

X-ray absorption study of the O 2*p* hole concentration dependence on O stoichiometry in YBa₂Cu₃O_x

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 (Received 10 June 1988)*

A detailed x-ray absorption study of the oxygen *K* edge of YBa₂Cu₃O_x is presented. A pre-edge peak is observed for all samples with $x \geq 6.4$ which we argue to be due to holes in the O 2*p* band. By comparison to Li_xNi_{1-x}O the x dependence of the number O 2*p* holes in YBa₂Cu₃O_x is determined.

INTRODUCTION

Since the discovery of superconductivity at elevated temperatures in oxidic copper compounds,¹ there has been an intense interest in the nature of the states close to the Fermi level induced by stoichiometry variations. Although there is a general consensus that these states are localized on the CuO₂ planes, there is still some discussion about whether these are primarily Cu 3*d* states or O 2*p* (ligand hole) states. A substantial amount of spectroscopic information²⁻⁶ suggests that the Cu *d-d* Coulomb interactions are very large (larger than the O → Cu charge transfer energy Δ) in which case the materials are in the charge transfer gap or O *p* hole region of the classification scheme suggested by Zaanen and co-workers.^{7,8} The most direct probe of the local O 2*p* unoccupied density of states is O 1*s* x-ray absorption spectroscopy (XAS). The dipole selection rules and the local character of the optical transition-matrix elements involving a core state assure us that only the local unoccupied states of O *p* character are probed. If the hole states at the Fermi level are of primarily O 2*p* character, a precontinuum edge peak should be visible in the O 1*s* XAS spectrum with an intensity proportional to the O 2*p* hole concentration. The first measurements displaying the presence of a prethreshold peak in YBa₂Cu₃O_x were presented by Yarmoff *et al.*⁹ using XAS and by Nücker *et al.*¹⁰ using electron-energy-loss spectroscopy. To our knowledge, however, there has been no systematic XAS study of YBa₂Cu₃O_x as a function of x , aside from the electron-energy-loss experiment which could be prone to electron-induced damage. Quite contrary to this there have been numerous investigations of the Cu 2*p* (Refs. 11 and 12) and Cu 1*s* (Refs. 13 and 14) edge from which a consensus has been reached that there is no detectable Cu³⁺ present although there are claims of the presence of Cu¹⁺. This also is consistent with the presence of holes in the O 2*p* band. In this paper we present a detailed XAS study of the O 1*s* edge for

YBa₂Cu₃O_x with x between 6.26 and 6.98 which covers the range for which these materials have T_c ranging from 90 to 0 K with antiferromagnetic order.¹⁵ These results are used to estimate the O 2*p* hole concentration as a function of x by comparing to the results obtained for Li_xNi_{1-x}O.¹⁶

MATERIALS

Pellets of YBa₂Cu₃O_x were made as follows. A mixture in the appropriate ratio of standard solutions of Y₂O₃ (Philips Maarheeze, The Netherlands) in diluted HNO₃ (pro analyze, E. Merck, Darmstadt, Federal Republic of Germany) and Ba(NO₃)₂ and Cu(NO₃)₂ (both pro analyze, E. Merck) in demineralized water was spray dried (Buechi 190, Flawil, Switzerland) using inlet and outlet temperatures of 230 and 180 °C, and a feed rate of ½ l/h. The powder obtained was calcined in air for 1 h at 550 °C to decompose the nitrates followed by 2 h at 900 °C. The calcine was ground with an agate mortar and pestle followed by a second heat treatment in air for 2 h at 950 °C. After this the powder was air quenched and reground and checked by x-ray diffraction to be more than 95% YBa₂Cu₃O_x. Pellets were pressed by preforming in a polymethylmethacrylate die, followed by isostatic pressing at 400 MPa. The pressed pellets were sintered for 6 h in pure O₂ at 950 °C followed by slow cooling. The sintered pellets with final dimensions of 11 mm in diameter and 8 mm thickness were then mounted in the furnace of a thermogravimetric setup described in Ref. 10. The initial atmosphere in this furnace was a mixture of O₂ and N₂ with an effective log₁₀(*p*O₂/atm) of -0.05. The absolute pressure and gas flow rate were kept constant at values of 1050 mbar and 200 sccm (cubic centimeters per minute at STP). The temperature was programmed as follows: 500 °C/h to 900 °C, followed by 1 h at this level to remove all adherent water and CO₂; 500 °C/h down to 400 °C,

followed by 4 h at this level for stoichiometry checking; 500 °C/h to levels of 500, 600, 700, 800, 900, and 1000 °C for complete equilibration and finally cooling to room temperature at 25 °C/h. During the final cooling the sample weight and accordingly the oxygen content were kept constant by direct digital proportional integrating control with the pO_2 of the furnace input gas stream. Homogeneous samples with a well-defined stoichiometry were obtained in this manner as no bulk oxygen transport had to occur during cooling. More details are given in Refs. 17–19. The stoichiometry parameter x for the $YBa_2Cu_3O_x$ samples as a function of temperature was obtained using the method of Ref. 17. This gave $x = 6.98$ for the sample equilibrated at 400 °C and $x = 6.26$ for the one equilibrated at 1000 °C. The samples were stored under argon. For the XAS measurements the pellets were cleaved under helium and glued onto a sample holder with TorrSeal and a tiny drop of conducting silver epoxy (Epo-tec H20E) for electrical contact.

To insert the samples in the vacuum chamber the samples were briefly exposed to air. *In vacuo* the samples could be scraped with an alumina file. The pressure was in the 10^{-9} -Torr range after a bake out at 80 °C. The measurements were done at BESSY, the Berlin synchrotron. The monochromator used was an SX700 (Ref. 20) which operated with an exit slit of 10 μ m giving a resolution of 400 meV at 500 eV. The absorption was determined by the total-electron-yield method. This probes a layer of 100 to 200 Å deep. The total yield was divided by the storage ring current recorded simultaneously. No correction was made for the energy-dependent photon flux in the oxygen edge region caused by contamination of the optics as it was found to be only about 2%. The absolute energy scale was determined by comparison with the data of Nücker *et al.*¹⁰

Although the XAS measured by the total electron yield

method is not extremely surface sensitive, one still must take precautions to prevent too much oxygen depletion during the measurements. To check for changes in oxygen content with time we measured the most oxygen-rich sample ($x = 6.98$) immediately after scraping and again at 15 min later. We could detect a small oxygen depletion, but it was negligible compared to the spread in x values measured. All the other samples were measured within several minutes after scraping.

RESULTS AND DISCUSSION

In Figs. 1 and 2 we present the spectra of the unscraped and scraped samples respectively for various values of x . In both sets of spectra we see the appearance of a peak at about 528.5 eV for $x \geq 6.40$ which grows in intensity as x approaches 7 which is indicative of an increasing O $2p$ hole count with x . Qualitatively the results prior to and after scraping are the same. The most significant difference is that the scraped samples exhibit an enhancement of the feature at 528.5 eV. This could be a result of the unscraped samples having lost some oxygen close to the surface. In addition to the pre-edge feature at 528.5 eV, we see a shoulder with small peaks around 530 eV which seems to be independent of x . This pre-edge feature is also present in insulating CuO .²¹ In insulating NiO a strong pre-edge peak is seen in the O $1s$ XAS spectrum.^{21,22} These structures are present in spite of the fact that these materials are insulators and therefore they cannot be attributed to O $2p$ holes at the Fermi level. These structures are due to Cu (d^{10}) or Ni (d^9) final states which are accessible via O $1s$ absorption because of the covalent mixing in the ground state. To be more explicit the ground-state wave function in the impurity or clus-

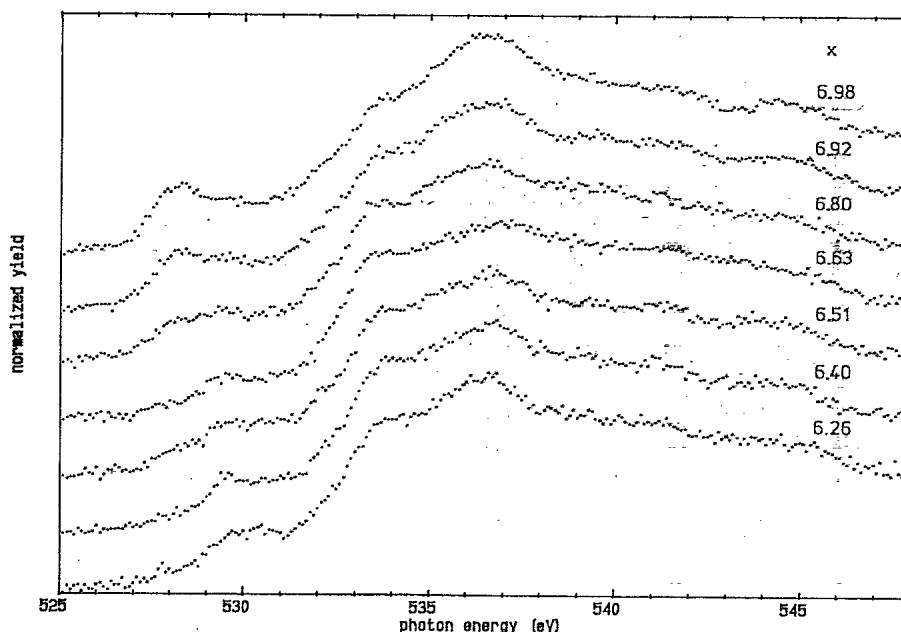


FIG. 1. Oxygen absorption edges of unscraped $YBa_2Cu_3O_x$ samples. A constant background was subtracted. Data were scaled by the integral between 530 and 548 eV. The spectra were shifted vertically for clarity.

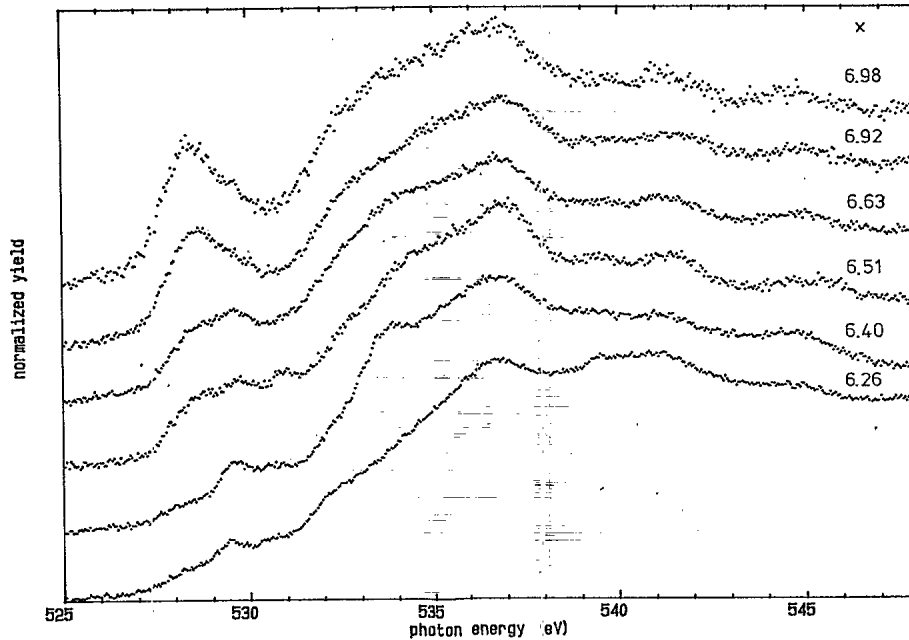


FIG. 2. Oxygen absorption edges of $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples after scraping. Spectra were scaled and shifted as in Fig. 1.

ter^{7,8} approximation valid for large U , is for CuO (Ref. 23)

$$\alpha |d^9\rangle + \sum_k \beta_k |d^{10}\underline{L}_k\rangle \quad (1)$$

and for NiO

$$\alpha |d^8\rangle + \sum_k \beta_k |d^9\underline{L}_k\rangle + \sum_{k,k'} \gamma_{kk'} |d^{10}\underline{L}_k\underline{L}_{k'}\rangle, \quad (2)$$

where \underline{L}_k is a ligand hole ($\text{O } 2p$ band) with wave vector k . For finite values of β we see that $\text{O } 2p$ "holes" are available for XAS even in the insulating samples although now solely because of hybridization and not because of true charge compensation. For $U \gg \Delta$, with use of Zaanen-Sawatzky-Allen (ZSA) (Refs. 7 and 8) arguments, a plausible form for the ground state, with holes added to achieve charge balance, for the CuO_2 layers would be

$$(\alpha |d^9\rangle + \sum_k \beta_k |d^{10}\underline{L}_k\rangle) \left| \prod_k^N \underline{L}_{k'} \right\rangle, \quad (3)$$

where the $\prod_k^N \underline{L}_{k'}$ represents the N hole states introduced because of charge balance which here are crudely treated as "spectators." These holes would be at the top of the valence band of the CuO_2 layers and therefore separated in energy by the band gap from the electron addition or conduction band states $|d^{10}\rangle$. We see from Eq. (3) that now two types of final electron addition states are available, namely,

$$(\alpha |d^9\rangle + \sum_k \beta_k |d^{10}\underline{L}_k\rangle) \left| \prod_{k'}^{N-1} \underline{L}_{k'} \right\rangle,$$

where a spectator ligand hole is filled and $|d^{10}\rangle \left| \prod_k^N \underline{L}_{k'} \right\rangle$, where a $|d^{10}\rangle$ state is reached via addition of either a d electron (as in $L_{2,3}$ XAS) or by addition of an $\text{O } 2p$ electron. Since the spectator ligand holes are at the top of the valence band these two states would be roughly separated by the band gap in the insulator although the different effects of the core hole in these two states could reduce the

energy separation somewhat. In $\text{YBa}_2\text{Cu}_3\text{O}_x$ the separation between these states is about 1–1.5 eV, which is close to the band gap of CuO of 1.4 eV as measured by a combination of photoelectron spectroscopy and inverse photoemission spectroscopy.²⁴ For $\text{Li}_x\text{Ni}_{1-x}\text{O}$ the separation of these two types of pre-peak structures is 3.2 eV which is 0.8 eV less than the band gap.²⁵ The continuum absorption starts at about 531 eV and shows structure characteristic of the band structure. The structure is only weakly dependent on x for the unscraped samples although some broadening of the structures is observed for increasing x . For the scraped samples we see larger changes in the continuum structure as x is varied. The most dramatic change is between $x = 6.26$ and $x = 6.40$. This could be due to the change from a tetragonal to an orthorhombic crystal structure.²⁶

Even though the energy resolution is not very good for the $\text{Cu } 2p$ edges, we present these data in Fig. 3 for comparison to other published results.²⁷ The shoulder for $x > 6.5$ on the higher-energy side is clearly visible next to the dominating "white" line at ~ 931 eV. The intensity of this so-called satellite structure grows with x making clear that it is related to the presence of holes in the CuO_2 layers for large x .

In order to get a better impression of the changes which occur with x we show in Figs. 4 and 5 the difference spectra with $x = 6.40$ for the unscraped and scraped samples, respectively. To obtain these difference spectra we normalized each spectrum to the integrated area between 530 and 548 eV after subtracting an energy-independent background. These difference spectra were then smoothed by splines. For the unscraped samples the dominant changes with x occur at the prethreshold peak at about 528 eV. For the scraped samples (Fig. 5) the sample with $x = 6.26$ is somewhat anomalous which we already discussed above. Aside from this we see the increase in the peak at about 528 eV with increasing x . The additional structure at 532

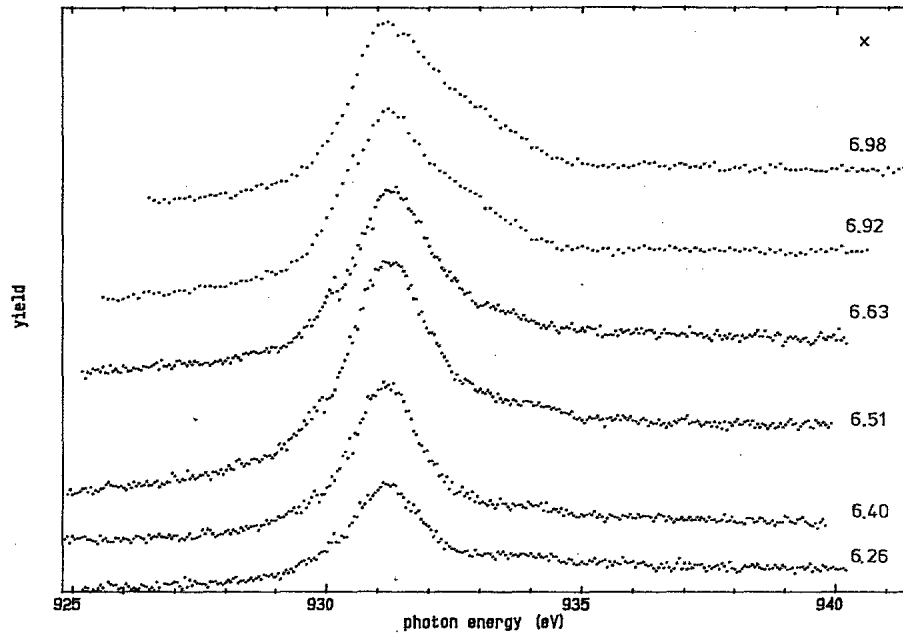


FIG. 3. Copper absorption edges of scraped $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples.

eV is due to the slightly different continuum onset in the $x=6.40$ sample indicating that something is happening between $x=6.5$ and 6.4 . This is perhaps not surprising since in the simplest picture, in taking Cu to be $2+$ and O to be $2-$, at $x=6.5$ no extra holes are required for charge compensation. For $x < 6.5$ then electrons are required for charge neutrality which could result in Cu^{1+} ($3d^{10}$) which are the first electron affinity states in the CuO_2 layers.²⁴

In Fig. 6 we have plotted the intensity of the peak at 528 eV in the difference spectrum versus the oxygen content x . The error bars are determined by simply trying

different normalizations and energy shifts. The straight lines are drawn to guide the eye and to point out that the density of O $2p$ holes extrapolates to zero for x somewhere between 6.5 and 6.3. From the data presented here it is not possible to reach any conclusions concerning possible plateaus as claimed for the superconducting transition temperature.¹⁵ This would require a much more detailed study involving many more samples.

As already mentioned above a strong prethreshold peak in the O $1s$ spectrum is also observed for Li-substituted NiO. From a detailed study of the electronic structure of NiO (Refs. 7, 8, 24, 28, and 29) we found that the first

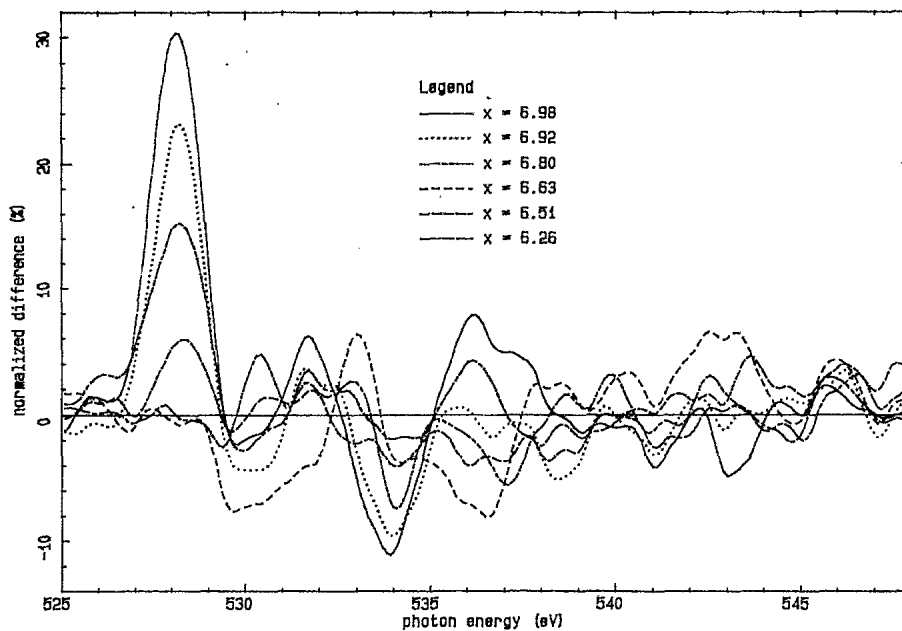


FIG. 4. Smoothed difference spectra of the scaled absorption edges of unscraped samples with respect to $\text{YBa}_2\text{Cu}_3\text{O}_{6.40}$ as a percentage of the mean height between 530 and 548 eV.

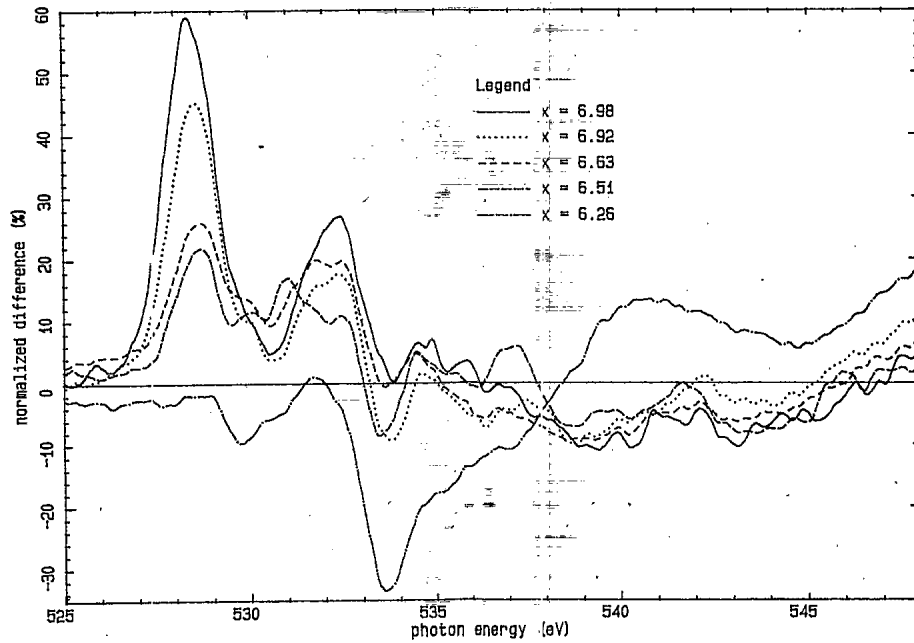


FIG. 5. Smoothed difference spectra of the scaled absorption spectra of scraped samples with respect to $\text{YBa}_2\text{Cu}_3\text{O}_{6.40}$ as a percentage of the mean height between 530 and 548 eV.

ionization states are of primarily O 2p character. This would suggest that in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ the number of holes introduced per Li ion would be close to 1. The intensity of the Li-induced O 1s prethreshold line can then be used to calibrate the data presented here. In Fig. 7 we show the intensity of the Li-induced peak versus now the O 2p hole concentration in NiO. The intensity of the prepeak is plotted as a fraction of the average intensity of the total O 1s absorption between 530 and 548 eV which is the same interval used to normalize the $\text{YBa}_2\text{Cu}_3\text{O}_x$ data above. In

the same figure we also show the data for $\text{YBa}_2\text{Cu}_3\text{O}_x$ where the hole concentration is calculated according to $\text{Y}^{3+}\text{Ba}_2^{2+}\text{Cu}_3^{2+}\text{O}_x^{2-h}h_{2(x-6.5)}$ where h designates a hole. As we cannot distinguish between different oxygen sites they are treated equivalently. We see that there is quite reasonable agreement demonstrating that the holes in $\text{YBa}_2\text{Cu}_3\text{O}_x$ are induced primarily in the O 2p band. The agreement with the $\text{Li}_x\text{Ni}_{1-x}\text{O}$ data for the scraped samples is even better if we assume the hole count to go to zero at $x=6.35$ instead of at $x=6.5$. This is perfectly

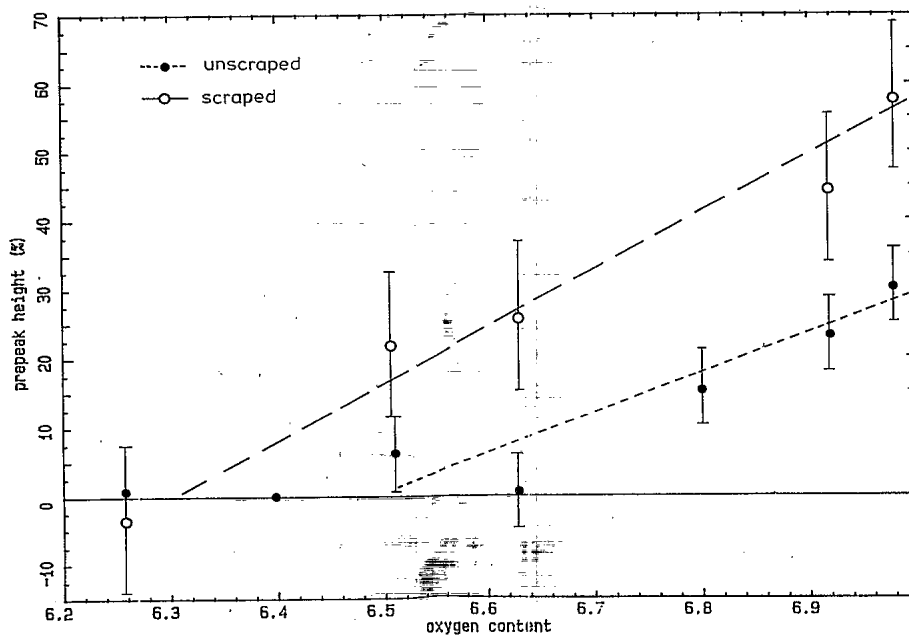


FIG. 6. Relative height of the 528-eV peak in the difference spectra as a function of oxygen content for scraped and unscraped $\text{YBa}_2\text{Cu}_3\text{O}_x$.

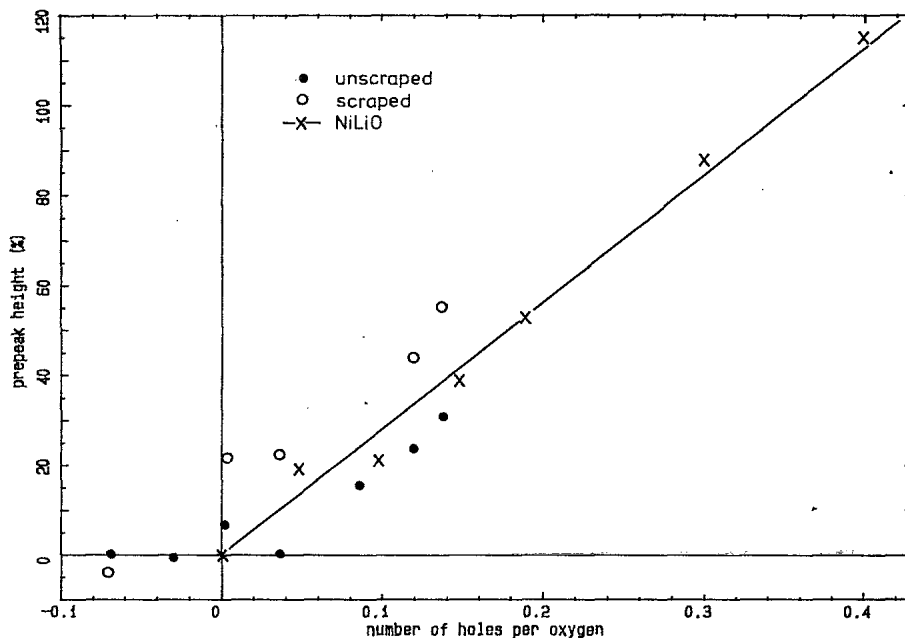


FIG. 7. Relative height of the Li-induced prepeak in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ and of the O-induced prepeak in scraped and unscraped $\text{YBa}_2\text{Cu}_3\text{O}_x$ as a function of the calculated O $2p$ hole number.

possible by adjusting the $[\text{Cu}^{2+}]/[\text{Cu}^{1+}]$ ratio. It gives better agreement with the thermodynamic data^{17,19} and is consistent with the presence of a phase transition²⁶ and the disappearance of superconductivity at $x = 6.35$.¹⁵

In conclusion, we have shown that the charge compensation in $\text{YBa}_2\text{Cu}_3\text{O}_x$ for $6.26 < x < 6.98$ occurs via holes in the O $2p$ band for large x and probably via electrons in Cu $3d$ states (d^{10}) for low x . The exact boundary cannot be determined from our data but could correspond to $x = 6.35$ where also the orthorhombic-tetragonal phase transition occurs.²⁶ A more detailed study involving much more samples is planned for the near future to determine the exact nature of the curve describing the hole concentration versus x .

ACKNOWLEDGMENTS

Thanks are due to W. H. M. Bruggink and M. M. E. Vantilt for preparing the samples. We are grateful to the Berlin Elektronenspeicherring für Synchrotronstrahlung (BESSY) for providing access to facilities. This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) and the Foundation for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for the Advancement of Pure Research (ZWO) and the Committee for the European Development of Science and Technology (CODEST) program.

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