

Intra-atomic versus interatomic processes in resonant Auger spectra at the Ti L_{23} edges in rutile

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The two components of the Ti $L_{23}M_{23}V$ Auger transition recorded on a stoichiometric rutile crystal are identified as $L_2M_{23}V$ and $L_3M_{23}V$ contributions. This assignment is evidenced by concordant data relative to resonances of the LMV decay at the Ti L_{23} thresholds and to Auger emission recorded in coincidence with the $2_{1/2}$ and $2_{3/2}$ photoemission at a photon energy far above the Ti L_{23} edges. The $L_3M_{23}V$ transition is shown to follow either the direct photoexcitation of a $2_{3/2}$ electron or the fast Coster-Kronig decay of a $2_{1/2}$ photohole. Although specific LMV contributions related to valence orbitals are identified, the long-suggested dual description of the $L_{23}M_{23}V$ Auger line as intra-atomic and interatomic transitions are discarded.

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I. INTRODUCTION

The chemical nature and environment of an element often manifest themselves through the occurrence of specific electronic transitions. In ionocovalent compounds, the severely depleted valence population of the cations favors the otherwise long-living interatomic core hole Auger decays, which is at the origin of many spectroscopic fingerprints, including characteristic Auger line shape¹ and electron-and photon-stimulated desorption of positive oxygen ions from oxide substrates.² It has been evidenced recently that core-level electrons of neighboring atoms can be direct actors in the resonant photoemission process of the excited atom which can have applications as a probe of the hybridization with the external orbitals of neighboring atoms.^{3,4}

In transition-metal oxides, the occurrence of interatomic transitions in Auger decays involving the valence electron has suggested making use of them to determine the surface stoichiometry.⁵ Indeed, this is a central need of the chemistry of ceramic surfaces, since the ability to produce a correct diagnostic about the nature of the chemical defects and to estimate their amount is often hampered by the lack in experimental means. In this respect, titanium oxide substrates, whose dominant type of defect is the oxygen vacancy, is the most tractable. Upon their removal from the lattice, oxygen ions leave their charge behind, so the creation of vacancies goes with the reduction of Ti^{4+} cations into Ti^{3+} and Ti^{2+} . It can thus be specifically characterized in photoemission⁶⁻⁹ and electron energy-loss measurements.⁷ Above all, the stoichiometry of the oxide has been shown to be directly related to the ratio of the two components of the Ti $L_{23}M_{23}V$ Auger transition.^{6,10} Due to its appearance when the metal is oxidized and its increase in intensity upon increasing the oxidation state of the metal, the low kinetic energy component is assigned to a so-called "interatomic $LMV(O)$ " decay,¹⁰ while the other component is associated to an "intra-atomic

$LMV(Ti)$ " process^{7,8,10} [$V(Ti)$ and $V(C)$ refer to Ti and O contributions to the oxide valence band]. This well-documented Ti LMV intensity ratio has been widely used to determine changes in stoichiometry of Ti compound surfaces⁵⁻¹⁰ as well as variations in surface oxygen composition upon metal deposition.¹¹ Such an interpretation is consistent with the expectation that a change in the oxygen vacancy concentration should affect the oxide valence band which involves the O $2p$ and Ti $3d$ hybrid orbitals at the origin of the Ti-O bond.¹²⁻¹⁶ However, in other argonlike systems, the LMM Auger transition (the other intense decay of the L_{23} hole), yields to distinct lines attributed to L_2MM and L_3MM transitions,¹⁷ including the occurrence of a L_2L_3V Coster-Kronig (CK) decay which significantly reduces the intensity of the former. Therefore, the constant suggestion that the observed Ti LMV transition is a $L_3M_{23}V$ component whose shape is entirely dictated by the interatomic/intra-atomic ratio is questionable. Is this interpretation correct, or is the mechanism linking the Auger line shape to the titanium degree of oxidation more subtle?

The Ti LMV transition has been examined both on-resonance at the Ti L_{23} edges and off-resonance by coincidence spectroscopy on a stoichiometric $TiO_2(110)$ rutile surface which has been chosen since it is stable and can be reproducibly prepared. Resonant Auger is a well-suited technique to give a better insight into this Auger decay. Powerful probes of the electronic properties of matter, resonant spectroscopy experiments consist of studying spectra at different photon energies across an absorption edge with the use of the tunable photon energy offered by synchrotron radiation. Although quite accurate as a method to analyze the nature of Auger decays, resonant Auger might be misleading when interpreting transitions occurring far away from absorption edges. To remove this ambiguity, off-resonance coincidence spectroscopy experiments have been done. In the following,

the assertion that the Ti $LM_{23}V$ Auger spectrum is constituted by two $L_3M_{23}V$ and $L_2M_{23}V$ main lines, and not two intra-atomic and interatomic decays, will be discussed.

II. EXPERIMENT

Experiments were performed at the ALOISA beamline¹⁸ of the Elettra Synchrotron Light Source in Trieste. During the resonant Auger experiment, the s -polarized radiation was impinging at grazing incidence (~ 6 deg). In the photon energy range of 450–810 eV which has been used herein, the photon resolving power was around 5000. Resonant Ti LMV Auger spectra were recorded at normal emission using the ALOISA 30 mm hemispherical analyzers whose energy resolution was set to 360 meV, leading to an overall experimental bandpass lower than 380 meV.

The contributions of the L_2 and L_3 photohole in the LMV decay in nonresonant conditions were determined by recording the LMV Auger spectrum in coincidence with the $2_{1/2}$ and $2_{3/2}$ photoelectrons, with a photon energy of 810 eV lying about 350 eV above the Ti L_{23} edges. Two of the seven hemispherical electron analyzers hosted in the ALOISA chamber were tuned at fixed kinetic energy on the maximum of the $2_{1/2}$ (or $3/2$) photoemission peak, with an energy resolution of 2.2 eV, in order to integrate as much as possible over the photoemission peak. The other five were scanning the Auger region with an energy resolution of 2.5 eV in order to get the best compromise between maximum angular acceptance and good timing and energy resolution.

Once mounted in the vacuum chamber, the surface of the $\text{TiO}_2(110)$ crystal was cleaned by ion bombardment. The sample was then annealed at 900 K for 15 mn under vacuum to achieve electrical conductivity by creating bulk oxygen vacancies and subsequent population of the Ti $3d$ orbitals. As a result, the color of the crystal switched from transparent to dark blue. The working surface was obtained by further annealing at 770 K under oxygen at a pressure of 1×10^{-6} mbar and cooling under oxygen. Its composition was judged to be close to the stoichiometric TiO_2 , since its Ti $2p$ photoemission spectrum only shows a unique component associated to a titanium oxidation degree of four (the limit of detection of this method is estimated to 1 at. %).

III. RESULTS AND DISCUSSION

The Ti $2p$ absorption spectrum collected from the stoichiometric $\text{TiO}_2(110)$ surface, which is shown in Fig. 1(a), meets the already published data^{19,20} and calculations.²¹ The multiplet spectrum from the $2p^63d^0$ to $2p^53d^1$ excitation of the Ti^{4+} in octahedral symmetry involves seven lines.²² Van der Laan²¹ has identified the four main peaks in the absorption spectra as the following final states: $2_{3/2}3d\pi$, $2_{3/2}3d\sigma$, $2_{1/2}3d\pi$, and $2_{1/2}3d\sigma$. The $3d\sigma$ states, i.e., e_g -like states, lie at the higher energy because the associated bonding orbitals are directed toward the oxygen atoms. In rutile, the distortion of the Ti site from octahedral to D_{2h} results in a more complex multiplet whose more visible effect is the splitting of the e_g -like peak, as evidenced by com-

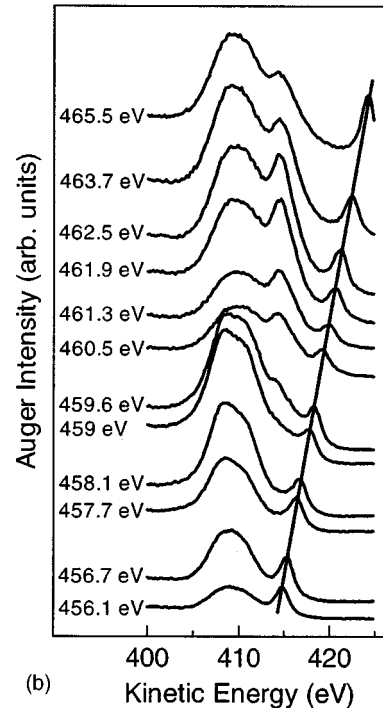
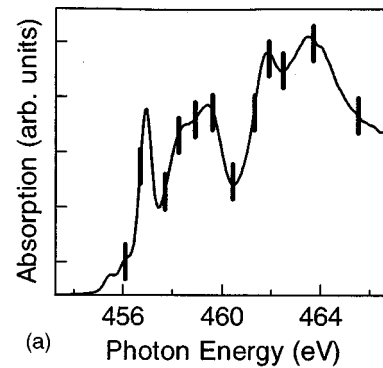


FIG. 1. (a) Full line: absorption spectrum in the Ti $2p$ threshold region. Vertical bars indicate energies at which the Auger spectra shown in (b) have been recorded; (b) $L_{23}M_{23}V$ Auger spectra recorded at the photon energies indicated in (a). The straight line indicates the position of the Ti $3p$ photoemission line, whose kinetic energy varies with photon energy.

parison with the absorption from the undistorted Ti site of SrTiO_3 .²¹

A. Resonant Auger electron spectroscopy

Resonant Ti $L_{23}M_{23}V$ Auger spectra have been recorded at various photon energies through the Ti L_{23} threshold region, by steps of about 0.6 eV. The probe photon energies, which are ranging between 455 and 467 eV, are shown by vertical bars in Fig. 1(a). The intensities of the spectra shown in Fig. 1(b) have been normalized with respect to the intensity of the incident photon beam measured on a grid. Spectra involve (i) peak at a kinetic energy which follows the photon energy and (ii) structures in the 405–416 eV kinetic energy range. The dispersing peak, whose maximum is shown in

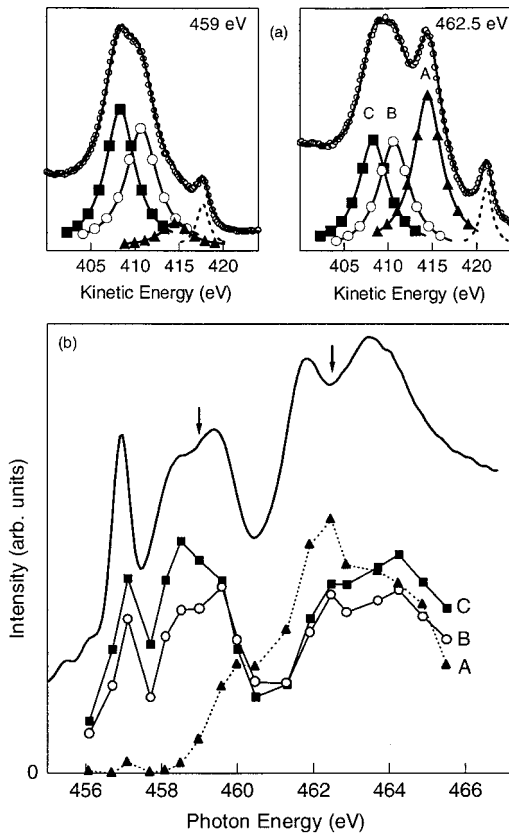


FIG. 2. (a) Decomposition into four components of the $L_{23}M_{23}V$ Auger spectrum recorded at a photon energy of 460.4 eV, including the photoemission $3p$ line (dashed line) and three Auger components at constant kinetic energies, 408.3 eV (C: squares), 410.7 eV (B: circles) and 414 eV (A: triangles) (see the text). Two decompositions are shown for the Auger spectra recorded at the energies indicated by arrows in (b); note that although the relative intensities of the A, B, and C components differ strongly, the quality of the fit remains quite good; (b) intensity of the A (triangles), B (circles), and C (squares) components of the $L_{23}M_{23}V$ Auger transitions through the Ti $2p$ threshold region.

Fig. 1(b) by a straight line, is peaking at a binding energy of 41.5 eV. It is assigned to the resonant Ti $3p$ photoemission line. The features observed in the 405–416 eV kinetic energy range are attributed to Auger LMV transition. The LMV spectra are dominated by salient features which appear at constant kinetic energies, a peak centered at 409 eV and a peak which shows up around 414.5 eV just before the L_2 edge.

By direct inspection of the Auger spectra shown in Fig. 1(b), it is clearly seen that the peak at 409 eV changes in shape upon scanning photon energy through the L_{23} region, which indicates that it involves different contributions. To get a better insight into the resonance behavior of the $L_{23}M_{23}V$ transition, the Auger spectra have been decomposed into three components A, B, and C [Fig. 2(a)]. The photoemission peak Ti $3p$, which appears at constant binding energy in the decomposition [Fig. 2(a)], is not discussed here. The high-energy Auger feature at 414.5 eV is labeled A. The 409 eV peak has been split into two contributions, which are labeled B and C, because it is the simplest way to account for several contributions with different resonance

behaviors. The choice of Lorentzian line shapes for A, B, and C is consistent with the fact that the linewidths are much larger than the experimental bandpass (0.38 eV) in all spectra under examination. It appears that Auger spectra can all be fitted with three lines at constant kinetic energy, 414.5 ± 0.2 eV, 410.7 ± 0.2 eV, and 408.3 ± 0.2 eV, with a unique and constant width of 2 ± 0.15 eV. The uncertainty of ± 0.2 eV corresponds to the scatter of the values derived from the fitting process.

However, no systematic shift in energy position could be evidenced, which means that there exist no feature which could be related to radiationless Raman regime in the resonant Auger Ti LMV spectra of TiO_2 across the Ti L_{23} edges. Such behavior is consistent with the trend observed along the series of the Argonlike d^0 ions.¹⁷ Raman-like decays, which dominate the absorption thresholds of highly ionic cations such as Ca^{2+} , become marginal as the degree of covalency increases.^{17,20} Recent papers have discussed the question of the relative intensity of the Raman-like to the Auger-like components by comparing the resonant behaviors of different compounds,^{23,24} the ratio between the two processes have been used to evaluate the charge-transfer time between absorbate and substrate.²⁵ Finazzi *et al.*²³ have recently shown the presence of a Raman-like Auger above the Cu L_3 edge in CuO, while in the case of Cu_3O , which is more covalent, they observe a normal Auger above the edge. The absence of Raman-like above the edge can thus be explained by the covalent character of the Ti-O bond which has been evidenced by valence-band resonant photoemission at the Ti $2p$ edges.¹⁵ Titanium being an early transition metal, i.e., with a high number of empty d states, the oxide TiO_2 exhibits a strong effective hybridization energy, which results in a strong covalency between the titanium $3d$ states and the oxygen $2p$ valence states.¹⁶ This covalent character of the Ti-O orbitals allows an effective delocalization of $3d$ electrons which substantiates the above observed absence of any sizeable Raman scattering at and above the Ti $2p$ threshold in TiO_2 .

The intensities of the peaks A, B, and C are reported in Fig. 2(b). Consistently with the direct observation, the structure A shows no intensity until the L_2 region is reached. It is associated to the $L_2M_{23}V$ decay. At variance, strong enhancements of B and C are observed not only when the photon energy is swept through L_3 , but also across L_2 . These are assigned to the $L_3M_{23}V$ channel. Their resonance regime arises from the existence of two routes for the creation of a $2_{3/2}$ photohole, either the direct absorption at L_3 or the decay of a $2_{1/2}$ hole via a L_2L_3V Coster-Kronig (CK) process. This fast process can be indirectly evidenced by the short lifetime of the L_2 hole with respect to that of the L_3 hole, i.e., the broadening of the L_2 manifold in the absorption edge spectrum.²² The quite high intensity of the $L_3M_{23}V$ Auger line at the L_2 threshold is indicative of the high probability of this CK decay. The decay of a $2_{1/2}$ hole via a LLV CK decay likely differs from the direct excitation of a $2_{3/2}$ electron. Indeed, if an Auger decay follows a CK decay, the atom ends in a three core holes final state, and, as observed in metals, the Auger electron is emitted with a lower kinetic energy than for a single Auger decay with a two core holes

final state. Nevertheless, for an insulator, in a CK process, a valence electron is excited to the empty states of the conduction band. Since these states are localized molecular orbitals, this electron lowers the influence of the valence hole. This can explain why, unlike in metals, we do not observe any three hole satellite associated with the L_3MV feature. The similar behavior of components B and C across the L_2 and L_3 edges, where they run parallel to the absorption profile, indicates that these features, which arise from the decay of the L_3 hole, cannot be differentiated by any particular contribution from either of the two routes leading to the creation of a $2_{3/2}$ photohole, i.e., the direct absorption at L_3 or the CK decay of a $2_{1/2}$ hole.

Rather subtle features are also observed in the intensities of the components A , B , and C , which cannot be explained with qualitative arguments. A complete analysis including multielectronic and crystal-field effects is required. We suggest that the origin of the B and C doublet is related to the shape of the valence band of TiO_2 . This band exhibits a two-peak spectrum with an energy separation of 2 to 3 eV showing two distinct resonances at the $3p \rightarrow 3d$ threshold.¹³ Reproducibly recorded at photon energy ranging from UV to x rays, it has been accounted for by calculations.²⁶ After a molecular orbital picture,¹⁴ the high (low) binding energy part of the density of states is dominated by contributions from σ (π) bonding hybrids. The observed energy separation of 2.4 eV between B and C supports the assignment of those peaks to Auger decays involving the components of the valence band. This doublet is not observed in the L_2MV line. Some decay processes allowed at the L_3 edge can be forbidden at the L_2 . Studies on samples with different stoichiometry will be undertaken to support this assumption, by measuring how changing the hybridization affects the LMV profile.

B. Auger spectra in coincidence with photoemission

The above picture of the LMV transition along $L_2M_{23}V$ and $L_3M_{23}V$ channels relies on a *a priori* decomposition of the spectrum into somewhat arbitrary components. Moreover, although being quite helpful in deciphering L_2 and L_3 edges, resonant features might be specific to the threshold region. To directly determine the respective contributions of the L_2 and L_3 photohole in the LMV decay in nonresonant conditions, this Auger spectrum has been recorded in coincidence with the $2_{1/2}$ and $2_{3/2}$ photoelectrons at a photon energy of 810 eV lying well above the Ti L_{23} edges.

The two coincidence spectra presented in Fig. 3 have been collected in three days of beamtime. The error bars are the square roots of the total coincidences i.e., true plus accidental. The true coincidence counts are obtained by integrating the coincidence peak area in the time spectra, the background of accidental coincidence being subtracted. The Auger spectrum in coincidence with $2_{3/2}$ photoemission is narrow and mostly located on the low-kinetic energy side of the $L_{23}M_{23}V$. The Auger spectrum in coincidence with $2_{1/2}$ photoelectrons is more complex. It clearly dominates the high kinetic energy side of the LMV transition. It is responsible for the shoulder seen even on the raw Auger line (Fig. 3)

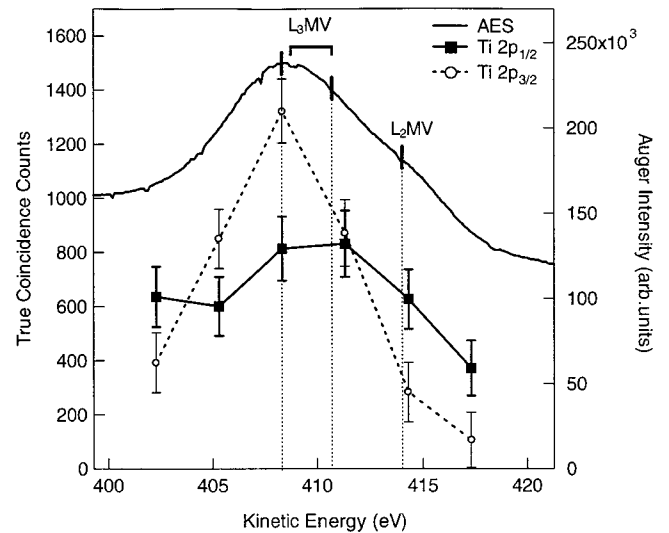


FIG. 3. Auger spectra in coincidence with $2p_{1/2}$ (squares) and $2p_{3/2}$ (circles) photoelectrons, at a photon energy of 650 eV, far above the Ti $2p$ edges. The Auger spectrum recorded at the same photon energy is also given (full line).

which gives rise, in the Auger derivative spectrum, to the feature which has long been attributed to the intra-atomic LMV transition.^{6,10} In addition, the extension of this coincidence spectrum over the central part and the low kinetic energy side of the LMV spectrum supports the occurrence of a L_2L_3V CK channel arising after the photoexcitation of L_2 electrons into a $3d$ orbital, to create a L_3 hole followed by a $L_3M_{23}V$ decay. Important CK decays have been already observed on $3d$ transition metals.²⁷

IV. CONCLUSION

It turns out that the distinction between interatomic and intra-atomic transitions is not relevant to explain the Ti LMV profile in stoichiometric TiO_2 . The conclusions drawn from the resonance of the LMV process in the Ti $2p$ threshold region nicely meet those derived from the examination of this LMV spectrum in coincidence with the $2_{1/2}$ and $2_{3/2}$ photoemissions at a off-resonance photon energy. The two main contributions to the $L_{23}M_{23}V$ Auger spectrum are due to the $L_2M_{23}V$ at kinetic energy of 414.5 eV and $L_3M_{23}V$ transitions around 409 eV. The $L_3M_{23}V$ decay follows both the direct photoexcitation of a $2_{3/2}$ electron and the fast CK decay of the $2_{1/2}$ photohole whose occurrence is directly evidenced by the coincidence experiments. While discarding the previous picture of the two LMV peaks to favor the L_{23} splitting, the above results suggest another fingerprint for the chemical composition of the oxide. Associated with the two-peak-shaped valence band, the two components at 410.7 and 408.3 eV of the $L_3M_{23}V$ transition can be related to the oxidation state of titanium. This signature of the TiO bond open a way to explain the Ti LMV line shape, although its change with the stoichiometry of the oxide is still to be understood.

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