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### Title

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### Author

Ferrer, S.

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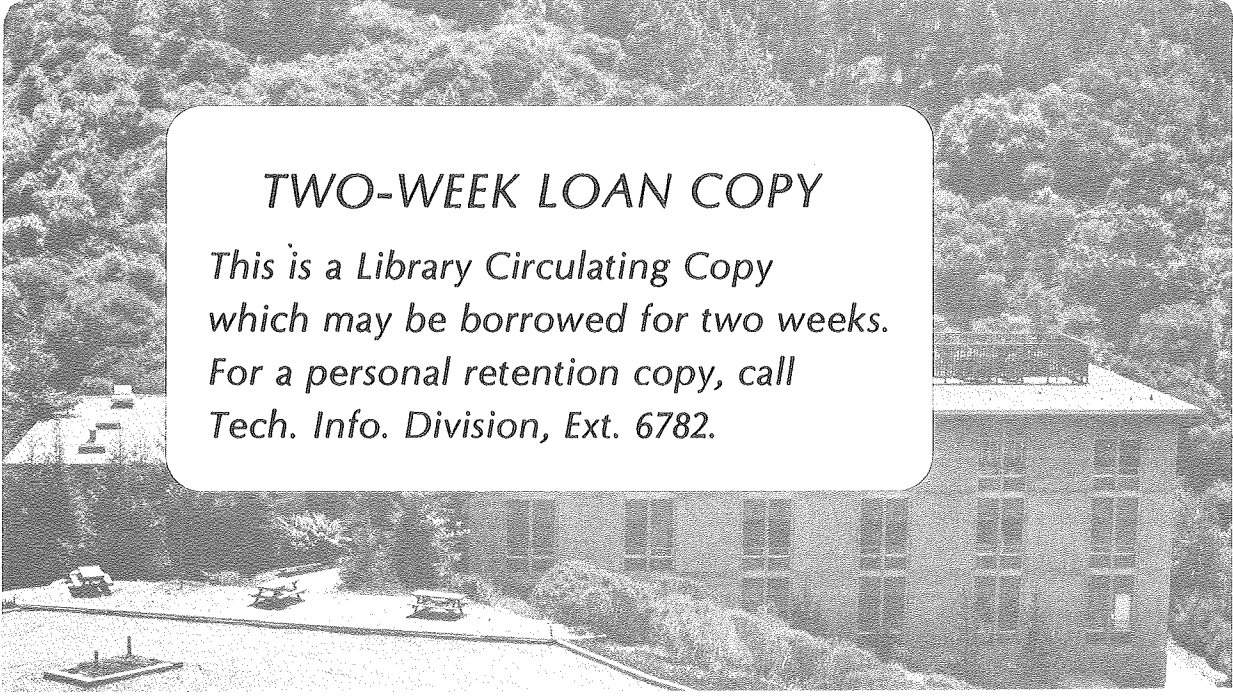
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S. Ferrer and G.A. Somorjai

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UPS STUDY OF THE ADSORPTION OF OXYGEN ON REDUCED  
SrTiO<sub>3</sub> SURFACES

S. Ferrer and G.A. Somorjai

Materials and Molecular Research Division,  
Lawrence Berkeley Laboratory, and Department  
of Chemistry, University of California,  
Berkeley, CA 94720, USA

Abstract

The adsorption of oxygen on a reduced SrTiO<sub>3</sub>(111) surface occurs in two distinct phases. At low exposures (less than 1 L), the adsorption leads to the incorporation of O<sup>-</sup> ions into the vacant lattice oxygen sites. At higher exposures a second different oxygen species adsorbs.

## Introduction

Several papers dealing with oxygen adsorption on SrTiO<sub>3</sub> and TiO<sub>2</sub> have been published (1-4), but the understanding of the oxidation process is still incomplete. In this paper we report an UPS study of oxygen adsorption on a reduced SrTiO<sub>3</sub>(111) surface. Evidence is presented for two different charged oxygen species on the surface. One appears to be adsorbed O<sup>≡</sup> ions in agreement with previous results (1), and the second appears to be superoxide ions that were detected independently by ESR studies. At low exposures, below ~1 L (=10<sup>-6</sup> Torr<sub>x</sub>sec) most of the oxygen adsorbs as O<sup>≡</sup> ions. At about 1 L the adsorption of this species ceases, and at higher exposures only the second oxygen species continue to adsorb.

## Experimental

A SrTiO<sub>3</sub> single crystal supplied by National Lead was used in this study. It was of (111) orientation (determined by Laue X-ray diffraction). Before inserting the crystal sample in the vacuum system it was reduced in a hydrogen furnace for several hours at 700°C resulting in a black colored specimen. The UHV system, electron analyzer, UPS, XPS, and AES equipment have been described in detail elsewhere (5,6). The mass spectrometer was a UTI model 100c. The base pressures was in the low 10<sup>-10</sup> Torr range and less than 1x10<sup>-9</sup> Torr during the UPS experiments. The UPS HeI spectra were recorded in two different ways: in the usual N(E) mode with analyzer pass energy of 25 eV using a conventional counting electronics equipment, and also in the dN/dE mode. In this second case the pass energy was also 25 eV and the modulation of the analyzer was 0.2 volts peak-to-peak. The detection was through a Lock-in amplifier operated in the same

way utilized to record Auger spectra in the  $dN/dE$  mode. The analyzer's sweeping rate was 0,03 eV/sec and the signal-to-noise ratio was  $\sim 30$ . This mode of operation was chosen because it is very sensitive to changes of line shape as well as to the appearance of weak emissions.

### Results

Figure 1 shows the UPS spectra from the clean  $\text{SrTiO}_3(111)$  surface,  $\text{Ar}^+$  sputtered, annealed at  $450^\circ\text{C}$  for a few seconds and subsequently cooled to room temperature. The upper curve shows the spectrum in the usual  $N(E)$  mode. It exhibits the emission due to the presence of  $\text{Ti}^{3+}$  ions at the surface at 0.6 eV below the Fermi level and a broad peak from  $\sim 3$  to  $\sim 8$  eV which corresponds to the O2p band. The bottom curve shows the same spectrum in the derivative mode. The Fermi level corresponds to the minimum in the emission of  $\text{Ti}^{3+}$  ions. The O2p band appears clearly resolved in two components which inflection points are located at 4.7 and 6.7 eV. (The splitting of the oxygen band is a general feature of the d-band perovskites, resulting in two components of  $\pi$  and  $\sigma$  symmetries (7).) A weak emission is also visible at  $\sim 13$  eV; however, its intensity is not well reproduced in different runs. Sometimes this feature is not observed for the clean surface and therefore we shall not discuss its characteristics.

The changes in the UPS,  $dN/dE$ , spectrum caused by oxygen exposure are depicted in Figure 2. The upper curve solid line shows the spectrum corresponding to the clean surface free of adsorbed oxygen and the dotted line shows the spectrum after 1 L of oxygen exposure. The following changes are noticeable: (a) the intensity of the  $\text{Ti}^{3+}$  emission

is visibly diminished; (b) the intensity of the whole O2p band measured as the peak-to-peak amplitude increases, (its line shape remains essentially unchanged indicating no new emissions); (c) at 10 eV a new emission appears (its intensity increases with oxygen exposure as shown in the inserts of Figure 2); and (d) the whole O2p band is shifted 0.3 eV toward the Fermi level.

The bottom part of Figure 2 shows the spectrum after 1 L exposure (continuous trace) and the spectrum after 100 L of O<sub>2</sub> exposure (broken trace). The intensity of the Ti<sup>3+</sup> emission is slightly diminished. The intensity and position of the O2p band do not change due to this 100-fold increase in exposure. However, the intensity of the 10 eV emission increases noticeably. The inserts in the bottom of Figure 2 show further increase of the intensity of this emission upon exposures to 340 and 1000 L of oxygen.

Figure 3 shows the changes of the concentration of Ti<sup>3+</sup> species (measured as the area under the Ti<sup>3+</sup> peak in the UPS N(E) mode with a linear background subtracted) and of the work function as a function of the oxygen exposure plotted in a logarithmic scale. The value of 100 in the ordinate gives the intensity of the Ti<sup>3+</sup> emission from the clean surface. Figure 4 shows the change of the peak-to-peak amplitude of the O2p emission in the dN/dE mode (mentioned above in (b)) and the increase of the 10 eV emission as a function of oxygen exposure.

After flashing the crystal (previously exposed to oxygen) at about 500°C in vacuum, the UPS spectrum was essentially identical to the spectrum corresponding to the clean surface. However, attempts to detect the desorbing oxygen species by our mass spectrometer, after oxygen

exposures of  $\sim 100$  L, were not successful.

### Discussion

The existence of two different phases of the initial oxidation process is indicated from the observations that are displayed in Figure 3. At low exposures (less than 1 L) there is a very rapid oxygen uptake that results in oxidation of  $\text{Ti}^{3+}$  to  $\text{Ti}^{4+}$  and an increasing work function. At higher exposures there are smaller rates of  $\text{Ti}^{3+}$  oxidation and work function increase, indicating a smaller sticking coefficient for oxygen. At low oxygen exposures, the peak-to-peak amplitude of the whole O2p band grows reaching a constant value at  $\sim 1$  L (Figure 3) which remains unchanged at higher exposures. The intensity of the oxygen-induced 10 eV emission is very small at low oxygen exposures, but it increases continuously during exposures greater than 1 L. This different behavior between the O2p and 10 eV emissions indicates that the increase in the intensity of the O2p band and the 10 eV emission correspond to two different oxygen species. The similarity in the line shapes of the O2p emissions from the clean surface and that from adsorbed oxygen obtained after 1 L exposure (Figure 2) strongly suggest that the species responsible for the increase in the O2p intensity are adsorbed  $\text{O}^{\equiv}$  ions, in agreement with the interpretation and data of V. Henrich *et al.* on  $\text{SrTiO}_3(100)$  (1). This interpretation is consistent with the strong charge transfer between the surface and the adsorbed species observed during low oxygen exposures, resulting in the oxidation of  $\text{Ti}^{3+}$  (Figure 3). As is apparent in Figure 4, the adsorption of  $\text{O}^{\equiv}$  ions predominates at low exposures. The oxygen species responsible for the 10 eV emission is also capable of charge transfer, but of



smaller magnitude, as indicated by the slower oxidation rate of  $Ti^{3+}$  (Figure 3) at higher oxygen exposures. Therefore, this species is also negatively charged. Due to the lack of gas phase UPS data for non-neutral species, a direct identification is not possible at present. However, ESR studies indicate that superoxide ions are common adsorbed oxygen species for many oxides, including  $TiO_2$  (8,9). As a consequence  $O_2^-$  is a good candidate to account for the UPS emission at 10 eV.

Previously published data (6) show that on a reduced  $SrTiO_3(111)$  surface, which has been Ar sputtered and annealed, there is a large concentration of  $Ti^{3+}$  ions in the surface region which was estimated to exceed 1 monolayer. Therefore, the concentration of oxygen vacancies at the surface is very high. Thus oxygen dissociates on the reduced surface at low oxygen exposures and incorporates into the crystal lattice by occupying the vacant oxygen lattice sites. Formally, we can write this process as

$$\frac{1}{2} O_2(g) + (2Ti^{3+}-Vo) \longrightarrow (2Ti^{4+}-O^-)$$

where  $(2Ti^{3+}-Vo)$  represents an oxygen vacancy (Vo) with two bound electrons which are mainly distributed on the positive Ti ions adjacent to the vacant lattice site. At higher oxygen exposures, the adsorption of  $O^-$  ions ceases and there could only be a chemisorption of superoxide ions. The rate of oxygen uptake decreases noticeably as evidenced by the breaks that appear in the  $Ti^{3+}$  and  $\Delta\phi$  curves in Figure 3 with increasing exposures. The break in the oxidation rate could also indicate the beginning of the oxidation of the  $Ti^{3+}$  ions located in the second  $Ti^{3+}$  layer. However, our present data cannot confirm which of these two models is correct. Since we could not detect oxygen desorption after exposure when the crystal was heated in vacuum, diffusion of oxygen into the bulk of the

crystal is the likely process of removal of chemisorbed oxygen.

The 0.3 eV shift of the O2p emission toward the Fermi level which appears after 1 L of oxygen exposure (Figure 2) is also visible in the O1s and Sr 2s XPS emissions. Therefore, this shift affects all of the photoemission peaks. We interpret it as due to a combination of two factors: (i) the decrease in relaxation energy of the electrons at the surface due to the oxidation of Ti<sup>3+</sup> (10), and (ii) the decrease of the binding energy (referred to the Fermi level) of the electrons at the surface region due to the appearance of a double layer induced by the oxygen adsorption (11).

#### Acknowledgements

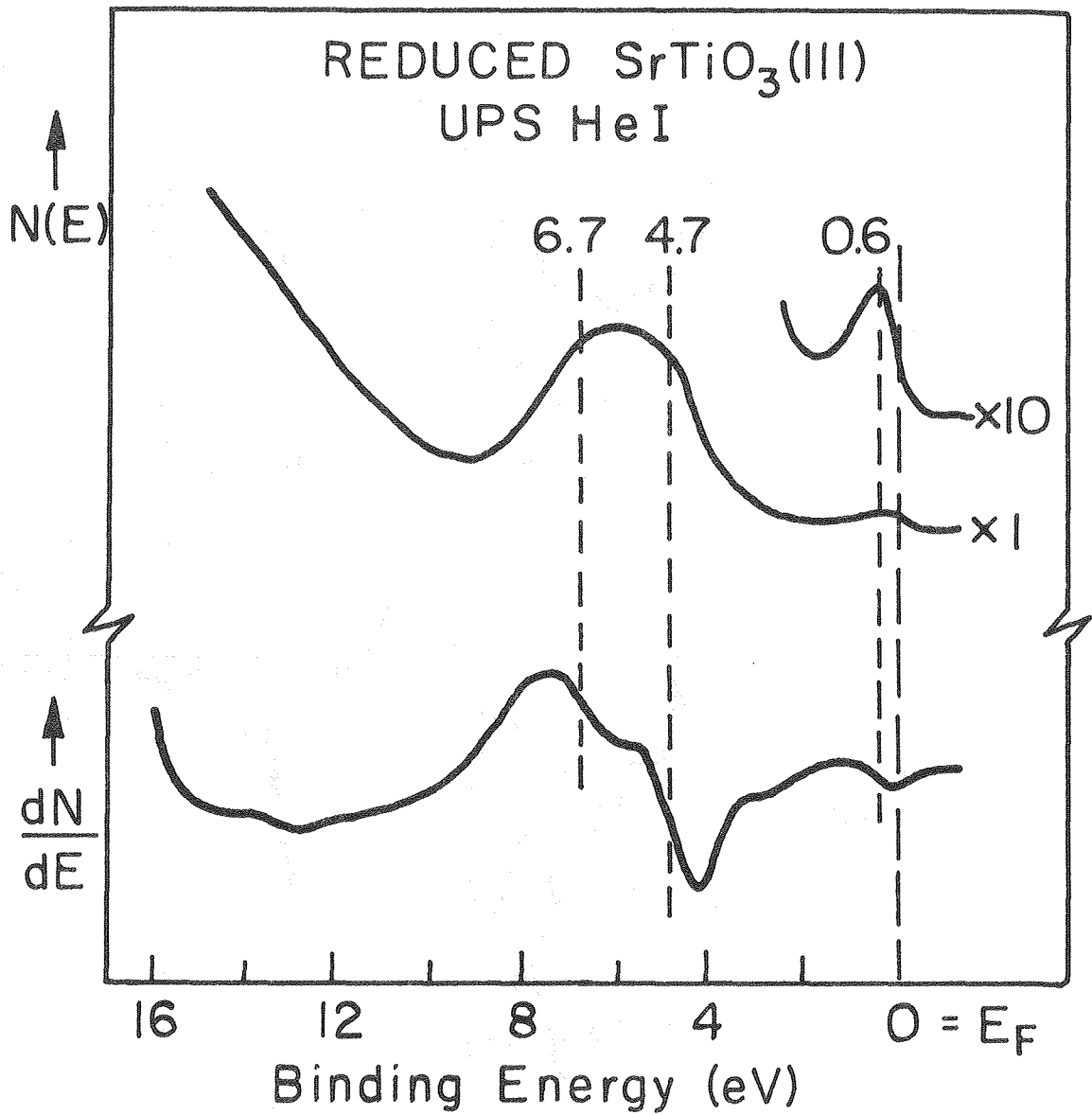
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Figure Captions

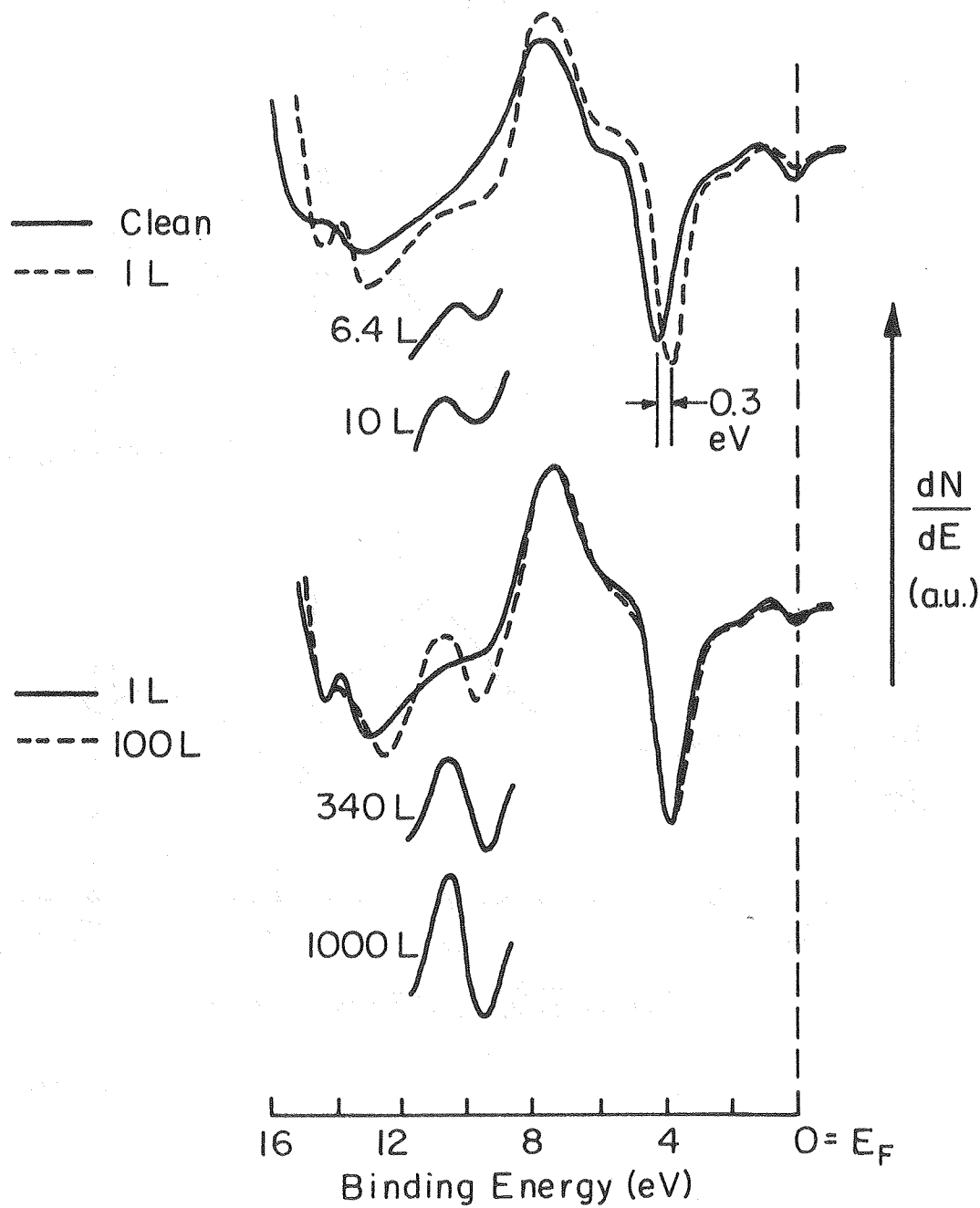
- Figure 1. UPS spectra of a reduced SrTiO<sub>3</sub>(111) surface in the N(E) mode (top) and dN/dE mode (bottom).
- Figure 2. Effect of the oxygen exposure in the UPS dN/dE spectrum of the reduced SrTiO<sub>3</sub>(111) surface.
- Figure 3. Variation of the change in work function (triangles) and of the Ti<sup>3+</sup> UPS N(E) intensity as a function of the oxygen exposure.
- Figure 4. Change of the peak-to-peak amplitude of the whole O2p band (triangles) and increase of the peak-to-peak amplitude of the 10 eV UPS emission (circles) as a function of the oxygen exposure. (The scales on the ordinate axis are both linear.)



XBL 808-5725

Fig.1

OXYGEN EXPOSURE ON REDUCED  $\text{SrTiO}_3(\text{III})$   
UPS HeI,  $dN/dE$  Mode  
mod. 0.2 V p-p



XBL 808-5724

Fig.2

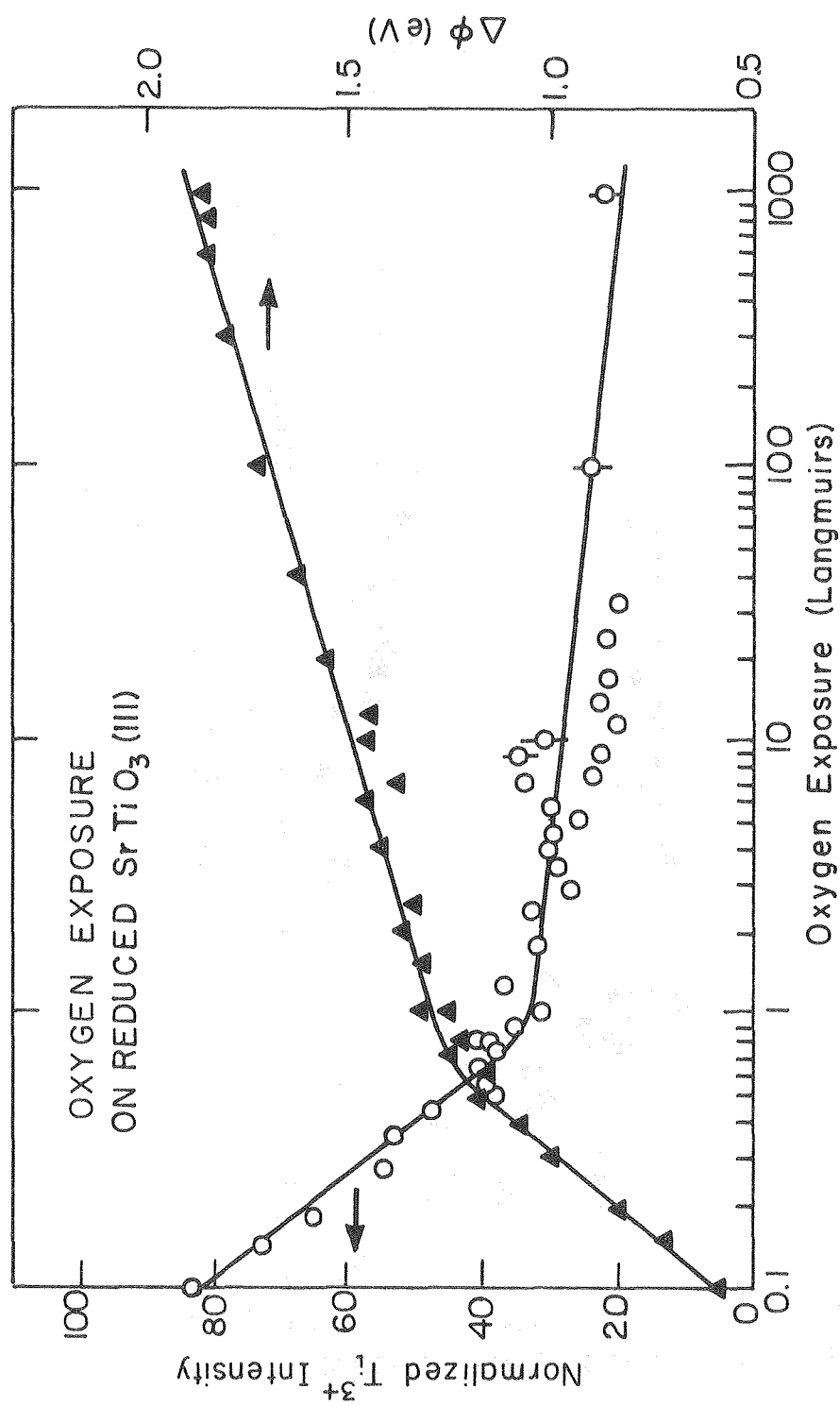
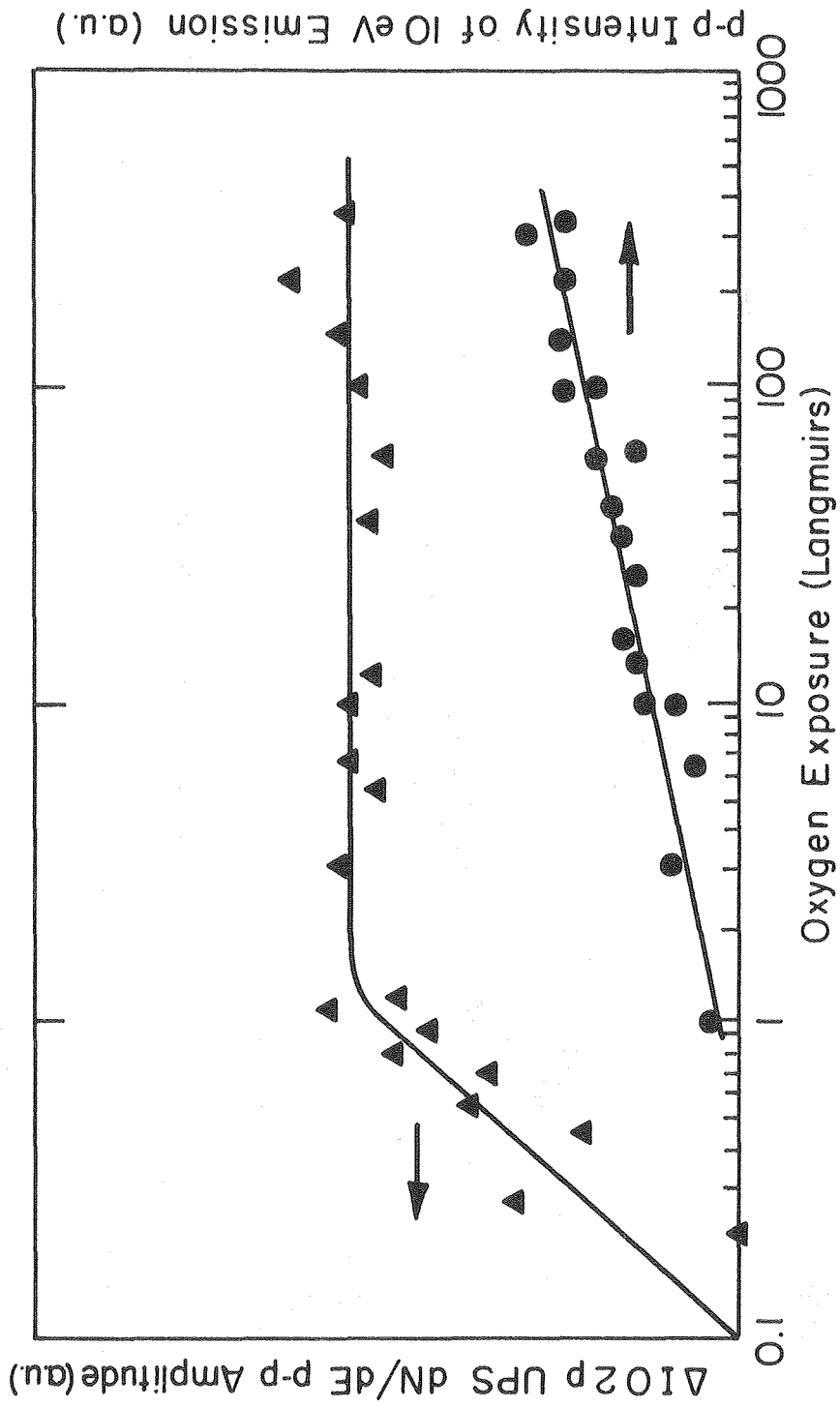


Fig.3

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Fig.4