | 30.0 | 2.2 | this peak is known to correspond to the lattice oxygen O ²⁻ in the HTS |
| | | 531.0 | 97.0 | 2.2 | this peak is due to O ²⁻ and strongly adsorbed oxygen species |
| | | 533.2 | 18.0 | 2.0 | hydroxide group OH ⁻ (no O ⁻ or O ₂ ⁻) |
| Ca _{0.5} Sr _{0.5} CuO ₂ (orthorhombic structure <i>Pmmm</i>) | Cu 2 <i>p</i> | 934.0 | 100.0 | 3.2 | the main line (Cu 2 <i>p</i> _{3/2} 3 <i>d</i> ¹⁰ <i>L</i> ¹) final state |
| | | | | | |
| | O 1 <i>s</i> | 529.3 | 58.0 | 2.0 | lattice oxygen O ²⁻ |
| 531.5 | | 97.0 | 2.2 | O ²⁻ and adsorbed species | |

source of Al *K*_α (*hν* = 1486.6 eV). The spectra were taken with an energy resolution of 1.2 eV. The data were analysed with a computer program, which performs satellite and background subtraction, smoothing and deconvolution (with Gaussian function), to obtain different components of the spectra. The investigated polycrystalline samples were prepared by conventional solid state synthesis. The obtained samples of orthorhombic structure were single phase, with lattice parameters consistent with the results of other X-ray diffraction (XRD) measurements. However, in Ca_{0.5}Sr_{0.5}CuO₂ where the partial replacement of Sr²⁺ with Ca²⁺ has taken place, the same lattice disorder occurs. The XPS spectra of the samples studied are shown in Figs. 1-4 and the results of their computer analysis are presented in Table.

From the integral intensity of XPS lines of the elements involved, a good agreement of the metallic cation content in samples with the initial nominal formulas Ca₂CuO₃ and Ca_{0.5}Sr_{0.5}CuO₂ was established. For both samples, the Cu 2*p*_{3/2}

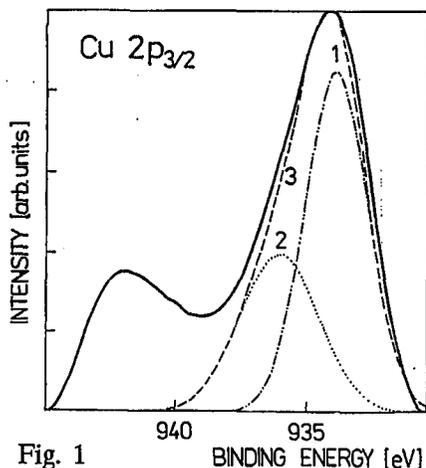


Fig. 1

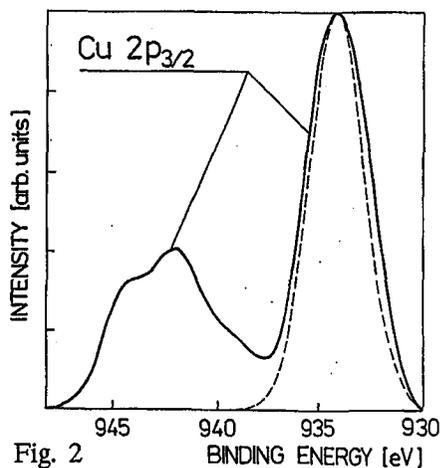


Fig. 2

Fig. 1. Analysis of the Cu $2p$ spectrum of Ca_2CuO_3 . The thick solid line is the measured spectrum, whereas the 1st, 2nd, and 3rd spectrum are the result of computer fit (see Table).

Fig. 2. Al K_α excited XPS spectrum of the Cu $2p$ levels in $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{CuO}_2$, $T = 300$ K. A dashed line labels computer fit.

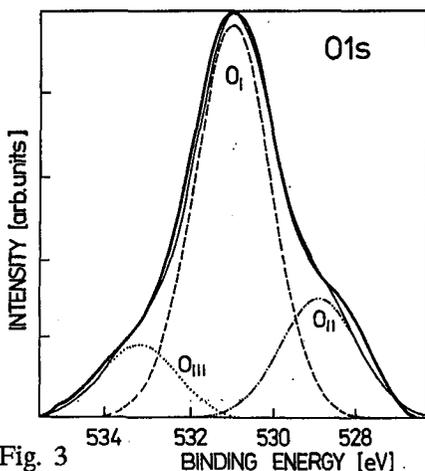


Fig. 3

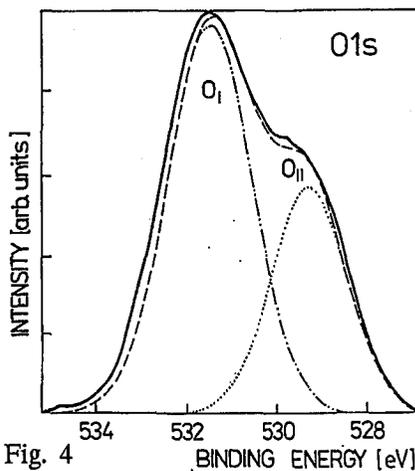


Fig. 4

Fig. 3. Analysis of the O $1s$ spectrum for Ca_2CuO_3 , $T = 300$ K. The thick line represents simulated spectrum obtained by superimposing of the three subspectra from different oxygen atoms (see Table).

Fig. 4. Analysis of the O $1s$ spectrum for $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{CuO}_2$.

core level spectra exhibited the same main peaks at the binding energy $\text{BE} \approx 934$ eV with a prominent shake-up satellite structure (Figs. 1 and 2). Also the values of energy separation between the satellite and the main peaks and the peak intensity ratios I_s/I_m for both samples are comparable. The intensity ratio of the satellite peak to the main one corresponds to the valence of Cu ions equal to $2+$ [4].

A detailed analysis of the Cu $2p_{3/2}$ main peak for Ca_2CuO_3 (Fig. 1) shows two contributions separated by 2.1 eV indicating the presence of two kinds of copper ions $2+$ of different binding energies (see Table). The second peak with BE ≈ 936 eV is probably related to the presence of copper hydroxide.

To estimate surface degradation and oxygen contamination the O $1s$ peaks in both compounds were measured. The O $1s$ (XPS) spectrum of Ca_2CuO_3 reveals the presence of the OH^- component (Fig. 3). It is worth noting that the contaminant species on the surface like OH^- is visible even after additional treatment of the sample, for example annealing or ionic bombardment (Ar^+ ions).

The O $1s$ (XPS) spectrum recorded for $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{CuO}_2$ (Fig. 4) does not show the presence of hydroxide groups. We suppose that the specific nature of active sites and surface porosity influence the surface phenomena of wetting in Ca_2CuO_3 . These results indicate that the surface electronic structure is strongly influenced by the humidity of the atmosphere for (IC) Ca_2CuO_3 . The fitting of Ca $2p$ and Sr $3d$ (only for $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{CuO}_2$ sample) spectra showed that the valency state of Sr and Ca were $2+$ and were characteristic of the bulk bonding states in compounds studied.

In a separate study the magnetic active centres were investigated by EPR method at different temperatures (15–300 K) [5] for both samples. It was found that these centres have a character of Cu^{2+} -centres with axial symmetry for $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{CuO}_2$ (their population is very low relative to the total content of Cu ions). The principal values of the g -matrix of the Cu^{2+} -EPR spectrum are consistent with the geometric distortion of the chains, possibly a change in the Cu–O distances. For Ca_2CuO_3 we observed broad EPR spectrum (for $T > 77$ K) with a poor resolution of the two components. The samples studied were in semiconducting phases.

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