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HIGH ENERGY SPECTROSCOPIES OF Cu COMPOUNDS, INCLUDING THE NEW SUPERCONDUCTORS

M. GRIONI^{***}, J.C. FUGGLE^{*}, P.J.W. WEIJS^{*}, J.B. GOEDKOOP^{*},
G. ROSSI^{**}, F. SCHAEFERS^{***}, J. FINK^{****} and N. NÜCKER^{****}

**Research Institute for Materials, University of Nijmegen,
The Netherlands*

***LURE, Université Paris-Sud, F-91405 Orsay Cedex, France*

****Berliner Elektronenspeicherring-Gesellschaft für
Synchrotronstrahlung mbH (BESSY), D-1000 Berlin 33, F.R.G.*

*****Kernforschungszentrum Karlsruhe, Institut für Nukleare
Festkörperphysik, Karlsruhe, F.R.G.*

Abstract

High energy spectroscopies are well suited to address the controversial issue of Cu valence in the new high T_c superconductors, as they can discriminate between various possible Cu configurations (d^8 , d^9 or d^{10}). XAS, XPS and AES spectra of Cu^I , Cu^{II} and Cu^{III} compounds show that, as a result of hybridization, the actual Cu d-count can be quite different from what is expected from simple considerations based on the formal valence. A value of ~ 9.3 is inferred for the superconductors. Discrepancies in the published results are attributed to insufficient sample characterization; we propose to adopt the O 1s XPS signal as a standard probe of surface condition in these materials.

Introduction

For high energy spectroscopists the new high temperature superconductor materials are interesting because they give the opportunity to illustrate the power of their techniques and because they show interesting spectroscopic phenomena. The use of photoelectron spectroscopies (XPS, UPS, synchrotron PS), Auger spectroscopies (AES) and X-ray absorption and emission (XAS, XES) should be able to provide insight into questions such as: Is Cu^{3+} ($Cu d^8$) really present? Are peroxide-like species present? and, how important are electron correlation and hybridization (mixing) of the bands? Unfortunately, the rush of publications has led to discrepancies in the interpretation of the data, and even in published experimental data. The variations of results from nominally similar compounds in different laboratories is an indication of the complexity of these materials. The materials La_2CuO and $YBa_2Cu_3O_6$ are intrinsically semiconductors (optical

data indicate a gap of ~ 2 eV in La_2CuO_4 and somewhat less in $\text{YBa}_2\text{Cu}_3\text{O}_{7-1, 2, 3/}$). Moreover, "doping" with vacancies, increasing oxygen content, and substitution of La by Sr or Ba all introduce states into the gap. Clearly small and at present poorly defined changes in the dopant, as well as surface contamination, all lead to large changes in the physical and spectroscopic properties of the materials.

Results and discussion

Many of the prominent high-energy spectroscopies (XPS, AES, UPS) are surface sensitive techniques, and because of the nature of the new superconductors it is difficult to prepare surfaces of known composition. The situation will not improve until large, non-porous samples are more widely available for cleavage and fracture under vacuum. In our opinion the O 1s signal is one of the most important monitors of surface condition. Unscraped samples show a large O 1s signal at ~ 532 eV which may be attributed to hydroxide (they also show a large C 1s XPS signal). When we scrape a fairly compact sample of La_2CuO_4 or $(\text{LaSr})_2\text{CuO}_4$ that has been kept away from all moisture, we find that through scraping (with, we think, consequent fracture of most grains contributing to the XPS signal) we observe a single O 1s peak at 528.5 eV. If the freshly scraped samples are left in vacuum a shoulder grows in the XPS peak at ~ 531 eV (Fig. 1). This could be attributed to some sort of hydroxide formed by diffusion of small amounts of hydrogen from the bulk, or to the effect of oxygen vacancies in the lattice, or to unknown effects. In our publications we always refer to spectra from $(\text{LaSr})_2\text{CuO}_4$ samples which gave a single broad O 1s peak at 528.5 eV. The situation for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ compounds is more complex. We do strongly recommend publication of O 1s XPS spectra to provide a basis for comparison of spectra from different laboratories.

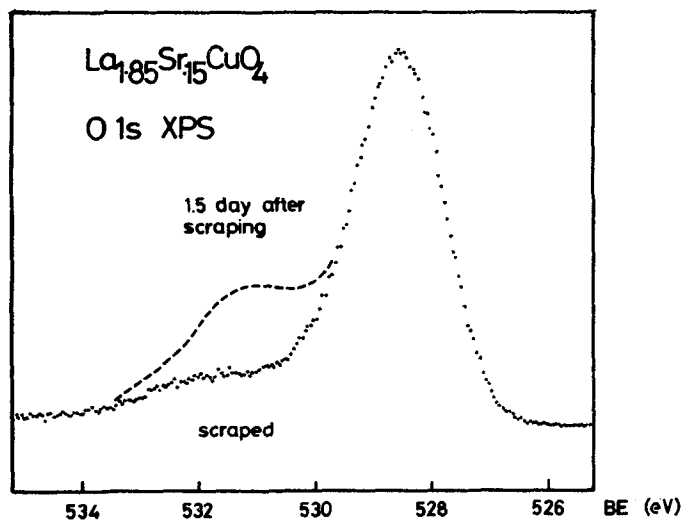


Figure 1: O 1s XPS signal from a superconducting sample, showing the effects of permanence under vacuum.

We have published elsewhere XPS spectra of the Cu 2p peaks /4/. They show large shake-up satellites, reminiscent of those found for CuO and Cu dihalides /5/. They are suggestive of a Cu d-count of approximately 9.3. We have not found any evidence for Cu^{3+} (d^8) in our spectra, and we have not been convinced by any of the literature we have seen which quoted high energy spectroscopic data as evidence for the presence of Cu^{3+} . We have also published /6/ our opinion that Cu LVV Auger spectra, satellites in valence band photoemission, and comparison of XPS valence bands with calculated density of states curves, all give evidence that the Coulomb interaction between the Cu 3d electrons is too high for the Cu d^8 configuration to contribute more than some percent to the total wavefunction in the ground state of the undoped materials, and that the oxygen atoms are not pure O^{2-} . We are not alone in these opinions /7-12/. The d^8 configuration may have a slightly higher weight in the superconducting (doped) materials, but this is not immediately obvious from the spectra.

Another technique which can give some insight into the electronic structure of Cu in its compounds is x-ray absorption. In Fig. 2 we illustrate the spectra of the Cu L_3 and L_2 edges at 932 and 952 eV. When it is available, the $2p \rightarrow 3d$ excitation channel is stronger than the $2p \rightarrow 4s$ channel. Thus divalent Cu ions, which are nominally Cu d^9 and have one d hole, give strong sharp peaks at the Cu L_3 and L_2 edges, whereas Cu^0 (e.g. Cu metal) and Cu^I , which are nominally Cu d^{10} , give no sharp peak. Thus if one can satisfactorily normalize the spectra, one could use the intensity of the peaks near the edges to estimate the Cu d-count in Cu compounds. We have not yet found a method of normalization of the

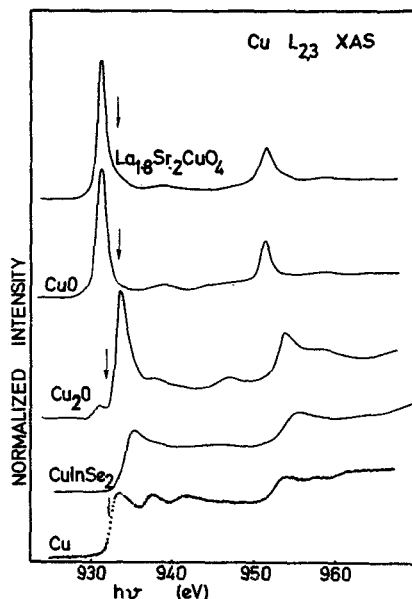


Figure 2 : Cu $L_{2,3}$ XAS spectra of nominally Cu^0 , Cu^I , Cu^{II} compounds, normalized to the same intensity below the edge, and of a high T_c sample. Arrows mark the corresponding XPS binding energies.

spectra satisfactory for this purpose, but it is clearly possible to differentiate between Cu^{I} and Cu^{II} compounds. Note that Cu_2O , which is nominally Cu^{I} , is a special case. The spectrum shows a weak feature at ~ 0930.7 eV due to CuO impurity, and then a strong peak at 933.7 eV. This latter is probably associated with a large concentration of Cu 3d character which is present in calculations of the unoccupied states (to be presented in a different paper). This shows that even Cu^{I} compounds need not be strictly d^{10} because of the effects of hybridization. Turning to $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$, we find a single strong peak at the edge. We find no second peak as observed in Cu^{III} complexes and compounds like NaCuO_2 /13, 14/.

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