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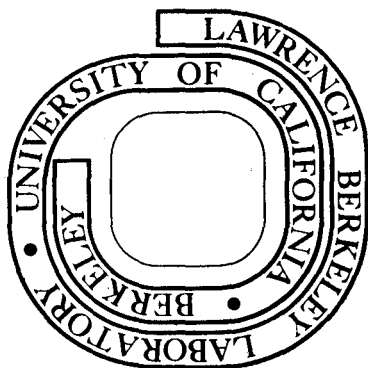
S. P. Kowalczyk, F. R. McFeely, L. Ley, V. T. Gritsyna, and
D. A. Shirley

July 1976

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The Electronic Structure of SrTiO_3
and Some Simple Related Oxides
(MgO , ZnO , Al_2O_3 , SrO , TiO_2)*

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Abstract

The valence band density of states (VBDOS) of the insulating oxides SrTiO_3 , TiO_2 , SrO , MgO , Al_2O_3 , and ZnO obtained by x-ray photoelectron spectroscopy (XPS) are reported. Qualitatively, the VBDOS of each of these oxides are similar to one another. These XPS results are compared with results from soft-x-ray emission spectroscopy (XES), ultraviolet photoemission spectroscopy (UPS), and theoretical calculations. There are some differences (in particular for TiO_2) between the XES and XPS results, which are probably due to matrix element effects enhancing different features of the VBDOS in the two techniques. The XPS results definitively clear up the question of the position of the O 2s level, which had been erroneously assigned in previous low-energy UPS measurements. Cluster-type calculations were demonstrated to give quite reasonable representation of the VBDOS for the above oxides.

I. INTRODUCTION

This paper will deal with the electronic structure of SrTiO_3 and several related oxides. SrTiO_3 crystallizes in the simple cubic perovskite structure. Its properties range from exhibiting ferroelectricity to becoming a superconductor at low temperatures. The perovskites have been studied with a wide range of experimental solid-state techniques.¹⁻¹¹ We have studied SrTiO_3 with x-ray photoelectron spectroscopy (XPS) under UHV conditions and with high resolution. In order to help understand the valence band density of states of SrTiO_3 , we have also studied several simple, related oxides, MgO , ZnO , Al_2O_3 , TiO_2 , and SrO which we will discuss first.

These oxides do not have occupied 3d bands (except ZnO , which has a filled, core-like d band). These materials are fairly ionic and their constituents approach a noble gas filled-shell configuration, thus both the band-structure and atomic pictures should give reasonable description of their properties.

II. EXPERIMENTAL

All the specimens of these materials except Al_2O_3 were high grade single crystals, which were cleaved in a glove bag filled with dry nitrogen and immediately inserted into the spectrometer vacuum without exposure to the ambient. This procedure has been demonstrated previously to yield very satisfactory samples for obtaining representative bulk density of states.¹² The Al_2O_3 crystal specimen was not prepared by cleavage but by in situ argon ion sputtering. The specimen was sputtered for approximately one hour at 1×10^{-5} torr of argon.

The beam voltage was 1 KeV. This treatment was enough to remove carbon contamination, as determined by scanning the Cls region. The 0 1s region yielded one nearly symmetric peak with no sign of a contaminant oxygen species.

The measurements were obtained with a Hewlett-Packard 5950A electron spectrometer.¹³ Monochromatized AlK α x-rays ($h\nu = 1486.6$ eV) were utilized as the excitation source. The vacuum of the spectrometer for these experiments was 5×10^{-9} torr or better.

III. RESULTS

A. MgO

MgO crystallizes in the NaCl structure. The XPS spectrum of its outermost levels is shown in Fig. 1. The valence bands consist of three groups of peaks. One, at about 18 eV from the top of the valence band, can be assigned to the O 2s levels on energetic grounds. A broad two-peak structure due to the O 2p-Mg3s bands extends from about 0 to 6.5 eV relative to the top of the valence bands. We will refer to this entire two-peak structure as the valence bands. The other oxides have quite similar spectra (see below).

There are several calculations available on the electronic structure of MgO. Tossell¹⁴ carried out SCF X α Scattered Wave calculations on MgO₆¹⁰⁻ clusters, obtaining both energies and charge distributions of the various levels. He found that the valence levels fall into three sets. There are 5a_{1g}, 4t_{1u}, and 1e_g levels which are O 2s non-bonding orbitals, then a set of bonding orbitals which are predominately O2p (5t_{1u}, 6a_{1g}, and 1t_{2g}), and finally a set of non-bonding O2p

orbitals ($1t_{2u}$, $6t_{1u}$, $2e_g$, and $1t_{1g}$). The oxygen 2s levels are predicted to be about 1 eV wide, which agrees well with the observed FWHM of this peak. The top two bands have an observed bandwidth of 6.5 eV. The calculated bandwidth of 3 eV is too small, as might be expected from a MO calculation. Tossell's calculation gives ~ 1.8 eV for the separation between the two groups of 02p bands, which compares with our measured separation of 2.5 eV. The separation between the 02s and the 02p bonding band is calculated to be 12.5 eV, while our results for the separation of the 02s band from the more tightly-bound valence band is measured to be 14 eV. Thus Tossell's calculation¹⁴ gives quite reasonable agreement with experiment.

There also exist several band-structure calculations for MgO.¹⁵⁻¹⁹ Cohen and collaborators have performed EPM¹⁵ calculations. We have seen previously that EPM calculations have yielded quite good results for the outermost valence bands in many compounds.¹² The EPM calculation gives a band width of ~ 5.0 eV and separation of ~ 3 eV for the two peaks in the valence band, both in good agreement with our observations. The oxygen 2s band is placed about 19 eV above the more tightly-bound band, much too high. This is undoubtedly due primarily to using a non-local pseudopotential.^{12,20} Pantelides et al¹⁶ have carried out ab initio self-consistent Hartree-Fock energy-band calculations for MgO, which yield a band width of 10 eV, valence-band splitting of ~ 6 eV and the 02s band being 21 eV above the lowest band. All those results are far too high. Recently, Pantelides has discussed the use of an empirical tight-binding method (ETBM) for insulating rocksalt-type crystals.¹⁷ The ETBM calculation

predicts a bandwidth of 7.0 eV which agrees quite well with our observations. Finally, Walch and Ellis¹⁸ have studied MgO employing both a MO-cluster and an energy-band representation within the Hartree-Fock-Slater scheme. The cluster calculation gave a bandwidth of 4.9 eV and a valence band splitting of a little over 3 eV, while their band structure calculation gave 2.7 and 1.6 eV respectively. Both their calculations give the separation of the 02s level from the bottom most band as about 14 eV. Thus all the above calculations more or less reproduce the general features of the occupied density of states but none do extremely well in predicting all the features of the VBDOS.

Fischer has reported x-ray emission (XES) studies of MgO²¹ as have Fomichev et al.²² Fischer's spectra yield a bandwidth of about 7 eV (MgK β), a band splitting of \sim 2 eV (in both MgK β and OK spectra) and the 02s levels at 14.5 eV (MgK β '-MgK β separation) above the bottom valence band.²¹ Thus there is quite good agreement between the XPS and XES results. ZnO, which has a filled 3d band has been discussed in detail previously.¹² Its VBDOS is very similar to MgO (except for the presence of the Zn 3d level which is very core-like).

B. Al₂O₃

In this section, we report results from Al₂O₃. These measurements were part of a preliminary investigation of radiation damage due to ion implananation in Al₂O₃. The Al₂O₃ valence band spectrum given in Fig. 2 was from an Al₂O₃ single crystal which was flame fusion grown. This particular sample was an unimplanted specimen.²³ The energies of the characteristic features of the valence band are given in

Table I. As can be seen by comparing Figs. 1 and 2, the valence band of Al_2O_3 is qualitatively very similar to MgO . There is the two-peak valence band structure plus the more tightly bound peak due to the O 2s band.

As can be seen from Table I, there is quite good agreement with the x-ray emission results.²¹ The separation of the two peaks in the valence band is somewhat smaller in the XES spectrum than in the XPS spectrum. This difference is due most likely to matrix element effects enhancing different parts of the valence band in the two different experiments.

Two $\text{MSX}\alpha$ cluster calculations have been reported.^{14,24} They however do not agree well with each other (see Table I). Tossell's calculation is in better agreement with our experiment. However, as in the case of MgO , Tossell's calculation gives a much too narrow valence bandwidth.¹⁴ The total valence bandwidth (from the top of the valence band to the bottom of the O2s band) is approximately 26 eV, while XES gives a bandwidth of ~ 27 eV.²¹ This compares to the theoretical value from $\text{MSX}\alpha$ calculations of 16 eV.^{14,24} The band structure calculation of Douglas also gives a bandwidth of about 16 eV.²⁵

C. SrO

SrO has been studied relatively little. We present XPS results in Fig. 3. The spectra should be qualitatively similar to MgO , which is the case. In SrO, the Sr4p core level overlaps the O2s band. The bandwidth in SrO is about 10 eV and the splitting is about 4.5 eV, both surprisingly somewhat larger than what was observed in

MgO.²⁶ There are no detailed calculations for SrO. ETBM would predict a bandwidth of 5 eV¹⁷ which would appear to be in contradiction with our XPS results. The SrO results will be useful primarily in helping to interpret the levels due to Sr in the SrTiO₃ spectra.

D. TiO₂

We will now discuss briefly the results for TiO₂, which are shown in Fig. 4. There appear to have been no band-structure calculations for TiO₂. However, Tossell et al²⁷ have performed MO calculations using the SCF X α method for TiO₆⁸⁻ and there have been several band-structure calculations on TiO^{28,29} and one for Ti₂O₃.³⁰

The TiO₂ VB DOS is very similar to what was observed for MgO. There are two peaks in the valence band, separated by 1.9 eV. The total bandwidth is 5.5 eV. The more tightly bound O2s level has a FWHM of 2.5 eV, and lies 15.0 eV higher than the lower valence-band peak. This agrees fairly well with the MO cluster calculation of Tossell et al.²⁴ The X α calculation has a roughly 2 eV wide O2s non-bonding band (5a_{1g}, 4t_{1u}, and 1e_g) which is about 11.5 eV more tightly bound than the bonding orbitals (5t_{1u}, 6a_{1g}, and 1t_{2g}) which are predominantly O2p. These bonding orbitals are separated from the non-bonding orbitals by 3.0 eV. The total valence bandwidth is about 5.5 eV. While we cannot make direct comparison with a TiO₂ band structure, band structure results for TiO and Ti₂O₃ yield bandwidths of ~ 4.5 eV and separation of O2s to O2p of 14 to 14.5 eV.^{28,30}

Low energy UPS investigations of TiO₂ have been performed by Derbenwick.⁹ His results give a bandwidth of ~ 5.2 eV and a 1.7 eV splitting which are in excellent agreement with our XPS results.

However, due to using low energy photons, the 02s level was mistakenly assigned to be only 2.8 eV above the "bonding" 02p bands, an assignment which is clearly not supported by our XPS results. Our results are for the most part qualitatively consistent with the XES results of Fischer^{31,32} and Holliday.³³ However, a detailed comparison shows much disagreement. Fischer's TiL_{III} emission spectrum has two features separated by 2.5 eV which he labels C and D and assigns to the 02s levels. Our 02s peak exhibits no sign of such structure. A peak split by 2.5 eV would be readily noticeable. The $TiK\beta''$ spectrum of Blokhin and Shuvaev³⁴ falls at about the same energy as feature C in Fischer's TiL_{III} spectrum³² and is featureless. The bandwidth obtained from Fischer's TiL_{III} spectrum is 15 eV (features G, A, and F) which is considerably larger than what we obtained. Furthermore the separation between his features A and F is 4.0 eV, far larger than anything possible in the XPS spectrum. Just considering features A and G yields a bandwidth of ~ 9 eV and separation of features of about 2.3 eV, which would be more consistent with the XPS results. Furthermore the separation of features C and G is about 12.5 eV and that between feature D and G is 15.0, suggesting that feature D is the "02s" band and features G and A are the 02p derived valence bands. However the separation of C from A is 14.8 eV. The oxygen K emission has two features separated by 2.2 eV.³² Blokhin and Shuvaev's $TiK\beta_5$ spectrum had a width of 4.63 eV and ~ 1.7 eV splitting.³⁴ A further examination of the TiL XES results is called for. The differences between the two spectra must certainly be due to matrix element effects.^{35,36} Such differences have been employed in the

past to determine the variation in atomic character across the valence bands in diamond and graphite.³⁶

E. SrTiO₃

It might be expected that the SrTiO₃ VB DOS be similar to TiO₂ since in both cases Ti is octahedrally coordinated to oxygen. Optical properties² and soft x-ray emission³³ of these two materials have been shown to be very similar. Our XPS results shown in Fig. 5 are similar to the oxides discussed above. The O2s band overlaps with the Sr4p band, but from relative intensity arguments the high binding-energy shoulder shown in Fig. 6 is probably the O2s band. The p bands are 6.5 eV wide. There appear to be several features in the VB DOS but details of these features will have to await higher resolution studies.

Two major features, separated by 1.9 eV, are resolved in the valence bands. The O2s band is separated from the 4.5 eV feature by ~ 14.5 eV. There are no detailed experimental results for the total valence bands of SrTiO₃ other than some earlier XPS results, which were done under poorer vacuum conditions and obtained with much poorer signal to noise.¹⁰ Theoretical studies include band-structure calculations by Kahn and Leyendecker³⁸ (LCAO-tight binding), Mattheiss³⁹ (APW), Soules *et al*⁴⁰ (*ab initio*-SCF-LCAO, also a cluster calculation was performed by these authors) and Wolfram *et al*.⁴¹ (LCAO).

On the basis of UPS ($h\nu \leq 11.6$ eV) work, Derbenwick⁹ proposed a density of states for SrTiO₃. The topmost band is in reasonable agreement with our results. The UPS results yielded a bandwidth of 5.5 eV with two principal features separated by 2.3. However, as in the case of TiO₂, Derbenwick places the O2s band much too low

(3.5 eV above the bottom peak of the 2p band). Blokhin and Shuvaev³⁴ on the basis of TiK β 5 x-ray emission spectrum give a bandwidth of 3.55 which is too narrow, probably because of different selection rules in XES.³⁶

Kahn and Leyendecker³⁸ calculated only the p bands for SrTiO₃. Their calculation determined the bandwidth to be 4.5 eV. The calculations of Wolfram et al⁴¹ yielded a bandwidth of 4 to 4.5 eV. Soules et al⁴⁰ calculated the bandwidth to be 5.86 eV; however, their calculated 02s bandwidth of 5.2 eV is much too large. Mattheiss' calculations³⁴ give a bandwidth of 3.5-3.8 eV, with about 2.0 separation of the principle features in the density of states. His 02s band is about 1 eV wide and ~ 14.8 above the valence band.

Soules et al⁴⁰ also carried out a calculation on an isolated TiO₆⁸⁻ cluster which gave fairly similar results to their band structure calculation, with the valence band being wider by about 2 eV (i.e., ~ 8 eV wide). This result along with the similarity of SrTiO₃ and TiO₂ XES spectra, suggests that short range order is an important factor in determining the VBDOS of these materials.

IV. CONCLUSIONS

These simple oxides appear to be fairly well understood. The VBDOS spectra are all very similar. The results as well as comparison with theory are summarized in Table I. Both band structure and cluster calculations appear to give adequate qualitative descriptions of the electronic structure although there is room for improvement in all the calculations. Some differences between XES and XPS results

were evident and deserve further detailed investigation. These differences may be due to matrix element effects and could possibly be clarified with variable photon energy photoemission studies. These measurements have located the O2s levels fairly accurately. Since the VBDOS of these oxides are very similar, these spectra may serve as fiducial points in obtaining the partial d-density of states in compounds with d-electrons. Such a procedure has already been employed in the case of transition metal difluorides, where alkali fluorides were used to deconvolute out the F2p contribution from the transition metal difluoride VBDOS.⁴² This is important for compounds which have d-electrons since neither band-structure nor atomic type calculations work particularly well.⁴²

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Footnotes and References:

- * This work was done with support from the U.S. Energy Research and Development Administration.
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Table I. Comparison of XPS VB DOS Results for the Oxides with Calculations and X-ray Emission Results.

Method	Ref.	Valence Bandwidth (eV)	Δ VB (eV) ^a	Δ O2s-VB (eV) ^b
<u>MgO</u>				
MSX α	14	3	1.8	12.5
EPM	15	5.0	3	19
SCHF	16	10	6	21
ETBM	17	7.0	--	--
MO-Cluster	18	4.9	3	14
HF band-struct.	18	2.7	1.6	14
XES	21	7	2	14.5
XPS	^c	6.5	2.5	14
<u>Al₂O₃</u>				
MSX α	14	3.1	2.9	12.7
MSX α	24	1.4	0.9	14.7
XES	21	11	2.2	13.5
XES	^d	10.6	2.0	13.3
XPS	^c	11.6	3.2	13.6
<u>TiO₂</u>				
MSX α	27	5.5	3.0	11.5
UPS (hv<11.6eV)	9	5.2	1.7	2.8
XES (TiL _{III})	32	~ 15	4.0 ^f	16.1 ^g
XES (TiK β ₅)	34	4.6	1.7	--
XPS	^c	5.5	1.9	15.0

Table I. (continued)

Method	Ref.	Valence Bandwidth (eV)	Δ VB (eV) ^a	Δ O2s-VB (eV) ^b
			<u>VO₂</u>	
APW	e	5.5	2.0	--
XPS	37	5.6	1.7	--
			<u>SrTiO₃</u>	
SCF-TB	40	5.9	~ 3	14.5
APW	39	3.7	2.0	14.8
TB	38	4.5	--	--
	41	4.5	--	--
UPS (h ν <11.6eV)	9	5.5	2.3	3.5
XES (TiK β ₅)	34	3.6	--	--
XPS	c	6.5	1.9	14.5

^a Separation between the two major features in the valence band.

^b Separation between O2s peak and the more tightly bound feature in the valence band.

^c This work.

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Table I. (continued)

^f Separation of features F and A in Ref. 32.

^g Separation of feature A from the average position of features C and D in Ref. 32.

Figure Captions:

- Fig. 1. XPS spectrum of the outermost levels in MgO.
- Fig. 2. XPS spectrum of the valence region of Al_2O_3 .
- Fig. 3. XPS spectrum of the outermost levels in SrO.
- Fig. 4. XPS spectrum of the outermost levels in TiO_2 .
- Fig. 5. XPS spectrum of outermost levels in SrTiO_3 (upper panel).
XPS spectrum of the valence region of SrTiO_3 (lower panel).
- Fig. 6. XPS spectrum of the O2s and Sr4p region in SrTiO_3
(upper panel).
XPS spectrum of O1s region in SrTiO_3 (lower panel).

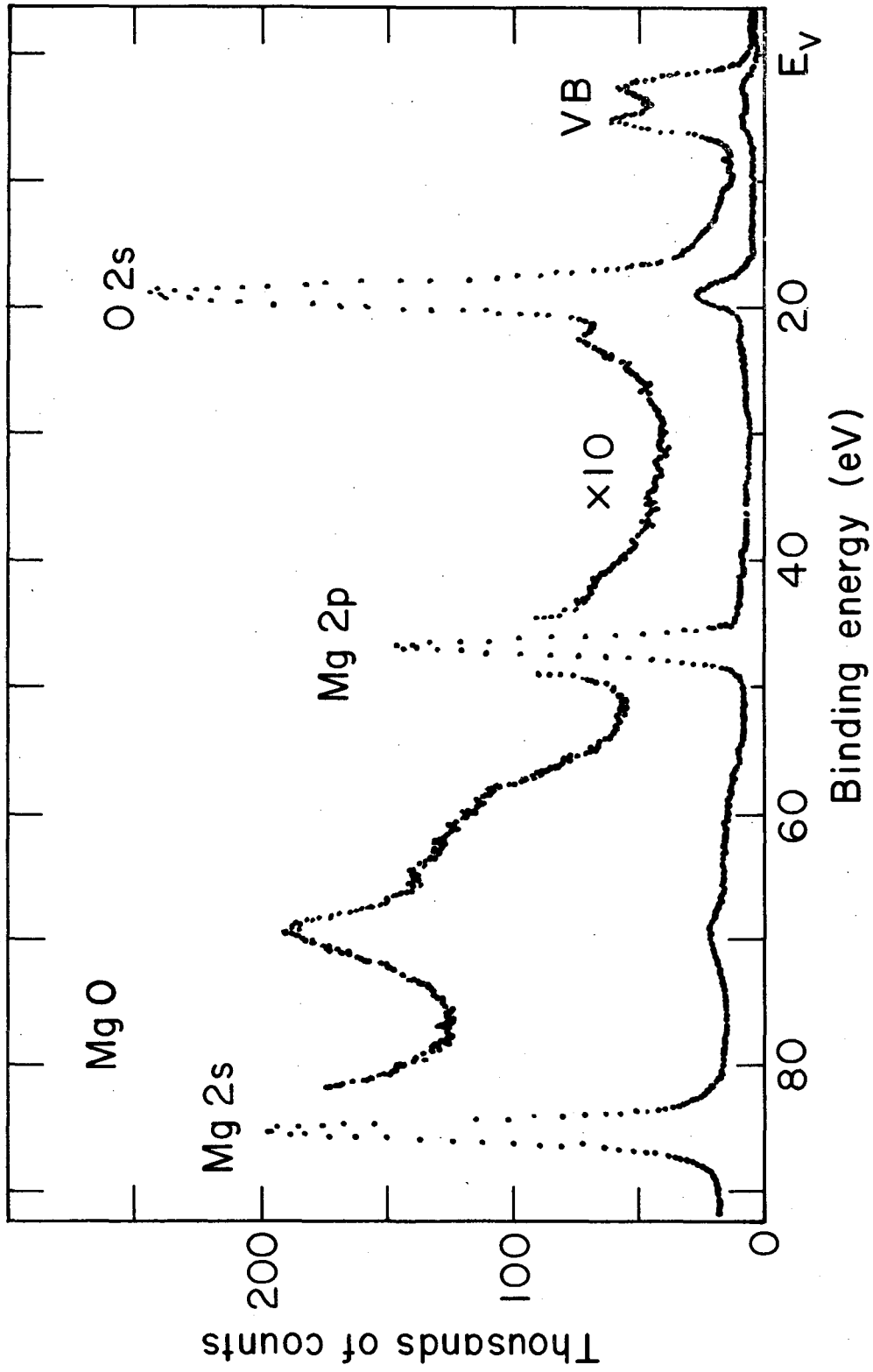
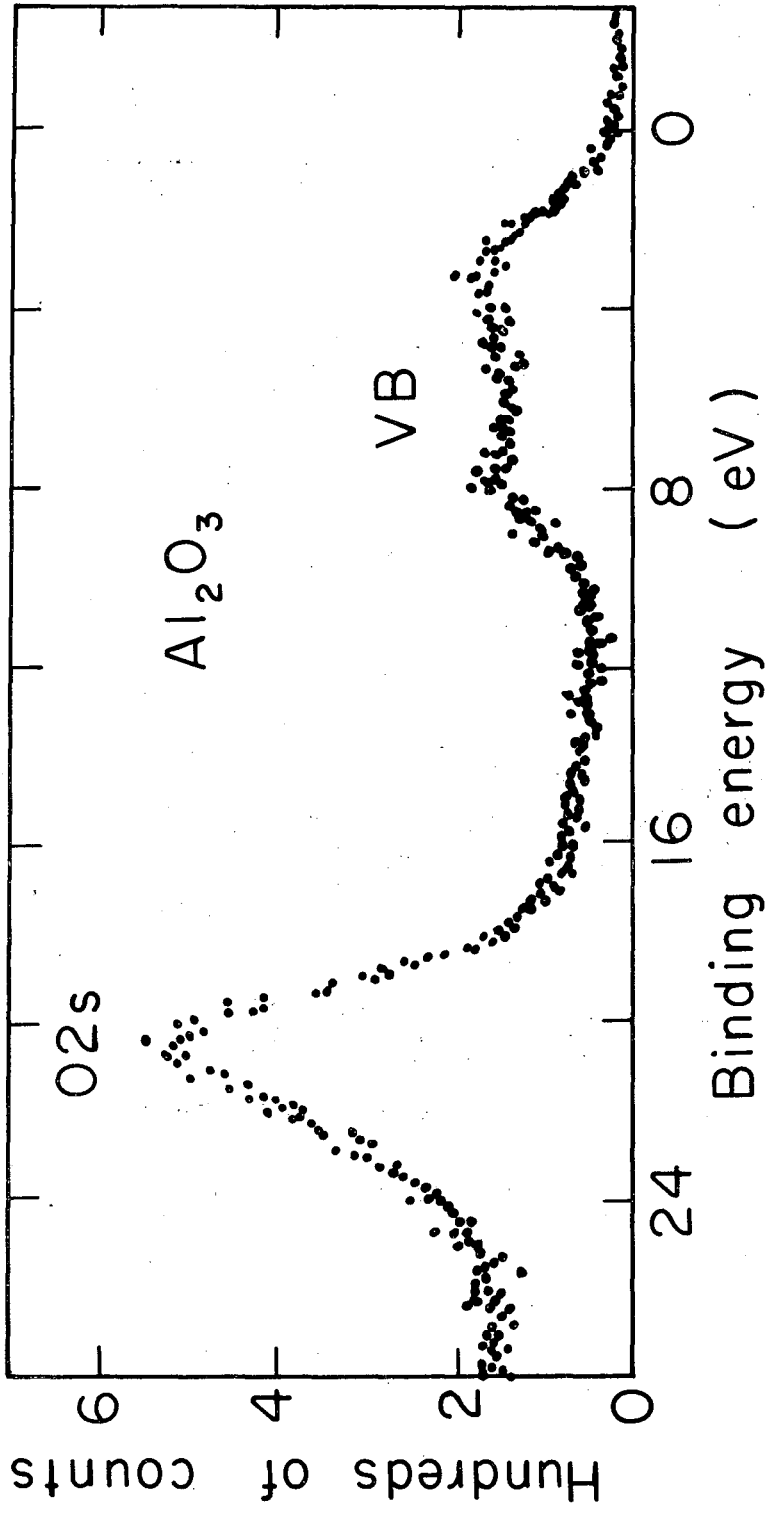


Fig. 1

XBL 757-3398



XBL 766-2983

Fig. 2

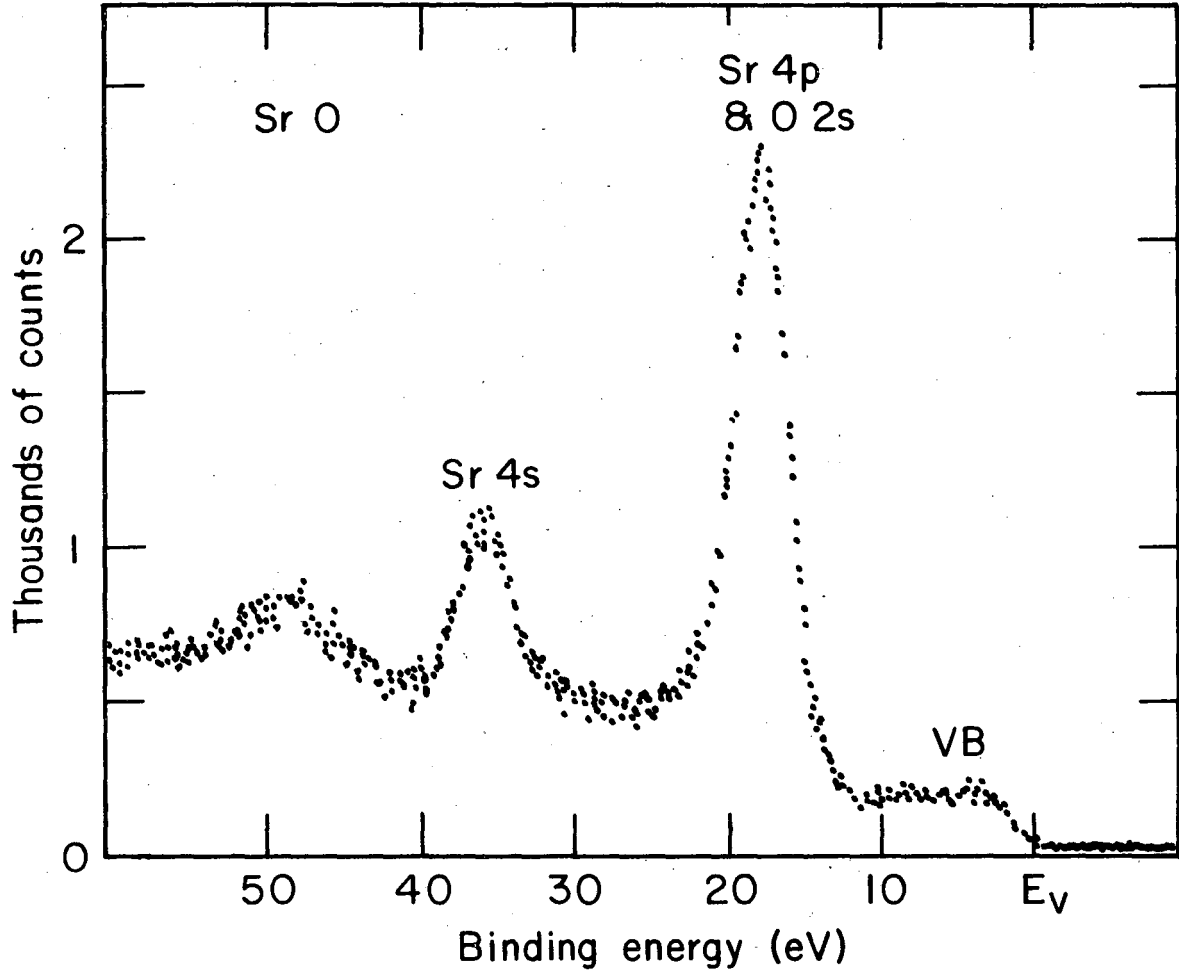
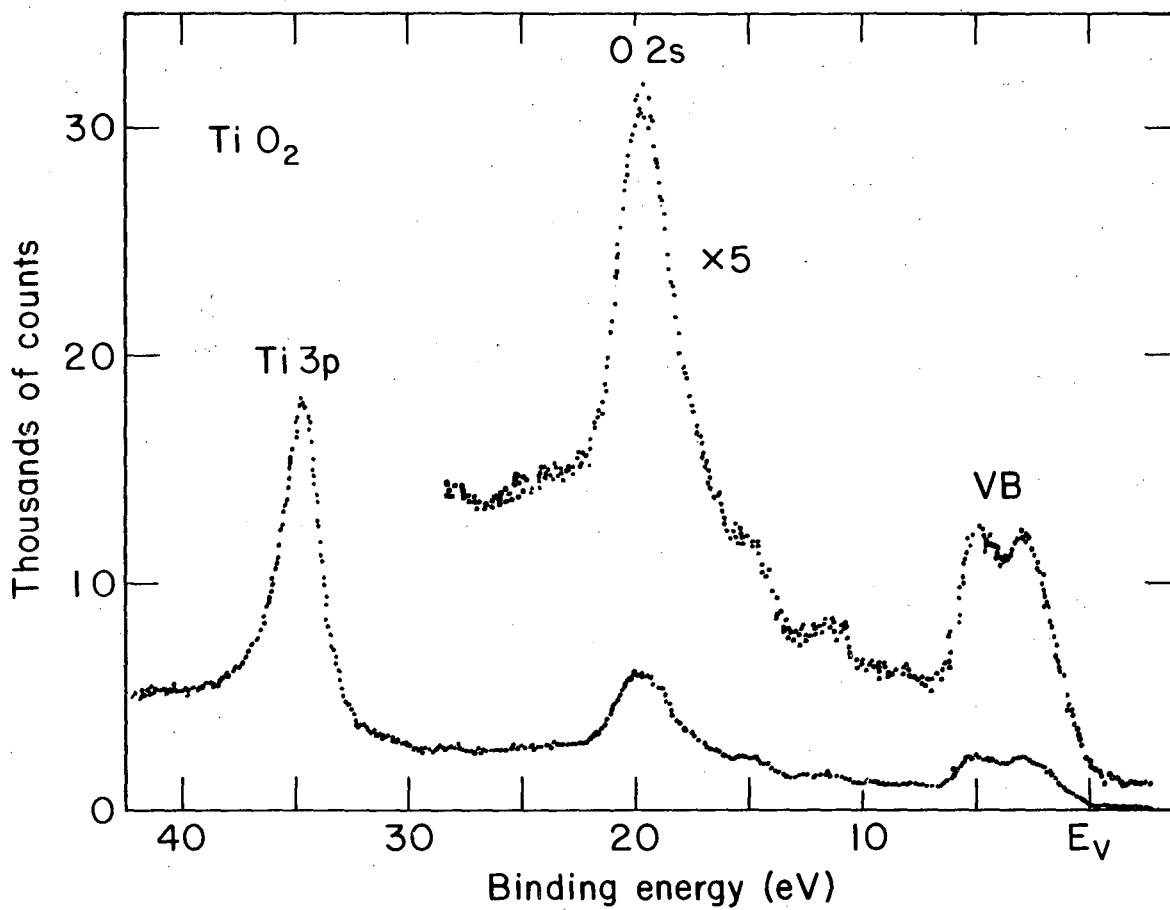


Fig. 3

XBL757-3410



XBL 757-3400

Fig. 4

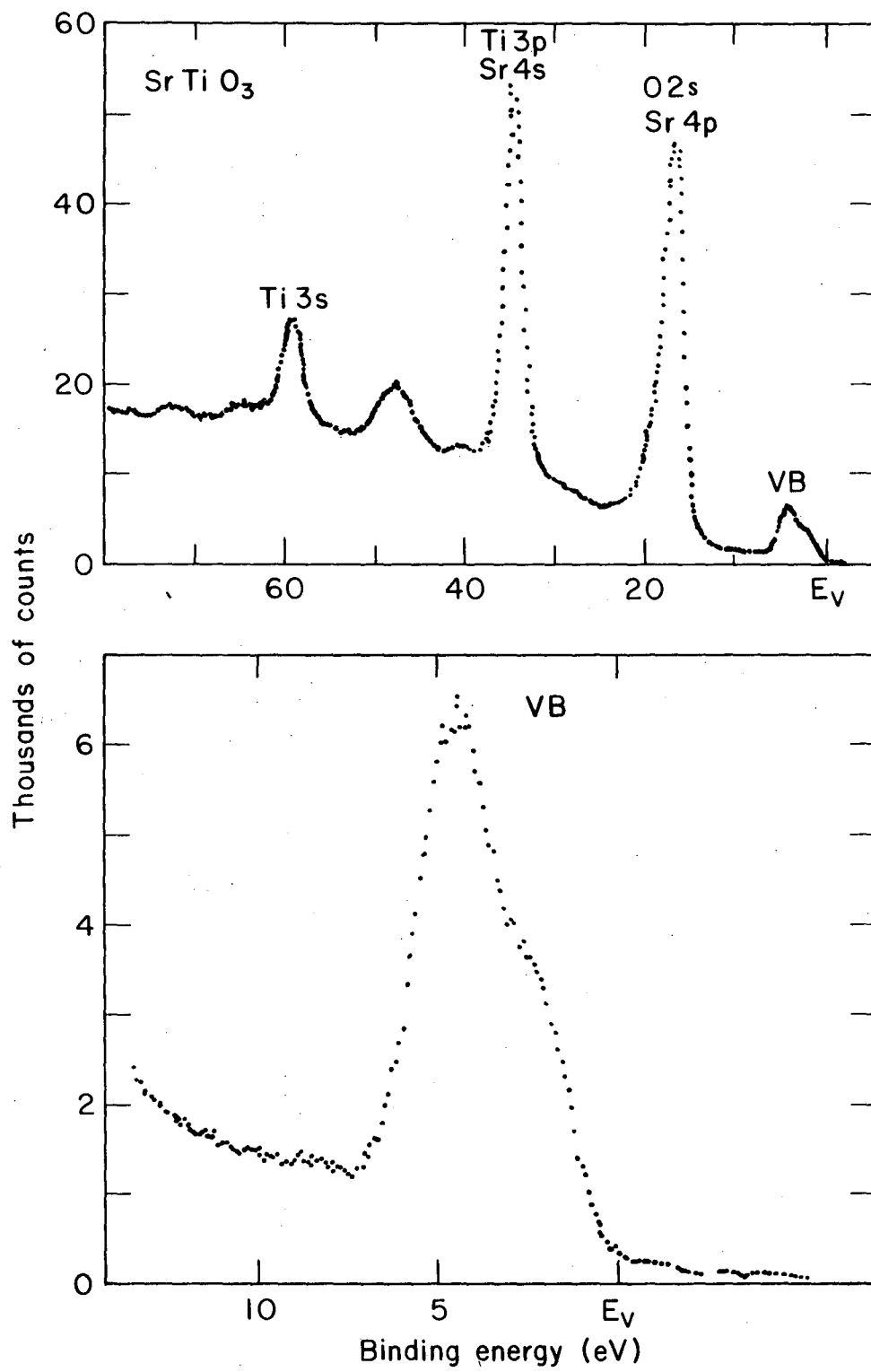


Fig. 5

XBL 757-3396A

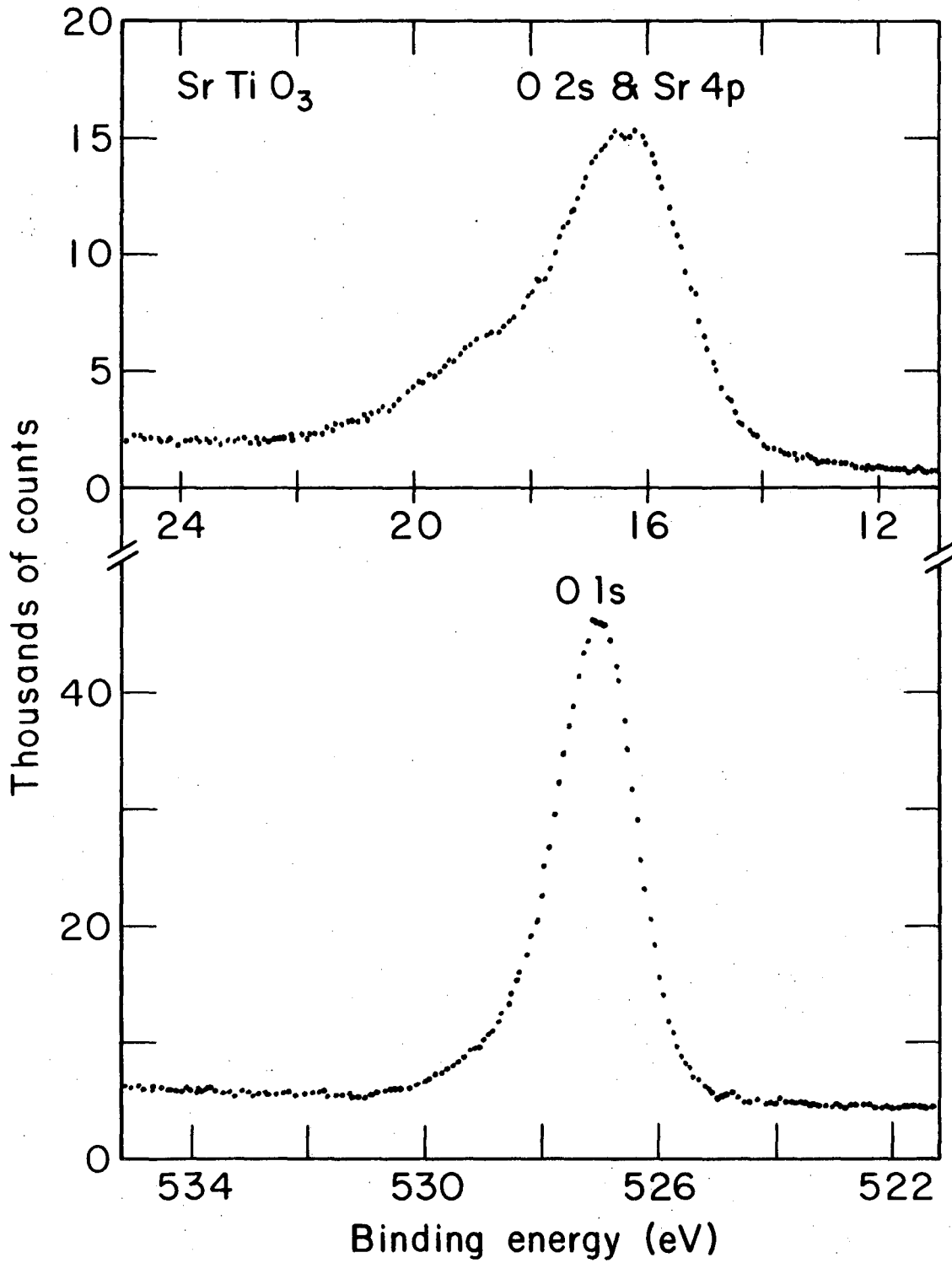


Fig. 6

XBL757-3412

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