Evidence for double valence fluctuation in metallic oxides of lead

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The possible role of double valence fluctuation in both lead and oxide ions with reference to metallization in oxides of lead is examined by x-ray-photoemission spectroscopy, ultraviolet-photoemission spectroscopy (UPS), and ^{207}Pb NMR studies. The double valence fluctuations may be viewed as $Pb^{4+}+2O^{2-}\rightleftarrows Pb^{2+}+O_2^{2-}$. While the insulating oxides PbO, Pb_3O_4, and Sr_2PbO_4 show a single oxide ion, O^{2-} characterized by O(1*s*) at 529.7 eV, the insulating peroxide BaO_2 is characterized by the ion O_2^{2-} with a single O(1*s*) at 533 eV. The metallic PbO_2, $BaPbO_3$, $BaBiPbO_3$, and $SrPbO_3$ showed the occurrence of both O^{2-} and O_2^{2-} ions. The valence band in these compounds has also been studied by UPS, and clear evidence for the coexistence of O^{2-} and O_2^{2-} is seen in PbO_2. A simultaneous study of ^{207}Pb NMR suggests that the Pb ion could also exist in mixed-valence states. Qualitative arguments are presented to rationalize the existence of such mixed valences of the anion in metal oxides in general and their role in superconductivity.

INTRODUCTION

The recently discovered phenomenon of high-temperature superconductivity[1-4] followed a model for superconduction arising from bipolaron condensation proposed by Chakraborthy.[5] Shaforth *et al.*[6] seem to be the first to predict the possibility of a superconducting state arising from a Bose condensation of tightly coupled pairs. Several mechanisms[7-9] have been proposed for the observation of the high T_c's such as the resonating valence-bond model, the spin-density wave model, etc. A satisfactory explanation is still being sought. Prior to the era of high T_c superconductivity, Hirsch and Scalapino[10] proposed a double valence fluctuation model in which *two* degenerate states differ by two electrons instead of by the one electron found, for example, in rare-earth systems. The basic mechanism is one in which the transfer of an electron to a cation pushes a pair of cation electrons to neighboring anion orbitals so that subsequent transfer of an electron to the cation does not lead to Coulomb repulsion from the original pair of electrons. Hirsch and Scalapino show that, unlike the bipolaron model where the critical parameter is the electron-phonon coupling constant, double valence fluctuation is entirely electronic in origin and T_c is of the order of $J_{\rm eff}/k_B$ which can be very high. The model of Hirsch and Scalapino involves both cation and anion. It is appealing in the light of the fact that high-temperature superconductivity is found in oxides with the perovskite structure in which cation-cation interaction has to be directly mediated by the oxygen anion.

Oxygen species varying by two electrons such as O^{2-}, O_2^{2-}, or O_2 are well known. The double valence fluctuation in oxides may be visualized in terms of the equilibrium

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

Ions such as Pb, Bi, Sn, etc., have the property that stable valence states also differ by two electrons, such as Pb^0, Pb^{2+}, and Pb^{4+}, Bi^{3+}, and Bi^{5+}. Oxides of Pb such as $BaPb_{1-x}Bi_xO_3$ also show superconductivity.[11] The question arises whether purely double valence fluctuations can give rise to metallicity itself before one considers their role in superconductivity. With this in mind, we have examined the photoelectron spectra of several oxides of lead to see if the metallicity in some of these systems may be attributed to a double valence fluctuation. We take advantage of the fact[12,13] that the O(1*s*) valence band in x-ray (XPS) and the photo emission spectroscopy O(2*p*) valence band in He II ultraviolet photoemission spectroscopy (UPS) show distinct features which distinguish O^{2-} from O_2^{2-} species. Our results clearly show a correlation between metallicity and mixed valence of oxide ions. NMR studies on ^{207}Pb support our conclusions. The results of these investigations are presented below. Part of this paper was presented earlier.[14]

EXPERIMENTAL

X-ray and uv photoelectron spectra were recorded in ESCA-3 Mark-II spectrometer of VG Scientific Ltd. Powder samples were pressed into thin pellets and the spectra were taken at 300 K without any argon ions etching or heating the samples in the spectrometer. This was done to prevent dissociation or reduction. The ternary oxide systems such as $BaPbO_3$, $SrPbO_3$, Sr_2PbO_4, etc., were prepared by the decomposition of the carbonates (at 1000 K) obtained as coprecipitates by the addition of a solution of the metal nitrates to an excess carbonate solution. The compounds were characterized by x-ray diffraction studies.

RESULTS AND DISCUSSION

In Fig. 1(a), the O(1*s*) region of orthorhombic PbO, PbO_2, and BaO_2 are given. The spectra of PbO is characterized by a single O(1*s*) peak at 529.7 eV with Pb($4f_{7/2}$)

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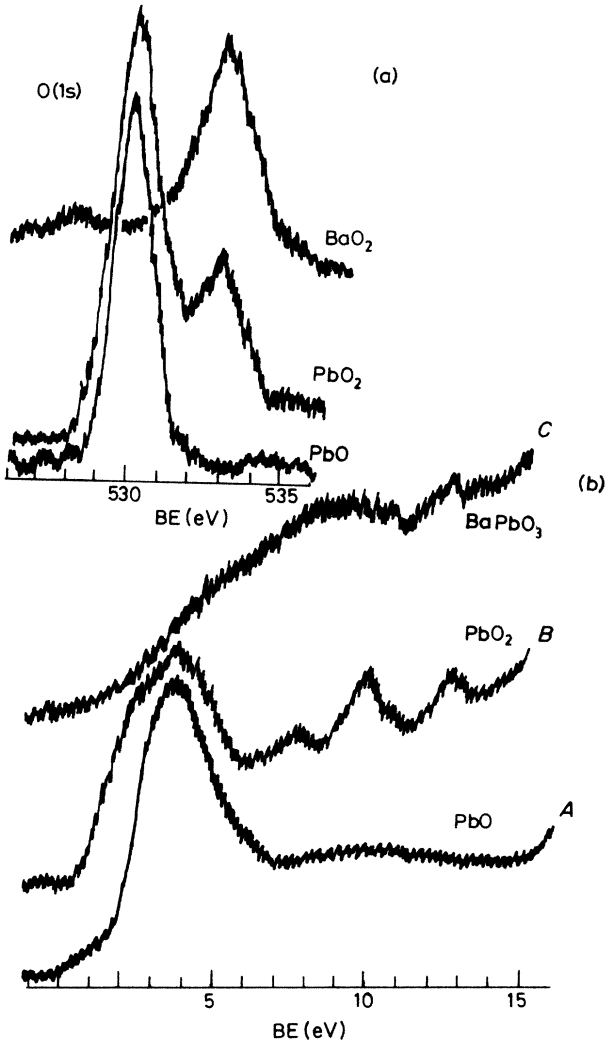

FIG. 1. (a) Al K_α XPS O(1s) region of PbO, PbO_2, and BaO_2. (b) He II UPS valence-band region of PbO, PbO_2, and $BaPbO_3$. BE is the binding energy.

at 138.0 eV.[15] The O(1s) peak is clearly due to an oxide ion O^{2-}. The O(1s) in BaO_2 however clearly shows a peak at 533 eV which can be assigned to O_2^{2-}, since BaO_2 is a peroxide. The spectrum of PbO_2 interestingly shows the two O(1s) peaks, at 529.7 and 532.7 eV suggesting the simultaneous presence of both oxide and peroxide ions. These peak intensities are entirely reproducible and comparable to those reported earlier.[16] The relative intensities of the oxide and peroxide peaks is about 2:1.

Oxide ions, O^{2-} with $2p^6$ electronic configuration should give a single $2p$ final state upon photoionization and, hence, a single O($2p$) band which is usually peaked at 4–6 eV. This indeed is observed in the case of PbO as shown in Fig. 1(b). The maximum of the O($2p$) band occurs at around 4 eV as expected. The valence-band spectra of PbO_2 [Fig. 1(b)] show, besides the peak at 4 eV due to O^{2-}, features due to three additional maximum at 7.4, 9.7, and 12.7 eV. Such species have been observed in $Ag+O_2$, $Au+O_2$, and $Pt+O_2$, etc., by Kamath and Rao[12] and these peaks have been assigned to $2p\pi_g^4$, $2p\pi_u^4$, and $2p\sigma_g^2$ corresponding to a O_2^{2-} ion. Photoionization of $2p\pi_g^4$, $2p\pi_u^4$, and $2p\sigma_g^2$ in O_2^{2-} ion should give three bands.[17] Thus the O(1s) band at 532.7 eV in PbO_2 correlates well with the peroxide ion, O_2^{2-} from the expectations in the valence band. The peroxidelike species does not seem to be due to a surface species as the relative intensities of these two peaks are unchanged on changing the angle of collection.

In $BaPbO_3$ the three additional features are seen, though less clearly. What is important is the very small density of states near the top of the O($2p$) band [Fig. 1(b)]. In Fig. 2, we show the XPS O(1s) region of insulating Pb_3O_4, conducting $BaBiO_3$, $BaBiPbO_3$, and $BaPbO_3$ (resistivity: 10^{-1}–10^{-3} Ω cm at 300 K)[18,19]. For comparison, O(1s) of PbO_2 is also shown in Fig. 2. In Fig. 3, O(1s) and Pb(4f) regions are shown for insulating Sr_2PbO_4 (10^8 Ω cm at 300K) and fairly good conducting $SrPbO_3$ (1–10 Ω cm at 300 K).[17,18] What is interesting is that the oxides which are insulating show no peroxidelike species, while those that are good conductors do show a fairly intense O(1s) peak at about 532.5–533 eV. An interesting feature is that, in $BaPbO_3$, the ratio of peroxide to oxide is nearly 2:1, which seems to suggest that the formula of $BaPbO_3$ at least within the time scale of XPS is to be written as BaO_2+PbO with a Pb ion in the +2 state. That the species seen are not from the surface alone is borne out by the fact that the relative intensity of Sr(3d) in Sr_2PbO_4 to that in $SrPbO_3$ is about 2:1 (Fig. 3). Furthermore, by taking the relative intensities of

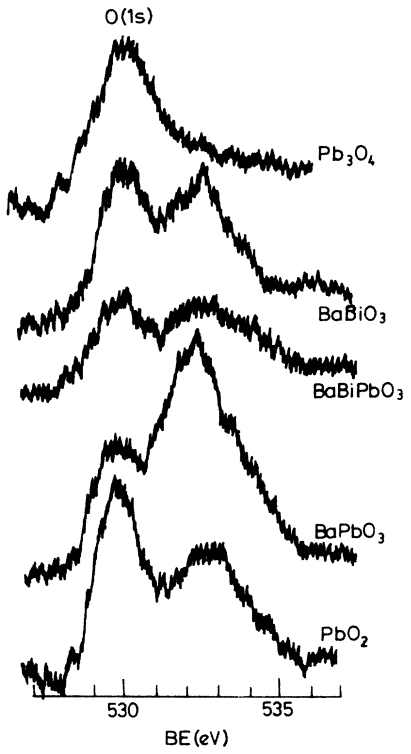

FIG. 2. O(1s) region of oxides of lead.

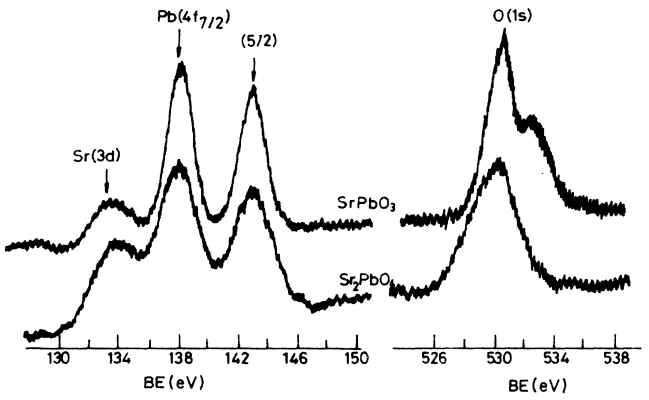

FIG. 3. O(1s) and Pb(4f) region of Sr_2PbO_4 and $SrPbO_3$.

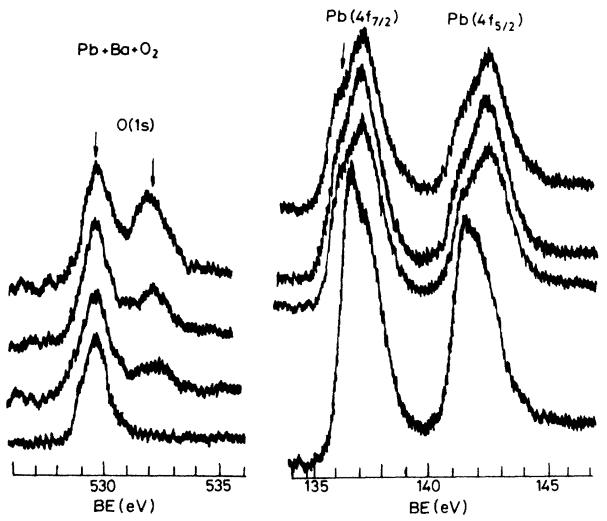

FIG. 4. O(1s) and Pb(4f) regions for Pb+Ba+O_2 system; surface concentration of Ba for curve from bottom to top are 0, 1×10^{14}, 2.5×10^{14}, and 3.8×10^{14} atom/cm^2.

Ba($3d_{5/2}$) and Pb($4f_{7/2}$) in $BaPbO_3$ and the corresponding photoionization cross sections, we have estimated the stoichiometry on the surface and find that the stoichiometry is correct within 10% of the bulk value. This is near the limits of accuracy of quantitative estimation using the XPS method. $BaBiO_3$, as well as the superconducting $BaPb_{0.75}Bi_{0.25}O_3$, also show peaks due to both oxide and peroxide ions (Fig. 2).

Samples prepared by the ceramic technique which involve higher temperatures of firing were found to have different stoichiometries at the surface. Thus samples of $BaPb_{1-x}Bi_xO_3$ prepared by the ceramic technique were found to be predominantly BaO_2 at the surface. We have prepared single crystals of $BaPbO_3$ using KCl as flux and find that even in this case the surface is rich with BaO_2. Scratching or cleaning the samples *in situ* after evacuation always gave us a peroxide-rich species in these ceramic samples. Our experience with single crystals is not in agreement with the single-crystal results of Wertheim *et al.*[20] who have, however, not reported the surface composition of their crystals. We note that cleaving crystals which are rarely obtained in large sizes, such as those of $BaPb_{1-x}Bi_xO_3$, may not be a sufficient criterion for obtaining the correct information, as sometimes the crystal cleaves easily at the point where inhomogenities are present; therefore, the surface examined need not correspond to the composition expected.

We sought to examine if the O_2^{2-} species can be generated on the surface. Barium from a getter source was deposited on a Pb surface and then oxygen was exposed. It is well known that oxygen exposed to a Pb surface gives only PbO at 300 K.[15] In Fig. 4, we show the changes in the O(1s) and Pb(4f) region when dry oxygen was exposed to a Ba covered Pb surface for different barium concentrations. On the barium covered surface, O^{2-}, as well as peroxidelike O_2^{2-} peaks, is clearly seen. On barium itself, an intense peak at 528.0 eV develops which is identified with BaO.[21] A small peak at this energy can be seen in Fig. 1 for BaO_2. Thus, a Ba covered Pb surface shows the possibility of a mixture of PbO- and $BaPbO_3$-type oxides. It is interesting to note that even a Pb(4f) region shows more and more of a Pb^{2+} peak as the Ba concentration is increased. Binding energies of core levels of Ba, Pb, and Sr and the O(1s) are summarized in Table I. Even though a formal oxidation state of Pb in PbO_2 should be 4+, Pb($4f_{7/2}$) is observed at about 0.3 eV lower compared to PbO. Similarly, Pb($4f_{7/2}$) binding energy in $BaPbO_3$ is similar to that in PbO_2.

The photoelectron spectroscopy studies therefore establish, in our opinion, the mixed-valence nature of the oxide ions. This mixed valence of the anions could induce or coexist with mixed valency in the lead ions. All the core levels of lead remain, however, essentially the same. We, therefore, examined the NMR signal from ^{207}Pb. Some of the chemical shifts obtained are given in Table II. The shifts obtained with Sr_2PbO_4 are the highest reported so far for ^{207}Pb in an oxide matrix and reflect the truly quadrivalent character of the lead ions, in this compound. The mixed valence of lead ions[21,22] is seen in the insulating Pb_3O_4. However, in PbO_2, a single NMR line is seen although XPS shows two distinct oxide species. This would indicate a valence fluctuation of the Pb ions so that, in the NMR time scales, we obtain a single line. This is, perhaps, also the case in $SrPbO_3$ where we also obtain a single NMR line. The chemical shift in this compound is smaller compared to Sr_2PbO_4 indicating a lower formal valence state of the Pb ions. The decrease in chemical shift as the conductivity increases is usually interpreted in terms of a Knight shift. In conjunction with our XPS results, this is also consistent with a decrease in the formal oxidation state.

The possibility of double valence fluctuation may be looked at from the point of view of ionic radii. In $BaPbO_3$, for example, the perovskite a parameter is 4.30 Å.[23] This compares well with the distances expected from ionic radii[23] of Pb^{4+} and O^{2-}, (0.78 and 1.40 Å, respectively). Since the ionic radius of Pb^{2+} on octahedral coordination is 1.19 Å, the double valence fluctuation should mean an effective radius of 0.96 Å for an oxygen ion or an O—O distance of 1.92 Å in the peroxide species.[24]

TABLE I. Core-level binding energies of oxides of lead in eV. The values are accurate within ±0.2 eV.

Compound	Pb($4f_{7/2}$)	O(1s)	Ba($3d_{5/2}$)	Bi($4f_{7/2}$)	Sr(3d)
PbO	138.0	529.7			
PbO_2	137.6	529.7			
		532.7			
$BaPbO_3$	137.6	529.6			
		532.5			
$BaBiO_3$		529.3	779.6	158.4	
		532.4			
$BaPb_{0.8}Bi_{0.2}O_3$	137.6	529.3	779.6	158.4	
$SrPbO_3$	137.6	529.6			532.8
		532.5			
Sr_2PbO_4	138.0	530.0			132.8

The above studies, therefore, make a case for the possibility of the existence of double valence fluctuation involving both cations and anions. Since these oxides have no partially filled *d* orbitals, and since there is no significant density of states at the Fermi level [see Fig. 1(b)], the metallicity of the lead oxides would seem to arise from the double valence fluction. In a sense, we may consider the metallicity as due to a degenerate gas of bipolarons. Such a degenerate gas could be the precursor to a superconducting state.

Finally we examine the conditions for the formation of such peroxidelike species in the oxides. We adopt an argument similar to that proposed by Fasteas and Goodenough[25] for the instability of Fe_2S_3. According to them, the location of Fe^{3+} one-electron energy level within the valence band by the transfer of electrons from the valence band to the Fe^{3+} level which now becomes Fe^{2+}. The holes in the valence band reorganize to create S_2^{2-} dimers so that Fe_4S_3 becomes unstable to the disproportionation $Fe_2S_3 \rightarrow FeS + FeS_2$. The essence of the arguments of Fasteas and Goodenough[25] are attractive although these arguments fail when applied to $KFeS_2$, for example, where the Fe^{3+} ions are quite stable or to the dilute magnetic semiconductors such as $Mn_xCd_{1-x}S$, where the Mn^{2+} levels are located well within the valence band.[26] Apparently the on-site correlation energy for the metal ions *vis-a-vis* the depth of these levels from the top of the valence band is important in determining whether S_2^{2-} ions are formed or not.

It may be postulated that an O_2^{2-} or O^{1-} species would be obtained if holes are created in the oxide valence bands which are predominantly of O^{2-} character. These holes may be created in transition-metal oxides by the presence of empty $3d^n$ levels within the valence band. In the case of ions such as Fe^{4+}, Cr^{4+}, Co^{4+}, Ni^{3+}, and Cu^{3+} there seems to be evidence to show that the $3d^n$ energy levels of these ions are likely to be located within the valence band of oxides. The $3d^n$ energy levels of iron group transition metal ions with respect to the top of the oxygen valence band in TiO_2 obtained from photoconductivity studies[27] are shown in Fig. 5(a). The valence band of $LaBO_3$ (Refs. 28 and 29) are

TABLE II. ^{207}Pb solid state NMR chemical shifts.

Compound	^{207}Pb (ppm)
$Pb(NO_3)_2$	0
PbO (yellow)	7187, [a]6500[b]
PbO (red)	6500, [a]6700[b]
PbO_2	8257, [a]8600[b]
Sr_2PbO_4	−2352[c]
$SrPbO_3$	−2056[c]

[a]From Ref. 22.
[b]Reference 23.
[c]Present measurements.

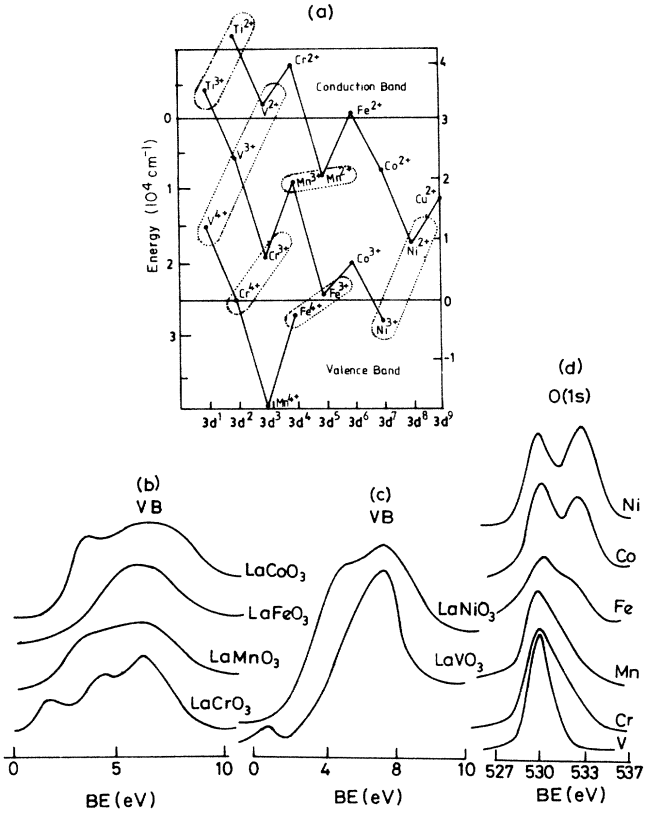

FIG. 5. (a) Location of $3d^n$ energies relative to the valence band and conduction band of TiO_2 (from Ref. 27). (b) XPS valence band from Ref. 28. (c) XPS valence band from Ref. 29. (d) O(1s) region from Ref. 30.

given in Fig. 5. While the $3d$ and O($2p$) bands are well separated in $LaVO_3$ and $LaCrO_3$, the metal d bands overlap with the O($2p$) band in other oxides. Correspondingly, the O($1s$) band becomes broader towards the higher binding energy as the metal $3d$ band merges with the O($2p$) band and two oxygen peaks are clearly seen in $LaNiO_3$ (Fig. 5). Fierro and Tejuca[30] ascribe the additional feature in the O($1s$) region around 531.5–532 eV to O^{1-} and not due to OH^- or CO_3^{2-} species. In our opinion, the growth of the additional feature in the O($1s$) region is a reflection of the tendency to create holes in the valence band by the overlap of the metal $3d$ band with the O($2p$) band. The results of Fierro and Tejuca are entirely reproducible. We have also seen that by decreasing the angle of collection to mere 10°, the relative intensities of the two O($1s$) peaks do not change significantly indicating that the oxygen species are likely to originate from the bulk. It is yet to be ascertained how much of the higher binding energy O($1s$) peak is due to surface oxygen. Further, the possible role of such mixed-valent oxide ions in the metallic compounds such as $LaNiO_3$ is yet to be studied.

A perusal of literature shows that in NiO and CuO, there are features in the higher binding energy side of O($1s$) band in the energy range 531–531.5 eV identified as due to O^- species.[31,13] These features have been associated with the mixed valence of an oxygen ion due to the presence of excess oxygen. It is to be pointed out that in oxides where a mixed valence of oxygen in O^{2-} and O^{1-} exists, the metal $3d$ and O($2p$) bands overlap.[32] We note from Ref. 32 that in NiO and CuO the $3d$ level is located well within the valence band. In such a case the removal of outer electron from Cu^{2+} to give Cu^{3+} should be unfavorable.

The stabilization of O^{1-} or O_2^{2-} species probably depends on the metal ion. In the case of metal ions such as Ni^{3+}, Cu^{3+}, one may obtain a single-electron transfer from the oxide ion to the metal $3d^{n+}$ ion to give O^{1-} and $3d^{(n-1)+}$ metal ion. In the case of ions such as Pb^{4+}, Bi^{5+}, it may be possible that two-electron transfers are required since Pb^{3+} and Bi^{4+} are less stable compared to Pb^{2+} and Bi^{3+}, respectively.

The formation of oxygen dimer when holes are introduced into the valence band has been rationalized by Ganguly[33] by assuming that the top of the valence band is antibonding in character. The formation of oxides and peroxide ions from oxygen molecule may be viewed as follows:

$$\text{Oxygen molecule } O_2\ (\pi^{*2},\sigma^{*0})+2e\rightarrow\text{peroxide } (O_2^{2-})(\pi^{*4},\sigma^{*0})\ ,$$

$$\text{Peroxide } O_2^{2-}(\pi^{*4},\sigma^{*0})+2e\rightarrow\text{oxide } O_2^{4-}(\pi^{*4}\sigma^{*2})\ .$$

Creation of holes in the valence band of essentially ionic oxides should thus lead to a reduction in the antibonding character which may manifest itself in the form of peroxide ion or other oxygen multimeric species. Small electron density at E_F and also at the O($2p$) region for O^{2-} ion in the He II UPS for $BaPbO_3$ [Fig. 1(b)] supports the above scheme of formation of peroxide ions. The model is different from the commonly accepted picture, based on the strong neutral metal-oxygen interactions where the valence band is bonding in character (for example, see Goodenough, Ref. 34).

Recent studies on high-temperature superconducting oxides of copper ($YBa_2Cu_3O_7$) have also shown evidence for the presence of peroxide species[35,36] with no Cu^{3+} ions. As mentioned earlier, it should be difficult to obtain Cu^{3+} species in oxide if we assume that the $3d$ level of Cu^{2+} is located within the valence band. The holes may instead create O^- or O_2^{2-} ions. The presence of peroxidelike species and any associated double valence fluctuation does not necessarily signal a low-temperature superconducting state since $BaPbO_3$ and PbO_2 are not superconductors. In $YBa_2Cu_3O_7$, there is evidence for a continuous increase in the amount of peroxolike oxygen species as the temperature is decreased from well above T_c with a concomitant increase in Cu^+ state. Apparently, the presence of double valence fluctuation is a necessary, but not sufficient, criterion for superconductivity.

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