Photoemission studies of the low-temperature reaction of metals and oxygen

S. L. Qiu, C. L. Lin, J. Chen, and Myron Strongin

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000

(Received 15 September 1989)

X-ray photoemission and synchrotron-radiation photoemission were used to study the reaction of metals and molecular oxygen at low temperatures. Combined core-level and valence-band measurements permit the identification of various oxygen species. When Li, Cs, K, and La are deposited on solid oxygen, an O $1s$ feature near 535 eV is observed and attributed to the superoxide species. Features ranging from 531.5 to 533 eV are also observed and identified as the peroxide species. In contrast to the case of Li and of most other metal oxides, for Cs or K "oxides" an O $1s$ feature is seen at 528 eV and attributed to the O^{2-} species in a metallic matrix.

I. INTRODUCTION

The study of the reaction of alkali metals and oxygen has been of interest over the years,[1-5] and because of the recent discovery of high-T_c materials fundamental studies of oxides have a renewed impetus. In this work, experiments on the formation of peroxides and superoxides when metals react with solid molecular oxygen are described. In the context of the high-T_c materials, various claims have been made for the observation of both peroxide[6] and superoxide species,[7] and some of the identifications are based on confusing data in the literature.[2,8] Of course, most of the previous studies of the molecular-oxygen species have involved oxygen adsorbed on metal surfaces, and there has been confusion over what particular oxygen species were actually observed. One of the aims of this work is to clarify some of these points.

The experiments in this paper are concentrated on the alkali metals for two reasons. First, the interaction of solid molecular oxygen and the alkali metals produces different molecular-oxygen species such as the peroxide and the superoxide. Second, the alkali metals have been used to form compounds such as $Li_xNi_{1-x}O$, which are of great interest in understanding the electronic structure of high-T_c superconductors.[9] The long-range intent of this research is to study whether CuO_2 layers and the local fourfold Cu-oxygen structure characteristic of the high-T_c superconductors can be constructed by reactions at low temperatures. It is intended to use the alkali metals and Ba, or La, to form metastable compounds below 35 K which could then be reacted with Cu or Ni to form stable oxides with Cu or Ni in a 2+ formal valence state. With proper doping, it is hoped that holes can be put on the oxygen sites as in the high-T_c materials. These experiments will be described in planned forthcoming publications and it is the purpose of the present work to carefully study the interaction of a variety of metals with molecular oxygen below 35 K to see if there are features common to a variety of systems. Besides the interaction of the oxygen on layers of metal, the interaction of the metal when deposited into an oxygen-rich environment, such

as solid oxygen itself, was also studied.

The experiments described here concentrate mainly on the x-ray-photoemission spectroscopy (XPS) spectra of the different metal-oxygen species. The interpretation of the valence-band spectra of oxygen on the alkali metals is somewhat controversial and our own work seems to support the work of Woratschek et al.,[4] who studied changes in the valence spectrum of Cs films as they were continuously oxidized. Recent work by Bertet et al.[5] relates features in the KO_2 (K superoxide) spectrum to the features of condensed O_2. The differences in interpretation will be discussed in the light of the XPS and some valence-band results obtain in this work.

II. EXPERIMENT

In this work the reaction of oxygen at about 35 K or below with films of Li, K, Cs, Ba, La, Cu, and Ag is studied. The films were deposited on a low-temperature Cu or Ta substrate at a pressure in the 10^{-10}-Torr range from a SAES getter source for alkali metals, and a tungsten basket source for Ba, La, Cu, and Ag. The cleanliness of the films was determined by the absence of a carbon or oxygen signal in the XPS spectrum. High-purity (99.999%) oxygen gas and a liquid-nitrogen trap were used to eliminate contamination of the oxygen. A standard continuous He-flow cyrostat provided the low-temperature environment. For the Cs and K experiments the temperature was estimated to be about 35 K or slightly higher. At these temperatures the high solid-O_2 vapor pressure allowed only a layer of physisorbed O_2 to be present. At temperatures below 30 K, where the vapor pressure is below 10^{-8} Torr, thicker layers of oxygen were easily obtained. Photoemission measurements and some of the XPS work were done with a standard PHI Al anode x-ray source and a Vacuum Science Workshop (VSW) HA-100 hemispherical electron-energy analyzer on beamline U7 at the National Synchrotorn Light Source (NSLS), at Brookhaven National Laboratory. Besides exposing the films to oxygen gas at low temperatures, some of the work was done by evaporating the metal into solid oxygen, which varied from one to three layers thickness.

On most runs a Ta foil was covered with an evaporated film of the metal to be studied. Ta was used as a substrate material since the film could be removed by resistively heating the Ta foil. On some runs, where it was desired to obtain the lowest temperature, the films were deposited onto the Cu holder. The metal film was usually made thick enough so that no Ta features were observed in either the XPS or the ultraviolet-photoemission (UPS) spectra. Because the measurements were done at low temperatures, it was assumed that diffusion of oxygen through an evaporated film to the Ta interface was negligible.

As the metal films were exposed to oxygen, various features were observed in the UPS and XPS spectra, and finally when the metal surface was reacted, additional O_2 deposition showed the characteristic valence and core-level features of physisorbed molecular oxygen. In some cases a characteristic oxide layer initially formed and further O_2 produced peroxide and superoxides before the features of molecular oxygen were observed. After a layer to a few layers of molecular oxygen were present on the surface, metal was then deposited back into the now oxygen-rich mixture and the various features were reobserved. Of course, in most cases the features from the initial oxygen-substrate reaction were also present and care was taken to observe the differences due to the deposition of additional metal atoms into the molecular oxygen. It should be emphasized that, on a few runs, deposition into thicker oxygen layers was studied with essentially the same results as those obtained for the thinner layers, and therefore the thickness of the oxygen layer is not thought to be of great importance in determining the position of the various oxide-related features. More will be said about this in the discussion of referencing. In some cases when the oxygen layers were very thick, the XPS features generated during metal deposition were not immediately observed and this is evidence that the metal deposited into the solid oxygen layers actually penetrates to the substrate surface or to a region near the substrate. It is especially interesting that the levels of both the superoxide and peroxide were not particularly sensitive to whether the species were near the top of the oxygen layer or near the interface. Again, this point will be discussed later. It is also interesting to mention that solid O_2 appears to be more "porous" than solid Kr and this may be due to a "fluffy" structure in the condensed molecular oxygen.

III. RESULTS

A. Oxygen 1s spectra and referencing

The main results of this work, which are shown in Figs. 1 and 2, give the O 1s spectrum for oxygen condensed on various metals, and also for the reverse experiment, where metals are deposited on solid oxygen. In the metal-rich regime, when oxygen is first condensed on the metal, the "oxide" is the first species that is observed. With further condensation of O_2 the "oxide" peak stays essentially constant and other peaks appear until the
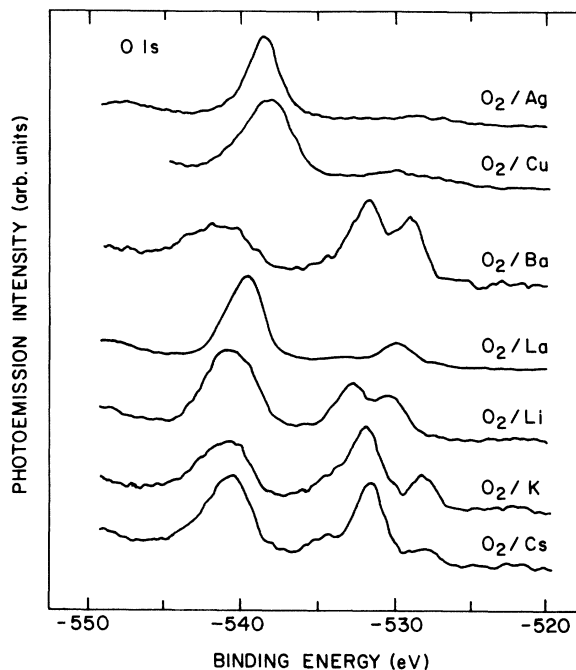

FIG. 1. Al $K\alpha$ XPS spectra of O 1s core level for molecular oxygen condensed on various metal substrates as indicated in the figure at 35 K or below. The temperature on the K and Cs substrates was about 35 K and only small amounts of molecular oxygen collected on the surface at this temperature. Note at about 35 K or above the oxygen vapor pressure is high enough so only the first physisorbed O_2 layer is stable.

solid-O_2 feature grows dominant. All the spectra shown in Fig. 1 were recorded just before the reverse experiment was performed, i.e., before metal was deposited into the solid O_2. The thickness of the solid-oxygen layer for the different cases in Fig. 1 varies from one to three layers and no shift in the spectrum of the metal core levels due to surface charging is observed. Basically, four features are observed in the data. At the highest binding energy, the XPS spectrum of molecular oxygen is observed, followed by the superoxide, the peroxide, and finally various "oxide" phases. The justification for these identifications is addressed in the discussion. In Fig. 3, a summary of the various peak positions is presented. Before considering the interpretation of the data, a description of the characteristic spectra and referencing of the XPS spectrum is given in the following subsections.

1. Molecular oxygen

The O 1s features of solid molecular oxygen are seen in the range 541–538 eV when referenced to the Fermi level of the metal substrate. The ionization potential of the 1s core level of the oxygen molecule is 543 eV, and the observed differences from this value on various substrates can be explained as follows. When a noninteracting rare gas or molecular solid is condensed on the surface of a metal, the vacuum level of the molecule and the metal
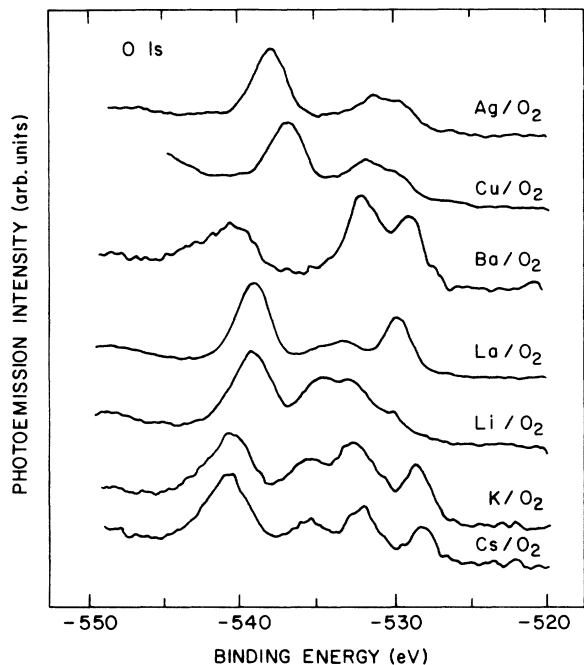
FIG. 2. Al $K\alpha$ XPS spectra of O $1s$ core level for various indicated metals deposited into solid oxygen at 35 K or below. The temperature for the K and Cs substrates was about 35 K and only about a monolayer of O_2 was present when the metals were deposited. In these spectra the superoxide becomes much more pronounced than in Fig. 1, where O_2 is condensed on the metal. In this case the metal is a dilute species in the physisorbed O_2.
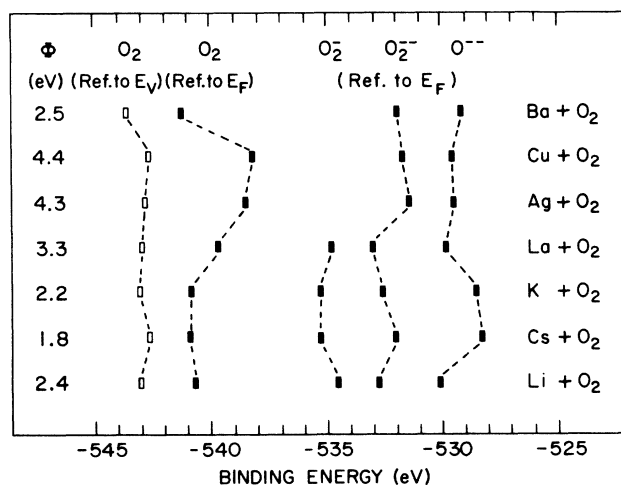

FIG. 3. Summary of various oxygen-related peak positions (rectangular bars) obtained from Figs. 1 and 2. The dashed lines are guides for the eye. The data listed on the left-hand side are the work functions of various metals as denoted on the right-hand side.

align.[10] As long as there is no charge transfer, this will be the case. Because of this, if, for example, the work function of the metal is about 4 eV, the O $1s$ peak of molecular oxygen will appear at 539 eV when referenced to the Fermi level of the substrate. In a photoemission measurement, where the sample and analyzer are grounded, the Fermi level of the substrate always appears at the same position, even when the substrate is changed. Since the vacuum level changes for the various metal substrates relative to the system ground, the O $1s$ is binding energies of adsorbates which are fixed to the substrate vacuum level also change relative to the Fermi level, and this variation is what is observed. The work function of various metals[12] studied in this work are listed on the left-hand side of Fig. 3. The data represented by open rectangles in Fig. 3 are obtained by adding the work function of the corresponding metal substrate to the binding energy of the molecular-oxygen $1s$ core level measured from the Fermi level. Clearly, the data in Fig. 3 for molecular oxygen on the different metal substrates are consistent with vacuum-level alignment. The small deviation seen for some data points is most likely due to the changes in the work function when oxygen is condensed on the metal substrate. Comparison of Figs. 2 and 1 reveals that the molecular-oxygen $1s$ peak shifts to lower binding energy in most cases when metal is deposited into the solid oxygen layer and new features appear. In contrast, the "oxide" peak from the underlying substrate does not shift. The shift of the molecular-oxygen features can be attributed to the removal of surface charge when the metal is deposited on the O_2 layer, or possibly to better screening of the O $1s$ core hole. The substrate-oxide features are under the surface charge sheet and the photoemission spectra would not be affected as much as the molecular oxygen. However, it is possible that the change in the vacuum level of the substrate upon the formation of the new species shifts the molecular-oxygen levels. Because of the alignment to the vacuum level, the peak position of molecular oxygen will be sensitive to the variation of the work function. For this reason, the data for molecular oxygen shown by the solid rectangles in Fig. 3, were taken from Fig. 1, whereas the data for the other features were taken from Fig. 2, where the data for metal on solid oxygen is given. It is only in this case the superoxide and peroxide features usually appear.

2. Superoxide and peroxide

A major result of these studies is the feature at about 535 eV which is attributed to the superoxide[13] where one electron is formally given to the oxygen molecule. Another feature in the regime from 531.5 to 533 eV is attributed to the peroxide, where two electrons are given to the oxygen molecule. We emphasize that we are not concerned with actual charge transfer, and discussions of electron donation are in the spirit of formal oxidation states. The justification for the assignment of these species will be discussed below, and the rest of the discussion here concerns the constancy of the XPS features. At first glance, the variation of the superoxide peak position appears similar to that of the solid molecular oxygen;

therefore, it might appear that the assumption of vacuum-level alignment for the superoxide feature is plausible. To verify the referencing for the superoxide species, we have performed an experiment in which the Li-superoxide species were formed over Ag and Li substrates, respectively, and although the O $1s$ peak for O_2 shifted, the same peak position for the superoxide was observed. This proves conclusively that the conjecture mentioned above cannot be true, since the vacuum levels of Ag and Li differ by about 2 eV. It would appear that in the case of the superoxide the constancy of the XPS peak position implies, as in the case of a metallic cluster,[14] that the Fermi level of the superoxide must be aligned to the Fermi level of the substrate. This means that there must be states around a Fermi level that can be "pinned" to the substrate Fermi level. For this to happen, the superoxide species must not be just single species, but a cluster of a superoxide phase which has enough states in the gap to provide alignment to the substrate Fermi level. This problem of referencing and the connection to the substrate is discussed in Ref. 14.

The peroxide case is thought to be similar. There is more variation in the XPS peak position than the superoxide, but since the variation does not correlate with what one would expect from the substrate work-function variation, we still argue that there is alignment to the Fermi level. The small variation in the peak position might, in fact, be due to variations in the amount of charge transferred to the oxygen molecule, even though the formal oxidation state is O_2^{2-} for peroxide. Since the oxygen molecule is close to dissociation in this configuration, there may also be variations in the bond length for the peroxides of different metals. In general, as more charge is transferred to the oxygen molecule, the core-level features shift to lower binding energy. It is then somewhat perplexing that the peroxide of Ag has the lowest binding energy. Possibly this case is characteristic of some state which is very close to dissociating into the atomic species.

3. The oxide

As already mentioned, the oxide features are first observed when oxygen is initially condensed on the clean metal films. It is interesting that in this regime significant shifts are observed for the O $1s$ peak positions of K and Cs oxides, as compared to Li,[13] Cu, and most other oxides. We attribute this to the fact that oxygen may go under the surface in the case of Cs (Ref. 4) and K, and this may lead to a more shallow binding energy because of the more effective screening in the metal. In the case of Li we argue that the lattice parameter is small enough, so the oxide remains on the surface and the characteristic binding energy of about 530 eV of the O $1s$ peak is found. It should be mentioned that O_2 on K was studied previously by Petersson and Karlsson.[2] They identify an oxide species at 528 eV which is consistent with our work. However, they also identify a species at 531.9 eV as molecular oxygen that is physiorbed. This is not quite right, since the present work shows the molecular species at 532 eV not physiorbed, but is probably a peroxide

species where charge is exchanged with the substrate. As previously discussed, the XPS peak for the physisorbed oxygen appears in the range 538–541 eV.

In concluding this subsection, we note that the oxide features do not correlate with the variation of the vacuum level. That is, a lower work function should make the peaks appear deeper, whereas for the case of Cs and K, with the lowest work functions, the oxide peaks have the lowest binding energies. In this case we argue that there is Fermi-level alignment, but there are many different oxides that can form with oxygen in the O^{2-} oxidation state.

B. Valence-band spectra

Although the work described above is fairly new, there are more detailed studies of the valence band of alkali metals after exposure to oxygen. Our own work parallels very closely the work of Woratschek et al.,[14] who studied both photoemission and deexcitation spectroscopy of the interaction of O and Cs. They found that small doses of oxygen caused the formation of O^{2-} ions which are under the surface and yield a photoemission feature at about 2.9 eV. Further exposure leads to Cs_2O_2 (the peroxide) with new features near 8 eV. Finally, the surface layer is completely transformed into CsO_2 (the superoxide), which then retards further oxygen penetration into the bulk. Of course, as the exposure increases, some of the initial peak positions are modified, but basically the situation is as described here. Our own data shown in Fig. 4 very closely parallel the data of Woratschek et al., even though our data were taken at about 35 K. Further-
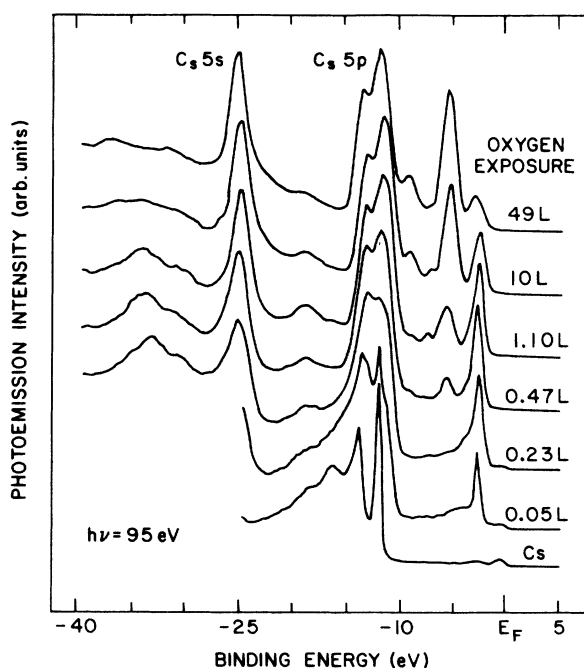

FIG. 4. Valence-band spectra taken at 95 eV photon energy for O_2/Cs at 35 K. The spectra are normalized to equal peak height of the Cs $5p$ level.

more, the identification of the species is made more plausible by the development of the features seen in the XPS spectra. First, the oxide, develops then the peroxide, and finally the feature near 535 eV due to the superoxide, as shown in Fig. 5. In the data of Bertel et al.,[5] the samples are exposed to large doses of oxygen where they reach a steady-state condition. They then argue that the observed features are the superoxide, which are similar to the molecular-oxygen features pulled down to the regime near E_F. Clearly, this is a great coincidence if the strongest features also occur below 3 eV in the initial-exposure regime, where XPS confirms there are no superoxide species occurring and that the peak is O^{2-}. Additional evidence for this view is provided by recent XPS results[13] for Li reacting with oxygen which show superoxide formation, but no feature near 3 eV in the valence-band spectrum. We have previously argued[13] that the position of the XPS feature for oxygen on Li, as compared to Cs and K, indicates that on Li, O^{2-} does not exist inside the metal as in the Cs (Ref. 4) case. This would explain the absence of the 3-eV feature for the Li case, and since the superoxide occurs it means that the 3-eV feature is *not* the $1\pi_g$ level of the superoxide. We emphasize again that the picture we find for Cs is similar to that presented by Woratschek et al.[4] It is possible that Bertel et al.[5] do not have a pure-superoxide phase, and that oxygen species in metal clusters are also present. No x-ray-diffraction or XPS data are presented in Ref. 5 to show there is pure superoxide.

In Figs. 6 and 7 we show valence-band results for O on K and Ba. The potassium features are similar to those found for Cs, and Ba also shows similarities, although in detail there are some differences. In the Ba case, the XPS
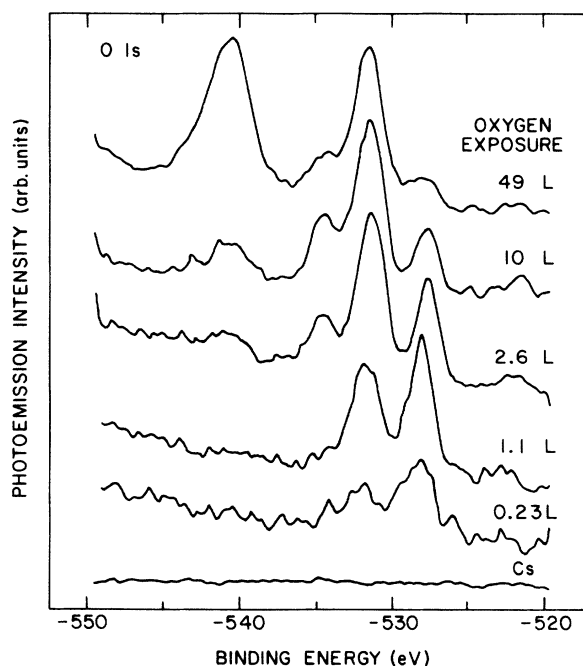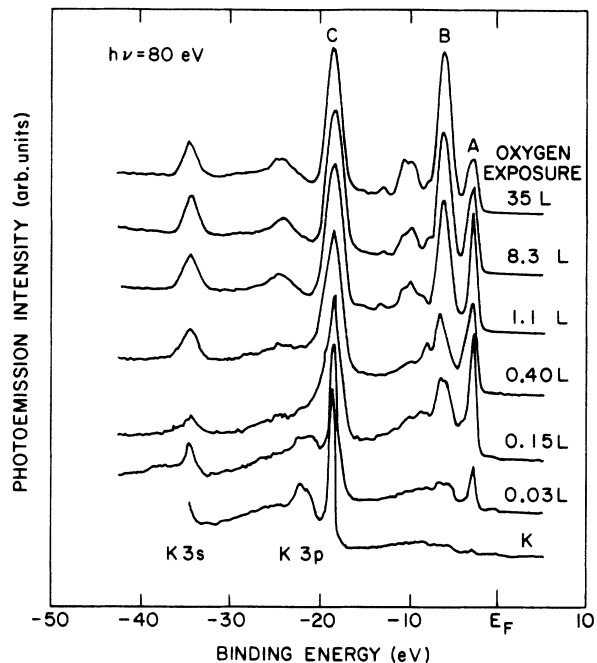

FIG. 6. Valence-band spectra taken at 80 eV photon energy for O_2/K at 35 K. The normalized intensities of peaks *A*, *B*, and *C* are plotted in Fig. 8.

spectra indicate peroxide forms, but there is no evidence of the superoxide. The absence of superoxide is also apparent in the Cu spectra. It is possible that the "even" metal-oxidation state does not favor the formation of the superoxide. In the case of Ag, there is also no superox-
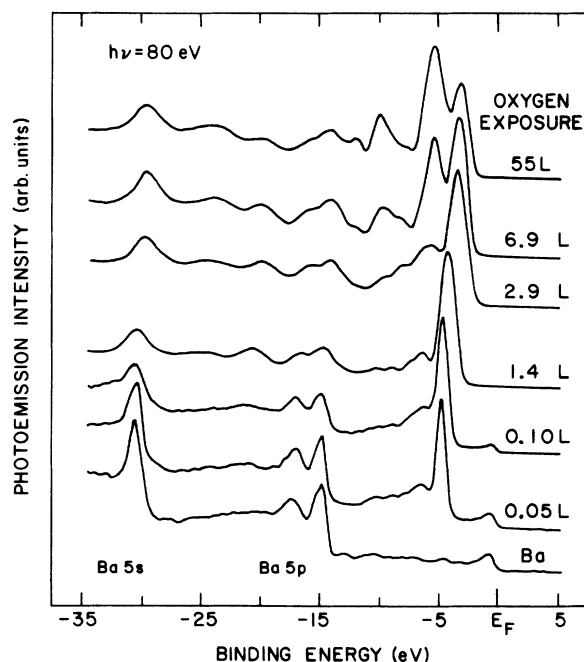

FIG. 5. O 1s core-level XPS spectra for O_2/Cs at 35 K. The spectra are not normalized to represent the increasing amount of O_2.

FIG. 7. Valence-band spectra taken at 80 eV photon energy for O_2/Ba below 35 K. The spectra are not to scale.

ide, but in this case it may simply be that a single Ag atom is not active enough in a chemical sense to donate an electron to an O_2 molecule.

C. Intensities and line shifts

Figure 8 shows intensity versus oxygen exposure for peaks A, B, and C as denoted in Fig. 6. It can be seen that peak A decreases in intensity with increasing oxygen exposure in the regime where B and C remain constant. In this regime, superoxide, peroxide and molecular-oxygen species are evident in the XPS spectra. This is also consistent with A being an O^{2-} species in the metal, which gets covered with successive products rather than the $1\pi_g$ level for the superoxide as suggested by Bertel et al.[5] In this subsection we also briefly point out that upon exposure to oxygen there is a significant increase in the photoemission intensity for both the alkali-metal and Ba core levels. As shown in Fig. 8, curve C, dramatic changes in intensity were observed at low coverages of oxygen, and the intensity of the K $3p$ level saturated above 1 L (1 langmuir $\equiv 10^{-6}$ Torr s) oxygen exposure. Similar effects are observed in work on Na.[3] There is also a shift to lower binding energy in some of the metal core-level peaks, especially in the case of Ba. Wertheim[15] has already discussed these shifts in the case of Ba and attributes them to a configuration change in the metal orbitals, and, in particular, to a change in the occupancy of the $5d$ orbitals. The data shown in Fig. 7 are somewhat anomalous in this regard. The initial amounts of oxygen on Ba yield an "oxide" feature at about 5 eV and measurements of the O $1s$ levels show a feature at 530 eV characteristic of the oxide. It is only when more oxygen is condensed on the surface that there is a shift to lower binding energy of the valence-band feature and, also, the Ba $5p$ and $5s$, as well as the $3d$ and $4d$, levels (not shown here). Also, at the same coverage the O $1s$ levels also shift to lower binding energy. This could just be a matter of obtaining enough oxide on top of the bulk Ba to see a significant shift. However, the fact that the oxygen features also shift brings up the alternate possibility that there is a change in final-state screening.[16]
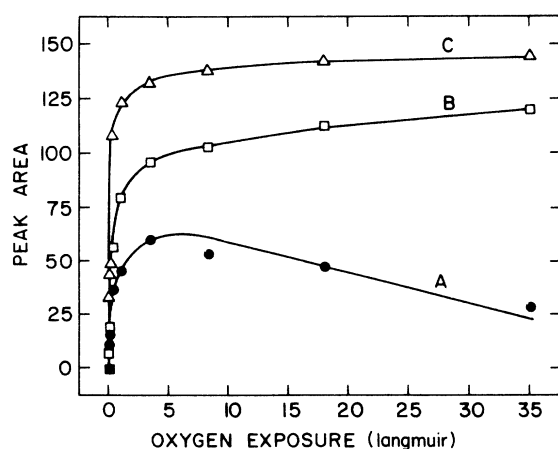

FIG. 8. Peak area vs oxygen exposure (1 langmuir $\equiv 10^{-6}$ Torr s) for peaks A, B, and C as denoted in Fig .6.

IV. DISCUSSION

A basic result of this paper is that the photoemission peak observed at about 535 eV is due to a superoxide species where an electron is donated to an oxygen molecule. There is no actual identification of this species, but the following arguments make it plausible. First, this oxygen species is at the highest binding energy besides the molecular-oxygen feature, and this means that this oxygen species has the smallest amount of charge per oxygen atom with the exception of molecular oxygen. Of course, of all the charged species we have discussed, the superoxide, indeed, has the smallest charge. Secondly, there is the plausibility argument based on the phase diagram. When oxygen is first put on the metal, the most metal-rich species forms, i.e., the oxide phases, followed by the next most oxygen-rich compound, the peroxide, and finally the superoxide. In the case of Li, detailed measurements[13] were done for the reverse case; we found that the first species that forms when metals are put on solid oxygen, i.e., the most oxygen-rich environment, is the superoxide, followed by peroxide, and finally the oxide. This picture is also found for experiments on other alkali metals, and, in particular, for Cs and K. We have excluded the ozonide, since its existence here seem improbable. It would appear most plausible that the initial metal in an oxygen-rich environment would donate an electron to the molecule rather than making the more complex ozonide where dissociation must also occur. Bertel et al.[5] have also argued against the existence of the ozonide in their experiments on the interaction of oxygen with alkali metals. It has already been mentioned that the constancy of the superoxide position with respect to the substrate Fermi level, even for different vacuum levels, implies a small cluster with states near the Fermi level, so there can be equilibration with the substrate chemical potential.

The case of the peroxide is somewhat more complex. In this case there is a variation in the energy of the O $1s$ feature, and presumably this is due to some variation in either the actual charge donated to the molecule or to a variation in the bond length between the oxygen atoms, or between the molecule and the metal. It is clear from Fig. 3 that this feature at 531.5 eV for Ag is closer to a peroxide or oxide feature and is not associated with the superoxide. In studies of molecular oxygen on Ag, Campbell[8] and others[17] have attributed this feature to the superoxide. This in itself is not a particularly important point, except that in work on high-T_c superconductors the observation of a species at this energy is taken as evidence for the superoxide,[7] and Refs. 8 and 17 are given as the basis of the identification.

It is interesting that both the peroxide and superoxide species have been invoked to explain some of the features in the XPS spectra of the hiigh-temperature superconductors. For the case of peroxide the identification at 532 eV is reasonable, except that it is clear that the observed features were not characteristic of the clean-surface and bulk superconductors. In the case of the superoxide, a somewhat smaller situation exists, and from the work presented here we emphasize that any superoxide species

should occur near 535 eV, and the feature observed at 532 eV in Ref. 7 is not superoxide.

In the case of the O^{2-} species we have been content to point out that the feature at 528 eV found for Cs and K is consistent with the picture of previous investigators where oxygen goes into the metal[4] and many different phases can form. Of course, it is somewhat interesting that this can happen at cryogenic temperatures. On the other hand, some of the oxides, like Li, Cu, and Ag, for example, show a feature at 530 eV and we argue that this is because the oxygen does not go into the bulk metal. It is interesting to note that different O $1s$ peak positions of the O^{2-} species due to two different environments are also observed in the high-T_c superconductors. Fowler et al.[18] report that high-quality metallic superconducting $YBa_2Cu_3O_7$ single crystals have the O $1s$ feature near 528 eV, whereas for the nonsuperconducting material it is near 529 eV or above. Thus in these cases, and probably in others, the O^{2-} species in a metallic environment appears at the same binding energy in the O $1s$ spectra.

In summary, the present work provides data showing characteristic features in the photoemission spectra of metals reacted with oxygen at 35 K or below. In some cases metastable species (i.e., superoxide or peroxide) are formed, and at least in the cases of Li and La the superoxide species are not stable at room temperature. These metastable species may be further reacted with Cu or Ni to form other species and these experiments are underway. It should be pointed out that although the photoemission spectra can enumerate the different species, there is little "fine" structure to identify specific compound formation, and most oxides appear fairly similar with a feature in the 530-eV region. On the other hand, absorption spectra of the O K edge show a wealth of information about holes and other features of oxide materials, and further experiments will exploit this.

[1]Paul E. Gregory, P. Chye, H. Sunami, and W. E. Spicer, J. Appl. Phys. **46**, 3525 (1975).

[2]L. G. Petersson and S. E. Karlsson, Phys. Scr. **16**, 425 (1977).

[3]P. L. Shek, X. Pan, Myron Strongin, and M. W. Ruckman, Phys. Rev. B **34**, 3741 (1986).

[4]B. Woratschek, W. Sesselmann, J. Kuppers, and G. Ertl, J. Chem. Phys. **86**, 2411 (1987).

[5]E. Bertel, F. P. Netzer, G. Rosina, and H. Saalfeld, Phys. Rev. B **39**, 6082 (1989).

[6]D. D. Sarma, K. Sreddhar, P. Ganguly,, and C. N. R. Rao, Phys. Rev. B **36**, 2371 (1987); Y. Dai, A. Mathiram, A. Campion, and J. B. Goodenough, ibid. **38**, 5091 (1988).

[7]J. W. Rogers, Jr., N. D. Shinn, J. E. Schirber, E. L. Venturini, D. S. Ginley, and B. Morosin, Phys. Rev. B **38**, 5021 (1988).

[8]C. T. Campbell, Surf. Sci. **173**, L641 (1986).

[9]P. Kuiper, G. Kruizinga, J. Ghijsen, G. A. Sawatzky, and H. Verweij, Phys. Rev. Lett. **62**, 221 (1989).

[10]D. Menzel, in Photoemission and the Electronic Properties of Surfaces, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, New York, 1978), p. 381.

[11]J. Colbert, A. Zangwill, Myron Strongin, and S. Krummacher, Phys. Rev. B **27**, 1378 (1983).

[12]See Table X in Photoemission in Solids II, edited by M. Cardona and L. Ley (Springer-Verlag, Berlin, 1978).

[13]S. L. Qiu, C. L. Lin, J. Chen, and Myron Strongin, Phys. Rev. B **39**, 6194 (1989).

[14]For a discussion of the effect of the substrate on the XPS peak positiions in clusters, see S. L. Qiu, X. Pan, Myron Strongin, and P. Citrin, Phys. Rev. B **36**, 1292 (1987).

[15]G. K. Wertheim, J. Electron Spectrosc. Relat. Phenom. **34**, 309 (1984).

[16]W. V. Lampert, K. D. Rachocki, B. C. Lamartine, and T. W. Haas, J. Electron Spectrosc. Relat. Phenom. **26**, 133 (1982).

[17]K. Prabhakaran, P. Sen, and C. N. R. Rao, Surf. Sci. **177**, L971 (1986).

[18]D. E. Fowler, C. R. Brundle, J. Lerczak, and F. Holtzberg, Surf. Sci. (to be published).