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Lack of Cu^{3+}, Pb^{4+}, and Bi^{5+} ions in metallic and superconducting oxides

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With a view to understand the oxidation states of metal ions involved in oxide superconductors, oxidation behavior of Cu, Pb, and Bi metals have been studied employing x-ray-photoelectron and ultraviolet-photoelectron spectroscopy. Pb and Bi have distinct $6p$ (0 to 4 eV) and $6s$ (7.5 to 10 eV) bands and upon oxidation, only the $6p$ electrons are ionized forming PbO and Bi_2O_3 with the simultaneous development of the $O^{2-}(2p)$ band (3 to 7 eV). We show that the $6s$ band of the metals lies below the $O^{2-}(2p)$ band, and hence $6s$ electrons cannot be ionized to form Pb^{4+} and Bi^{4+} as expected in PbO_2, $BaPbO_3$, $BaBiO_3$, and $BaPb_{0.75}Bi_{0.25}O_3$. Instead, these oxides are stabilized with lower valent O_2^{2-} along with O^{2-} ions with metals remaining in +2 and +3 states. Similarly, it is shown that the $Cu^{2+}(3d)$ band overlaps with the $O^{2-}(2p)$ band in the $YBa_2Cu_3O_{6.95}$ completely and the excess oxygen can be stabilized through lower valent oxide ions instead of Cu^{3+}.

INTRODUCTION

An insight into the valence states of cations or anions is crucial to the understanding of physical properties of inorganic compounds such as PbO_2, $BaPbO_3$, $BaPb_{1-x}Bi_xO_3$, $BaBiO_3$, and the recently discovered high-T_c oxides. The energies and dynamics of valence changes or fluctuations is particularly important in the understanding of metallization in these systems. In the usual Mott-Hubberd kind of theories[1-4] a single valence fluctuation involving only the metal ions is present:

$$M_i^{n+}+M_j^{n+} \rightleftarrows M_i^{(n-1)+}+M_j^{(n+1)} . \tag{1}$$

The relevant energy is the correlation energy U. The valence fluctuation in oxides, chalcogenides, pnictides, etc., may involve the ligands also,[5-8] as in

$$M^{n+}+L^{m-} \rightleftarrows M^{(n-1)+}+L^{(m-1)-} , \tag{2}$$

where $L^{(m-1)-}$ represents a hole on the ligand L^{m-}. Such a valence fluctuation would involve the ligand-metal charge transfer energy Δ. The interplay of U and Δ in metallization was first discussed by Zaanen, Sawatzsky, and Allen.[6] Recently, we have considered[7,8] a double valence fluctuation scheme involving a change by two electrons. In oxides we may express it in the form

$$M^{n+}+2O^{2-} \rightleftarrows M^{(n-2)+}+O_2^{2-} . \tag{3}$$

Equation (3) involves a dimerization of ligand holes brought about by a *direct* ligand-ligand hybridization as distinct from an *indirect* ligand-metal-ligand hybridization. Direct ligand-ligand hybridization is expected to be favored[9] in structures such as perovskites in which there is a close packing of oxygen especially when the spin-density on M^{n+} and $M^{(n-2)+}$ is small (small metal-ligand hybridization). Nonmagnetic M^{n+}-$M^{(n-2)+}$ pairs such as Bi^{3+}-Bi^{5+}, Pb^{2+}-Pb^{4+}, Sn^{2+}-Sn^{4+}, Tl^{1+}-Tl^{3+}, Cu^{1+}-Cu^{3+} (d^8, low spin), etc., in perovskite oxides could then participate in double valence fluctuation under certain circumstances. The paired electrons involved in such valence fluctuations could then be considered as bosons and it is of course extremely important to note that most of the oxides referred to above are superconducting.

X-ray- and ultraviolet-photoelectron spectroscopy (XPS and UPS) on $BaPbO_3$, $BaBi_{0.25}Pb_{0.75}O_3$, PbO_2, $BaBiO_3$, etc., seem to show evidence for the presence of a peroxide kind of oxygen with oxygen-oxygen bonding.[7,8] Further, NMR as well as photoelectron studies do not show clear evidence for the existence of Pb^{4+} or Bi^{5+} ions as suggested by the nominal composition assuming the valency of oxide ions as -2. Similarly, x-ray-absorption near-edge structure (XANES)[10,11] and XPS studies[12-14] do not show any clear evidence for the presence of Cu^{3+} ions in $YBa_2Cu_3O_{7-x}$ (1:2:3) or in $La_{2-x}Sr_xCuO_4$, instead there is some evidence for the presence of holes on oxygen. Rao, Ganguly, Hegde, and Sarma[15] were the first to suggest that dimerization of holes in O^{1-} forming O_2^{2-} is likely to be responsible for superconductivity in high-T_c Cu oxides from a comparison of the 1:2:3 with the $BaBi_xPb_{1-x}O_3$. Subsequently, Dauth *et al.*[16] have also found evidence of O_2^{2-} type of ion. Recent theoretical studies do take into account single-valence[17] and double-valence fluctuation[18] as in Eqs. (2) and (3). These results suggest that the equilibrium constant in Eqs. (2) and (3) is shifted towards the right in these compounds. The equilibrium constant is not specified for a given oxidation state but instead depends on the nature of the other cations present as well as the structural features. For instance, there is reason to believe that Pb^{4+} ions are stable[7,8] in Sr_2PbO_4 and that Cu^{3+} ions are stable[19] in $La_2Li_{0.5}Cu_{0.5}O_4$.

To a first approximation, the equilibrium constant may be considered to be determined by U, Δ, and the oxygen-oxygen hybridization energy, $E_{O\text{-}O}$. Δ is likely to be a function of the structure as well as the nature of the counter cations present. $E_{O\text{-}O}$ is likely to be a function of the O-O distance to a first approximation. U is also likely to be a function of the electron-phonon interaction. Thus, *a priori* it does not seem to be possible to predict the equilibrium constant of the above equations without taking into account all the factors mentioned above and which are difficult to evaluate. Nevertheless, it seems to us that one of the necessary conditions for the creation of holes on ligands is to have the M^{n+} level located well below that of the highest occupied anion level. Thus we would require the $6s$ levels of Pb or Bi or the $3d^8$ of copper to lie well below the top of the $O^{2-}(2p)$ band in order to obtain holes on oxygen.

The objective of this study is to study the oxidation of metals such as Pb, Bi, and Cu in order to obtain an understanding of the relative positions of the various metal and oxygen levels. An idea of electron transfer from metal to oxygen forming metal ions and oxide ions is used here and they are characterized by XPS and UPS techniques. These studies do indeed show evidence for the location of the metal levels of the higher oxidation states lying well below the top of the $O^{2-}(2p)$ band in agreement with our expectations. These results should become important in understanding the electronic structure of the newly discovered high-T_c Bi and Tl containing Cu oxides.

EXPERIMENT

He II uv and Mg K x-ray-photoelectron spectra were recorded in ESCA3 Mark II spectrometer of VG Scientific Ltd., U.K. Pure polycrystalline metals (Metals Crystals Ltd., Cambridge) in the form of 3-mm foil were cleaned *in situ* by argon ion etching until the impurity peaks from oxygen, carbon were not detectable from XPS $O(1s)$ and $C(1s)$ core-level spectra. Binding energies (BE) reported here are with reference to $Au(4f_{7/2})$ at 83.7 eV and they are accurate within +0.2 eV.

RESULTS AND DISCUSSION

To illustrate how XPS and UPS can be employed to show that metal valence electrons are transferred to oxygen in the oxidation process, a study of Ti to TiO_2 is described here. In Fig. 1, $Ti(2p)$ and $O(1s)$ regions are shown for clean Ti and Ti+O_2 forming TiO_2. The clean metal shows $Ti(2p_{3/2,1/2})$ at 454 and 460 eV and they are shifted by 5 eV on oxygen exposure. Correspondingly, a single $O(1s)$ peak at 530 eV develops. The binding energies of $Ti(2p)$and $O(1s)$ seen here match well with the bulk TiO_2.[20] In Fig. 2, the valence-band region obtained from He II UPS for Ti and TiO_2 are given. The valence band of Ti (curve A, Fig. 2) is centered around 1.5 eV from E_F and it spreads up to about 3.5 eV. On oxygen exposure, intensity of this band is totally decreased and a new band centered at 6.8 eV due to $O^{2-}(2p)$ develops. An extrapolation of the leading edge of the $O(2p)$ band in Fig. 2 shows that the top of the oxide ion band is 3.2 eV below the Fermi edge of the metal and this value agrees well with the band gap of TiO_2. When TiO, Ti_2O_3 are formed, one does clearly observe a partially filled $Ti(3d)$ band at or near E_F separated by a filled $O(2p)$ band with a single $O(1s)$ peak thus explaining the metallic property.[4,6,20] This experiment illustrates the formation of the TiO_2 with Ti in 4+ and oxygen in 2− valence states due to a transfer of four $(4s^2+3d^2)$ Ti valence electrons to two oxygen atoms. This is a simplified picture for an ionic oxide; however, there is partial ionic and partial covalent bonding in these oxides but the effective positive charge in Ti is equivalent to 4+.

Figure 3 shows He II UPS data of Pb metal before and after oxygen exposure. Clean Pb metal gives bands at 1.5, 3.5, and 7.5 eV with a series of peaks above 8.5 eV. The sharp peaks above 8.5 eV are due to $Pb(5d_{5/2,3/2})$ excited by He II β and He II γ radiation as indicated in Fig. 3. The Pb valence-band spectrum and the assignments agree well with the UPS study by Evans and Thomas.[21] The first two bands are assigned due to $Pb(6p)$ and the band at 7.5 eV is due to $Pb(6s)$ in accordance with the XPS as well as theoretical calculations.[22] On oxygen exposure, formation of PbO is seen[23] from a shift of $Pb(4f)$ peaks by 1 eV which can also be seen from the shift of $Pb(5d)$

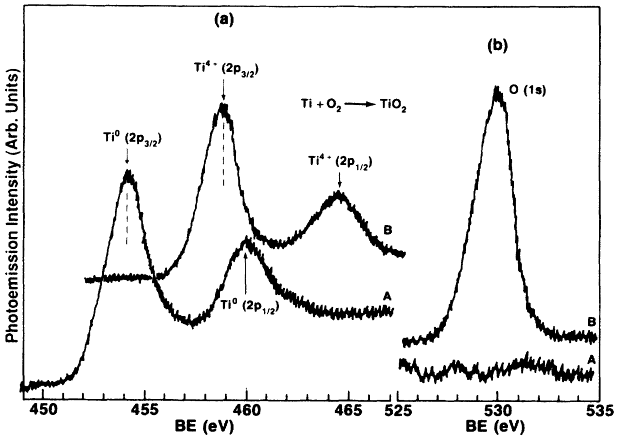

FIG. 1. (a) Plot of photoemission intensity vs binding energy (BE) in the $Ti(2p)$ and (b) $O(1s)$ regions for clean and oxygen exposed surfaces at 300 K.

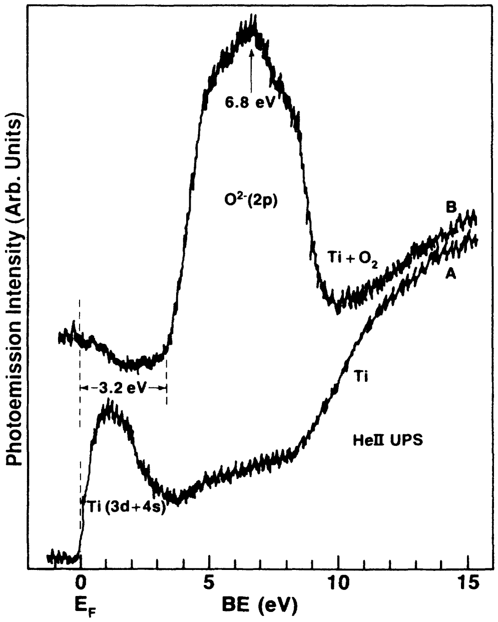

FIG. 2. He II UPS of Ti metal (A) and Ti+O_2 (1000 L oxygen exposure, where 1 L $=10^{-6}$ Torr sec) at 300 K.

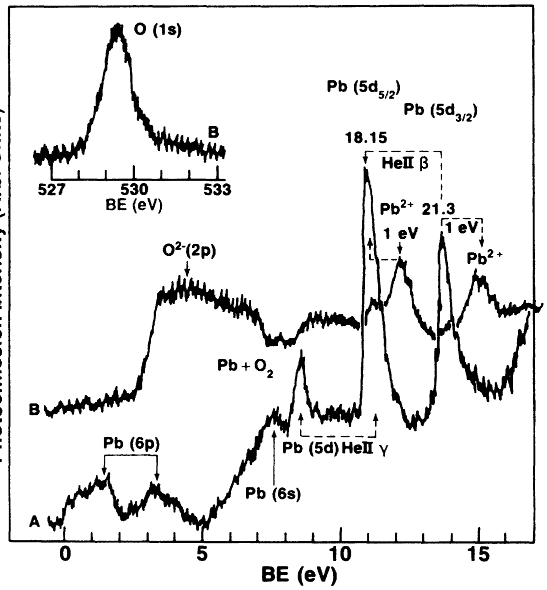

FIG. 3. He II UPS of Pb metal (A), and after 10^4 L oxygen exposure (B) at 300 K. O(1*s*) region is shown in the inset.

peaks from Fig. 3. This indicates that Pb(5*d*) behaves like a core level. The O(1*s*) region gives a single peak at 529.5 eV as shown in Fig. 3. The valence band now clearly shows the development of the $O^{2-}(2p)$ band spread over from 3 to 7 eV.

In Fig. 4, He II UPS data of Bi and Bi+O_2 are given. In Fig. 5, Bi(4*f*) and O(1*s*) regions are presented for the same conditions as in Fig. 4. The valence band of the metal shows two bands at 0.8 and 3.5 eV and bands at 9.2 and 10.3 eV. These two sets of bands are assigned to Bi(6*p*) and Bi(6*s*) in accordance with the XPS study as well as from theoretical calculations.[24] Upon oxidation, the $O^{2-}(2p)$ band develops with a peak at 4 eV. That Bi_2O_3 is formed on the surface is seen from the shifted Bi(4*f*) peaks by 2.2 eV along with a single O(1*s*) peak at

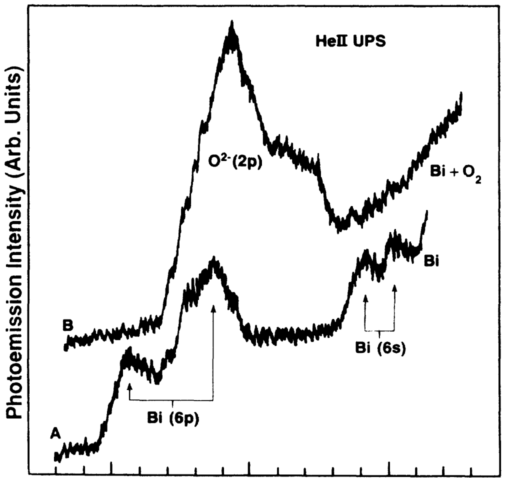

FIG. 4. He II UPS of Bi metal (A), and after 1000 L O_2 exposure (B) at 300 K.

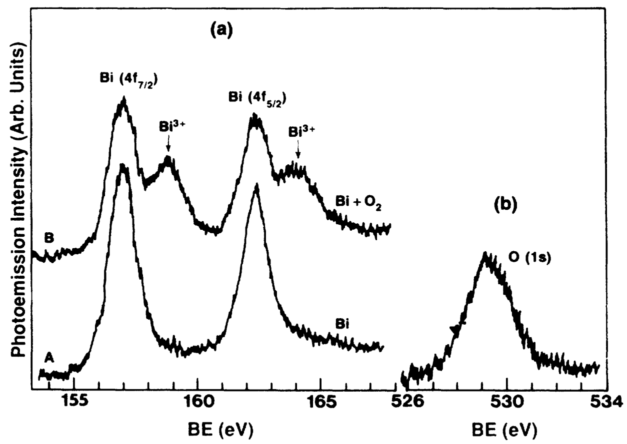

FIG. 5. (a) Bi(4*f*) and (b) O(1*s*) regions for conditions as in Fig. 4.

529 eV and these binding energies match well with the bulk Bi_2O_3 spectra and also from the reported values by Joyner *et al.*[25] It should be noted here that electron density of the first band of the metal disappears upon oxidation. On excess oxygen exposure, no new peaks developed in either the Pb(4*f*), Bi(4*f*), or O(1*s*) region. Nor was there any change in the valence band in the He II UPS. Therefore, no new oxide can be grown on the metal surfaces.

One simple way to find the band position of Pb metal can be to determine the shift of electron states from Pb atom to Pb metal. Ionization energies of the valence levels of Pb and Bi atoms in vapor state have been determined by Suzar and co-workers.[26–28] Thus, the ionization energies of Pb($6p_{1/2,3/2}$, $6s$, and $5d_{5/2}5d_{3/2}$) states are 7.42, 9.16, 14.59, 25.20, and 28.33 eV, respectively. In the solid state, Pb($5d_{5/2,3/2}$) are observed at 18.15 and 21.3 eV, respectively (see Fig. 3). Therefore, a shift of 7 eV takes place when Pb vapor metallizes due to the gain in the work function and relaxation energies. Hence, the 6*p* band of Pb should occur at 0.4 and 2.14 eV. These values are close to the observed values as in Fig. 3. Correspondingly, the Pb(6*s*) band should be seen at 7.6 eV which agrees well with the peak seen in Fig. 3. Perfect agreement in the shift of the Pb(6*s*) band shows that it behaves like a core level just as Pb(5*d*). When Pb is oxidized, Pb^{2+} ion is formed because the Pb(6*p*) band is above the O(2*p*) band edge. The 6*s* band is below the $O^{2-}(2p)$ band thus making it difficult for its ionization to form a Pb^{4+} ion unlike the case of Ti.

From a similar argument, the Bi(6*p*) band should occur at about 0.3 and 2.94 eV and Bi(6*s*) at 9.73 and 10.5 eV by comparing the ionization energies of Bi(6*p*) and Bi(6*s*) states in vapor[26–28] and Bi metal assuming the same amount of shift of 7 eV as in the case of Pb [Bi(5*d*) ionization energy in vapor phase is not available in the literature]. The agreement in the case of Bi(6*s*) is good. The first two bands are broad in the solid and the spin-orbit splitting and the assignment to Bi(6*p*) do agree with the earlier studies.[24] It is again clear that upon oxidation, $6p^3$ electrons are ionized forming a Bi^{3+} ion and the Bi(6*s*) band lies below the $O^{2-}(2p)$ band. This makes it difficult for a pure Bi^{5+} ion stable in an oxide. It is important to note that in the past, the presence of Bi^{3+} and Bi^{5+} ions have been proposed assuming a single valent O^{2-} in $BaBiO_3$.[29] While Bi is found in a +3 oxidation state, oxygen is found in a mixed valent state.[8,9]

It is also clear that even 6*p* bands in both Pb and Bi metals partially overlap with the O(2*p*) band. When oxidized, this overlap can be even more because metal levels are shifted to higher binding energies. Hence the oxides can be more covalent. The covalent nature of PbO and Bi_2O_3 is reflected in the extent of shift in 4*f* peaks. Generally, a shift of 1 to 1.25 eV to a higher binding energy is seen per unit increase in oxidation state in transition metals.[20] This can also be seen in the case of TiO_2 with a shift of 5 eV for a change in oxidation state of four. The Pb(4*f*) peaks are shifted by 1 eV for change in the oxidation state of two and Bi(4*f*) by 2.2 eV for +3 oxidation state indicating a lower chemical shift. This suggests that there is a higher degree of covalency in these oxides compared to TiO_2 and many oxides such as NiO.

In Cu metal, the 3*d* band is below 2.6 eV from E_F. Upon oxidation at 200 °C at low oxygen pressure, Cu_2O is easily formed and the Cu(3*d*) band is still seen at 2.6 eV and the $O^{2-}(2p)$ band occurs at 6.2 eV; the O(1*s*) peak is at 530 eV (see for example, Fig. 3 of Ref. 30). Thus, further oxidation to Cu^{2+} state is possible.

In CuO, $Cu^{2+}(3d)$ and $O^{2-}(2p)$ bands are seen at 4 and 5 eV and the O(1*s*) region shows the main peak at 529.7 eV with a shoulder at 531.5 eV as shown in Fig. 6. The two oxygen peaks are assigned to O^{2-} and O^{1-} from XPS and UPS studies.[30] It is to be noted that the Cu(3*d*) band is shifted to higher binding energy by about 1.5 eV compared to that in Cu_2O. Further, the O(1*s*) peak is shifted to a lower binding energy; correspondingly, the $O^{2-}(2p)$ band is shifted to lower energy. A shift of O(1*s*) to a lower binding energy is an indication of the shift of the $O^{2-}(2p)$ band. In TiO_2, O(1*s*) is at 530 eV and O(2*p*) is at 6.8 eV; in Bi_2O_3, O(1*s*) occurs at 529 eV and O(2*p*) peaks at 4.5 eV. In Al_2O_3, O(1*s*) is at 532.5 eV and O(2*p*) is at 7.5 eV. Thus, in CuO, overlap of $Cu^{2+}(3d)$ with the $O^{2-}(2p)$ band has begun for Eq. (2) to become operative. According to Zaanen, Sawatzsky, and Allen,[6] CuO is classified as a charge-transfer semiconductor. The XPS O(1*s*) showing the presence of O^{2-} and O^{1-} species and the Cu(2*p*) region showing satellites attributed to a ligand-to-metal charge transfer[31] ($2p^6 3d^9 \rightarrow 2p^5 3d^{10}$) does in fact experimentally demonstrate the validity of Eq. (2).

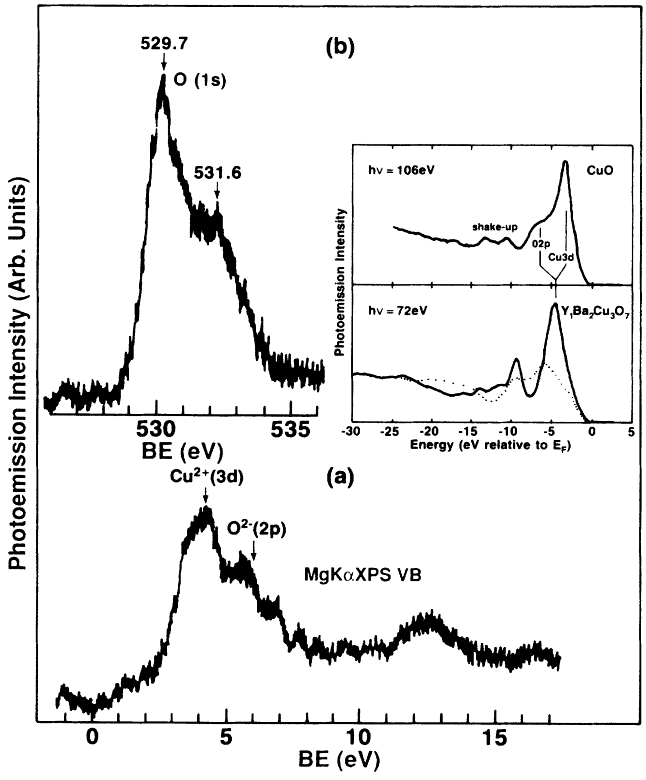

FIG. 6. Mg *K* XPS of O(1*s*) and valence band of CuO. Inset shows valence-band region of CuO and $YBa_2Cu_3O_7$ oxides taken from Ref. 32.

In the 1:2:3 compound, the first O(1*s*) peak occurs at 528.5 eV,[12,13,16] which means the $O^{2-}(2p)$ band should further shift to a lower binding energy. In such a case, Cu(3*d*) and O(2*p*) bands completely overlap as has been experimentally observed[13,32] (see inset of Fig. 6). The center of gravity of the valence band is at 4.5 eV. The lower binding energy of O(1*s*) at 528.5 eV seems to be affected by the influence of other cations in the 1:2:3. The O(2*p*) band is generally broad as can be seen in the case of TiO_2; typically, it is about 3 to 4 eV. Hence the top of the valence band in 1:2:3 can very well be due to $O^{2-}(2p)$. Since the $Cu^{2+}(3d)$ and O(2*p*) bands are exactly overlapping as can be seen from the inset of Fig. 6, there will be no preference to ionize electrons from Cu(3*d*) energetically. Therefore, formation of the Cu^{3+} ion in the 1:2:3 in the spirit of Ti^{4+} is difficult and this explains the failure to find the Cu^{3+} state in the superconducting oxides.

Crystal structure of 1:2:3 clearly shows two Cu-O distances; it is 1.89 Å [Cu(1)-O(1)] in the chain and 2.02 Å [Cu(2)-O(2)] in the plane.[33] It has also been proved that the oxygen in the chain is essential for the compound to become superconducting. The O-O distance in the chain is 2.67 Å giving a 1.33-Å size for this oxide ion which is smaller than 1.42 Å for the oxide ion in the plane. Smaller oxide ion is suggestive of O^{1-} type in the chain paving way to dimerization. It should be noted that the Cu-O distance of 1.89 Å is found in Bi as well as Tl containing high-T_c oxides.[34]

Our results therefore clearly indicate that the 6*s* levels of Bi^{3+} or Pb^{2+} ions or the $3d^8$ level of the Cu^{3+} ion lie well below that of the top of the $O^{2-}(2p)$ band. This then could provide a necessary criterion for the creation of holes in the valence band when Bi^{3+}, Pb^{2+}, or Cu^{2+} ions are further oxidized.

A generalization of the metal (*d*) band overlapping with the $O^{2-}(2p)$ band can lead to a simple explanation of why only the Ag^{1+} ion is stable and Ag^{2+} ion is not formed in oxides. The Ag(4*d*) band is at 4.5 eV and on oxidation, the O(2*p*) band also occurs at 4.5 eV. Thallium is another metal which can occur in +1 and +3 state. From the positions of 6*s* levels in Bi and Pb metals at 10 and 7.5 eV, Tl(6*s*) should occur at about 5 eV and therefore, it is a clear case for the occurrence of double valence fluctuation in Tl_2O_3 and a preliminary XPS study shows two O(1s) peaks at 528.7 and 532.7 eV with Tl in +1 state.[35] In fact, this oxide is metallic in nature. It would be interesting to examine the oxidation states Tl and oxygen in the superconducting thallium containing Cu oxides. A closer look at the oxidation process as viewed from the valence electron transfer to oxygen can indeed be fruitful and the work is in progress in this direction.

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[1] N. F. Mott, Philos. Mag. **6**, 287 (1961).

[2] J. Hubberd, Proc. R. Soc. London, Ser. A **277**, 237 (1964); **281**, 401 (1964).

[3] J. A. Wilson, Adv. Phys. **21**, 143 (1972).

[4] J. B. Goodenough, Prog. Solid State Chem. **5**, 149 (1972).

[5] P. Ganguly, Ph.D. thesis, Bordaux University, 1984 (unpublished).

[6] J. Zaanen, G. A. Sawatzsky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[7] P. Ganguly, M. S. Hedge, R. A. Mohan Ram, and K. Sreedhar, in *Proceedings of the Fifth International Conference on Valence Fluctuations, Bangalore, India, 1987,* edited by S. K. Mallik and L. C. Gupta (Plenum, New York, 1987).

[8] P. Ganguly and M. S. Hegde, Phys. Rev. B **37**, 5107 (1988).

[9] P. Ganguly, in Proceedings of the Solid State Symposium BARC, Bombay, 1987 (unpublished).

[10] A. Bianconi, J. Budnic, A. M. Flank, A. Fontaine, P. Lagarde, A. Marcelli, H. Tolentino, B. Chamberlin, L. Michel, B. Raveau, and G. Damazeau, Phys. Lett. A **127**, 285 (1988); see also A. Bianconi *et al.*, Int. J. Mod. Phys. **1**, 207 (1987).

[11] F. Baudelet, G. Collin, E. Dartyge, A. Fontaine, J. P. Keplar, G. Krill, J. P. Itie, A. Revcolvski, H. Tolentino, G. Tourillen, and M. Verlaguer, Z. Phys. B **69**, 141 (1987).

[12] D. D. Sarma and C. N. R. Rao, J. Phys. C **20**, L659 (1987).

[13] D. D. Sarma, K. Sreedhar, P. Ganguly, and C. N. R. Rao, Phys. Rev. B **36**, 2371 (1987).

[14] W. K. Ford, C. T. Chen, J. Anderson, J. Kwo, S. H. Liou, M. Hong, G. V. Rubenacker, and J. E. Drumheller, Phys. Rev. B **37**, 7924 (1988).

[15] C. N. R. Rao, P. Ganguly, M. S. Hegde, and D. D. Sarma, J. Am. Chem. Soc. **109**, 6893 (1987).

[16] B. Dauth, T. Kachel, P. Sen, K. Fischer, and M. Campegna, Z. Phys. B **68**, 407 (1987); **70**, 137 (1988).

[17] Y. Guo, J. M. Langlois, and W. A. Goddard III, Science **239**, 896 (1988).

[18] B. K. Chakraverthy, D. Feinberg, Z. Huang, and M. Avogon, Solid State Commun. **64**, 1147 (1987).

[19] P. Ganguly and K. Sreedhar (unpublished).

[20] C. N. R. Rao, D. D. Sarma, S. Vasudevan, and M. S. Hegde, Proc. R. Soc. London, Ser. A **367**, 239 (1979).

[21] S. Evans and J. M. Thomas, J. Chem. Soc. Faraday Trans. 2, **71**, 313 (1975).

[22] F. R. Mcfeely, L. Ley, S. P. Kowalczyk, and D. A. Shirley, Solid State Commun. **17**, 1415 (1975).

[23] R. W. Joyner, K. Kishi, and M. W. Roberts, Proc. R. Soc. London, Ser. A **358**, 223 (1977).

[24] L. Ley, R. A. Pollak, S. P. Kowalczyk, R. Mcfeely, and D. A. Shirley, Phys. Rev. B **8**, 641 (1973).

[25] R. W. Joyner, M. W. Roberts, and S. P. Sing-Bhopari, Surf. Sci. **104**, L199 (1981).

[26] S. Suzer, M. S. Banna, and D. A. Shirley, J. Chem. Phys. **63**, 3473 (1975).

[27] S. Suzer, J. Chem. Phys. **72**, 6763 (1980).

[28] S. Suzer, S. T. Lee, and D. A. Shirley, J. Chem. Phys. **65**, 412 (1976).

[29] D. E. Cox and A. W. Sleight, Acta Crystallogr. B **35**, 1 (1979).

[30] M. S. Hegde and M. Ayyob, Surf. Sci. **173**, L635 (1986).

[31] D. C. Frost, A. Ishitani, and C. A. McDowell, Mol. Phys. **24**, 861 (1972).

[32] J. A. Yarmoff, D. R. Clarke, W. Drube, U. O. Karlsson, A. Taleb-Ibrahini, and F. J. Himpsel, Phys. Rev. B **36**, 3967 (1987).

[33] J. M. Williams, M. A. Bano, K. D. Carlson, U. Geiser, H. C. Ivy Kao, A. M. Kini, L. C. Porter, A. J. Schultz, R. J. Thorn, H. H. Wang, M. Whangbo, and M. Evain, Acc. Chem. Res. **21**, 1 (1988); see also C. N. R. Rao, J. Solid State Chem. **74**, 147 (1988).

[34] M. A. Subramainan, J. C. Calabrese, C. C. Toradi, J. Gopalakrishnan, T. R. Askew, R. B. Flippen, K. J. Morrissey, U. Chowdhry, and A. W. Sleight, Nature **332**, 420 (1988).

[35] M. S. Hegde (unpublished).