

## Oxygen Chemistry in Copper Oxides: Evidence for $O^-$ Species†

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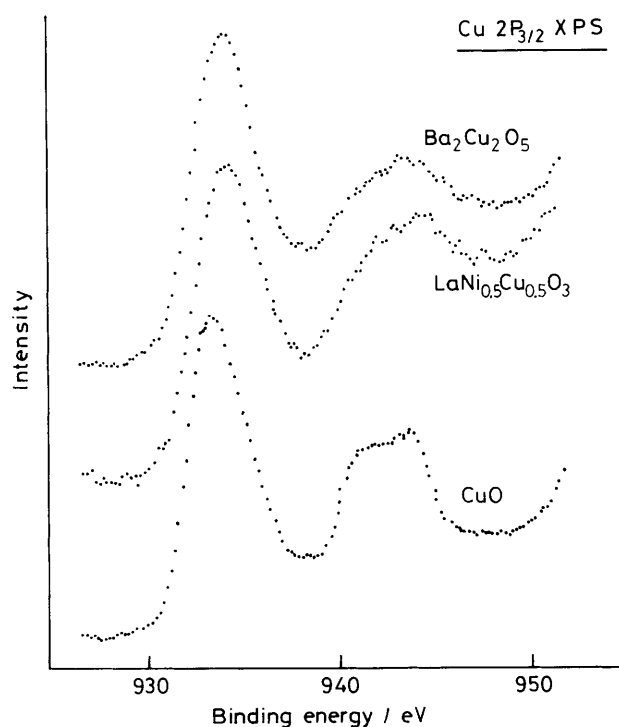
Core-level spectroscopic studies suggest that cuprates nominally supposed to contain  $Cu^{3+}$  ions are likely to have the excess positive charge on oxygen instead, giving rise to  $O^-$  type species (oxygen holes).

We generally assume a charge of  $-2$  for oxygen in metal oxides. However, this is strictly only correct for purely ionic oxides. Recent investigations on superconducting  $YBa_2Cu_3O_7$  have revealed that Cu in this cuprate is not present in the  $3+$  state. Instead, the excess positive charge in this oxide resides on oxygen, giving rise to  $O^-$  type species; these holes play an

important role in the superconductivity of this cuprate.<sup>1–5</sup> We considered it important to examine whether such holes on oxygen are present in other oxides containing copper nominally in the  $3+$  state. For this purpose, we have carried out an X-ray photoelectron spectroscopic study of  $Ba_2Cu_2O_5$  and  $LaNi_{0.5}Cu_{0.5}O_3$  where Cu is in the  $3+$  state according to stoichiometry.

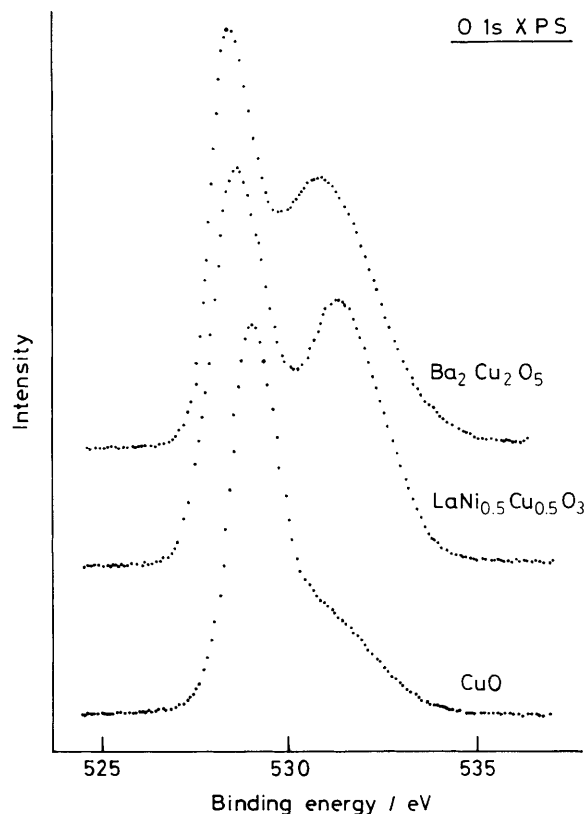
The oxide  $Ba_2Cu_2O_5$  was synthesized under high pressure,<sup>6</sup> and  $LaNi_{0.5}Cu_{0.5}O_3$  was prepared using a procedure developed in this laboratory.<sup>7</sup> The Cu 2p and O 1s core-level

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**Figure 1.** X-Ray photoelectron spectra of the Cu  $2p_{3/2}$  region of CuO,  $\text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$  and  $\text{Ba}_2\text{Cu}_2\text{O}_5$ .

spectra were obtained with a VG ESCA3 MarkII spectrometer using  $\text{Mg-K}\alpha$  (1253.6 eV) radiation. Since these ceramic cuprate samples have well-known problems<sup>8–11</sup> with surface impurities such as carbonate, we have taken special care to minimise the effects from such contaminants. Scraping the sample surface extensively has yielded single O 1s peaks in certain instances, but this is not always reproducible. Furthermore, time-dependent changes are also encountered even with thoroughly scraped surfaces. We have taken considerable care to obtain reproducible results with the best possible surfaces of these oxides. For this purpose, we used freshly prepared, well-sintered samples which were then vigorously scraped *in situ* under high vacuum ( $5 \times 10^{-10}$  Torr) at 300 K using an inert alumina file to remove surface contaminants. In spite of such precautions, small amounts of carbonate could be detected in the C 1s core-level spectra, possibly due to its presence at the grain boundaries. The ratio of the integrated intensities of the C 1s (due to the carbonate) and O 1s bands was, however, considerably less than 1 in 30 in every case after scraping. We have further taken into account even the presence of this small amount of carbonate impurity in interpreting the O 1s spectra. Using several bulk carbonate samples as standards, we could derive  $7.1 \pm 0.1$  as the intensity ratio between the O 1s (531 eV feature in  $\text{CO}_3^{2-}$ ) and C 1s (289 eV) in the carbonates. Making use of this experimental O 1s/C 1s ratio for carbonates, we could estimate the contribution from the carbonate impurity to the total O 1s intensity at 531 eV in the copper oxides on the basis of the observed C 1s intensity. Even after the carbonate contribution was subtracted out from the O 1s spectrum, both  $\text{Ba}_2\text{Cu}_2\text{O}_5$  and  $\text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$  showed considerable intensity in the 531 eV region (up to 20% or more of the total O 1s intensity). We consider this 531 eV intensity to be intrinsic to these copper oxides. This was, however, not the case with CuO which showed negligible intensity at 531 eV.



**Figure 2.** X-Ray photoelectron spectra of CuO,  $\text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$ , and  $\text{Ba}_2\text{Cu}_2\text{O}_5$  in the O 1s region after subtracting the intensity due to carbonate impurity (see text).

In Figure 1 we show the Cu  $2p_{3/2}$  spectra of  $\text{Ba}_2\text{Cu}_2\text{O}_5$ ,  $\text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$  and CuO. The spectra exhibit two features. The main feature at the lower binding energy ( $\sim 934$  eV) is due to the lowest energy configuration in the core-hole state (or the well-screened state) and essentially has the  $2p^53d^{10}$  configuration. The satellite or the poorly-screened feature at  $\sim 942$  eV corresponds to the excited state primarily involving  $2p^53d^9$  configuration.<sup>12</sup> The relative intensities of these two features are governed by the charge-transfer excitation energy,  $\Delta$ , between Cu 3d and O 2p derived states and the hybridization strength,  $V$ , between them. We find that the relative intensity of the satellite with respect to the main feature is significantly lower in  $\text{Ba}_2\text{Cu}_2\text{O}_5$  (0.3) and  $\text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$  (0.4) than in CuO (0.5). This reduction in the satellite intensity is most likely to be due to higher  $V$  or the shorter Cu–O bond in the  $\text{Cu}^{3+}$  oxides.

Another important difference between the Cu  $2p_{3/2}$  satellite peaks in the nominal  $\text{Cu}^{3+}$  oxides and in CuO is that it is much broader in the former (see Figure 1). This is likely to be due to the presence of the additional holes in the oxygen 2p level compared to CuO. The presence of the extra holes in the ligand band reduces the structure and increases the width of the satellite peak.<sup>13</sup> It is noteworthy that the features of the Cu 2p spectra of the two oxides nominally containing  $\text{Cu}^{3+}$  are not unlike those of the superconducting cuprates with covalent Cu–O bonds which contain hardly any  $\text{Cu}^{3+}$ . Thus, the Cu  $2p_{3/2}$  features in the spectra of all these copper oxides are essentially related to  $\text{Cu}^{1+}$ -like ( $3d^{10}$ ) and  $\text{Cu}^{2+}$ -like ( $3d^9$ ) configurations with a hole in the oxygen level. The  $2p_{3/2}$  feature of  $\text{Cu}^{3+}$  ( $3d^8$ ), expected around 20 eV higher than the main feature, is not seen in the Cu 2p spectra of these oxides.

Evidence for the presence of the excess positive charge on oxygen in  $\text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$  and  $\text{Ba}_2\text{Cu}_2\text{O}_5$  is provided by the O 1s spectra given in Figure 2. The spectrum of CuO essentially shows a single feature around 529 eV due to  $\text{O}^{2-}$  species. Besides the 529 eV main feature,  $\text{Ba}_2\text{Cu}_2\text{O}_5$  and  $\text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$  show a fairly intense feature around 531 eV even after subtracting out the contribution due to the  $\text{CO}_3^{2-}$  impurity as described earlier. Since oxygen hole species of the type  $\text{O}^-$  are expected<sup>14–16</sup> to have a binding energy around 531 eV, we conclude that such holes are present in these copper oxides, nominally containing  $\text{Cu}^{3+}$ , due to the high covalency of the Cu–O bond. The main conclusion from the present study is that the real state of a covalent Cu–O system in diverse oxides of copper is nearly the same, although for formal purposes one may assign different charges to Cu. Covalency in these oxides favours  $[\text{M}^{(n-1)}\text{O}^-]$  type of species in preference to  $[\text{M}^{n+}\text{O}^{2-}]$  species due to the small metal– $\text{O}^{2-}$  charge-transfer energy.

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