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Stoichiometry-related Auger lineshapes in titanium oxides: Influence of valence-band profile and of Coster-Kronig processes

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The ability to determine the nature and the occurrence of defects is a central need of ceramic surface chemistry. In titanium oxides, the Ti-LMV Auger decays line shape is very sensitive to the titanium degree of oxidation, and has long been empirically used as a qualitative probe of the stoichiometry. In the present work, resonant Auger and resonant valence-band measurements at the Ti-$L_{2,3}$ edges in TiO_2, TiO_{2-x} and metallic titanium provide a clear evidence that the evolutions of the Ti-LMV Auger line shape are due to drastic changes in the valence-band profile and in the probability of L_2L_3V Coster-Kronig decay processes when a fraction of titanium ions is reduced. Both are shown to be consequences of the filling of Ti-3d states near the Fermi level on defects sites. These conclusions are confirmed by Auger-photoelectron coincidence experiments.

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I. INTRODUCTION

The electronic structure of transition-metal oxides has been the subject of numerous theoretical and experimental studies. Indeed, depending on, e.g., the valence of the cation, the nature of the chemical bond, and the charge transfer from the cation to the ligand, a great variety of situations can be encountered. For their fundamental interest as well as for technological applications in the field of microelectronics, glass industry or magnetic storage, 3d elements oxides have been widely investigated, by all kinds of techniques sensitive to their structural defects or to their properties at surface, clean or after the depositions of thin metallic layers.

X-ray absorption spectroscopy (XAS) and electronic spectroscopies such as x-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy are among the most exploited tools for these studies, since they provide valuable information on both the electronic and crystallographic structures, including on possible local defects. The ability to produce a correct diagnosis about the nature and the amount of chemical defects is a central need of chemistry of ceramic surfaces because they create new electronic states, in particular in the gap, and perturb the reactivity.[1] In this respect, the occurrence of interatomic processes involving valence electrons in Auger decays has been used to determine, at least qualitatively, the surface stoichiometry of some transition metal oxides.[2] As an example, in Ti oxides, the relative intensities of the two main lines of the Ti $L_{2,3}M_{2,3}V$ Auger decay were shown to be clearly correlated to the surface stoichiometry of the compound.[3,4] This Auger spectrum mainly involves two components. Due to its appearance when the metal is oxidized, and its growing intensity while increasing the cation oxidation state, the low kinetic energy component has been assigned to a so called "interatomic L_3MV(O)" decay,[4] while the other component has been associated to an "intra-atomic L_3MV(Ti)" process.[4–6] Here, V(O) and V(Ti) refer to the O and Ti contributions to the oxide valence band, respectively. This well-documented Ti-*LMV* intensity ratio has been widely used to determine changes in the stoichiometry of Ti compounds surfaces as well as variations in surface oxygen stoichiometry after metal deposition.[2–7] Rao *et al.*[4] showed the coherent evolution of the Ti-$L_{2,3}M_{2,3}V$ Auger spectra through a series of compounds presenting a gradual reduction of the titanium ion from TiO_2 to metallic titanium. The spectrum evolves from mostly a unique line around 408 eV in TiO_2 to a unique line at around 414 eV in metallic titanium, the intermediate spectra presenting these two lines with varying relative intensities (Auger spectra from samples under examination herein are shown in Fig. 1).

To understand the link between the Auger line shape and the stoichiometry of titanium oxides, a detailed study of the Ti-$L_{2,3}M_{2,3}V$ Auger resonant behavior at the Ti-$L_{2,3}$ edges has been undertaken, as well as off-resonance coincidences measurements between Auger electrons and Ti-2p photoelectrons on a series of three samples: a stoichiometric TiO_2 crystal, a reduced-TiO_2 sample (TiO_{2-x}) and a polycrystalline metallic titanium plate. From our comprehensive study,

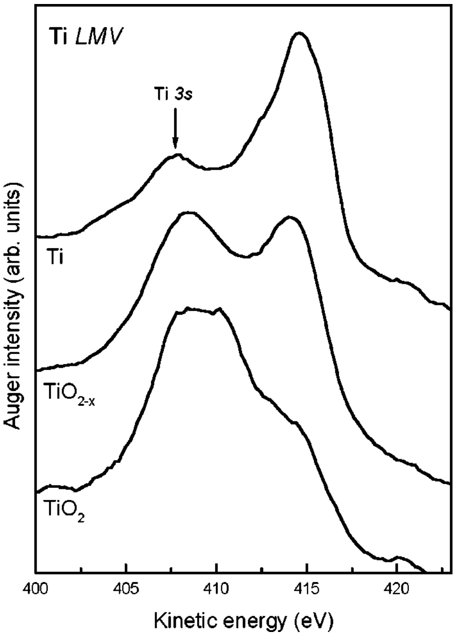

FIG. 1. Ti-LMV Auger spectra recorded off resonance in stoichiometric TiO_2 (bottom), reduced TiO_2 (TiO_{2-x}) (middle), and metallic titanium (top). The spectra measured on TiO_2 and TiO_{2-x} were obtained at 542 eV photon energy. On metallic titanium, the spectrum was recorded at 465.6 eV. Note that the feature seen at 407 eV kinetic energy in metallic titanium spectrum is the Ti-3s photoemission. The two other Auger spectra, which were recorded at higher photon energies are not contaminated by this photoemission peak.

the explanation of the relative intensities variations of the two Auger lines simply in terms of modification of the ratio between interatomic and intra-atomic $L_3M_{2,3}V$ processes can be ruled out. The occurrence of $L_2M_{2,3}V$ processes has also to be taken into account, and we will show that the contribution of such $L_2M_{2,3}V$ decays for Ti^{4+} ions is mixed with some $L_3M_{2,3}V$ decays due to reduced Ti species, complicating the understanding of the Auger spectrum. The valence band of the various compounds has been also studied, since it is involved in the $L_{2,3}M_{2,3}V$ Auger process, and must be at the origin of the sensitivity of this Auger process to the degree of oxidation of titanium. Indeed, the changes in the Auger spectrum will be shown to originate from filling of the 3d valence band states as well as to an increasing probability of the Coster-Kronig (CK) decay of the $2p_{1/2}$ core hole, both phenomena being due to the reduction of the Ti ion.

II. EXPERIMENT

Data were collected at the ALOISA beamline[8] of the Elettra Synchrotron Light Source in Trieste. The s-polarized light was impinging on the sample at grazing incidence ($\sim$6 deg). The resolving power was around 5000 in the 450–810 eV photon energy range used herein. The resonant Auger spectra were recorded using the ALOISA 33 mm hemispherical analyzers whose energy resolution was set to 360 meV, leading to an overall experiment bandpass of 380 meV. For the coincidence experiments, two of the seven analyzers hosted in the ALOISA chamber were tuned at fixed kinetic energy on the maximum of the $2p_{1/2}$ (or $2p_{3/2}$) photoemission peak, with an energy resolution of 2.2 eV, in order to integrate as much as possible on 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 time and energy resolution.

The TiO_2-rutile (110) sample used herein has been previously heated in vacuum at 900 K during 1 h. As a result, the rutile took a dark blue color and became conductive enough to avoid charging effects. The stoichiometric surface was obtained by further annealings at 800 K under an oxygen pressure of 1×10^{-6} mbar. Further details on the sample preparation are given in Refs. 7 and 9. All the spectroscopic measurements (Ti-$L_{2,3}$ XAS and Ti-2p XPS) which were performed on the samples obtained by this preparation procedure confirmed that the TiO_2 stoichiometry was restored on the depth probed by the photons, although we cannot exclude the occurrence of some structural defects at the very surface, such as those which have been observed by imaging techniques.[10] These defects are assumed to be marginal in the present measurements. The TiO_{2-x} sample was prepared by sputtering the stoichiometric TiO_2 (110) crystal with 1 keV Ar^+ ions during 15 mn (Ar pressure of 1×10^{-6} mbar, ionic sample current of 4 μA), in order to create oxygen vacancies near the surface. A 15 mn annealing at 400 °C in ultrahigh vacuum restored the surface reflectivity, needful for the coincidence measurements. The surface stoichiometry was characterized by monitoring both the Ti-2p XPS (which exhibits peaks corresponding to Ti^{3+} and Ti^{2+}) and the Ti-$L_{2,3}$ XAS spectrum. The latter is very sensitive to variations of the oxygen concentration, as shown by the strong changes in the spectrum recorded on TiO_{2-x} with respect to the stoichiometric TiO_2 spectrum (see top part of Fig. 2). The evolution of the XAS spectra with stoichiometry had been observed previously in TiO_2-anatase[11] and will be discussed later. This preparation method leads to quite reproducible surfaces.

The polycrystalline titanium sample was prepared by several argon ions sputterings followed by annealings at 670 K. Due to the strong reactivity of titanium, the cleaning procedure had to be often repeated, but small amounts of carbon were always detected by XPS. The high reactivity of the surface prevented any coincidence measurement on that sample because data collection time is too long compared to the clean sample lifetime.

In order to determine precisely the origin of the different contributions of the complex Ti-$L_{2,3}M_{2,3}V$ Auger spectra in TiO_2, we have recorded these spectra in resonance at the Ti-$L_{2,3}$ absorption edges. The goal is, by increasing the probability for the creation of a well defined core hole, to enhance the relative weight of a given contribution in the Auger profile. In nonresonant conditions, the $L_{2,3}M_{2,3}V$ Auger process can be described as follows: first, a 2p core hole is created by a photon whose energy is higher than the 2p binding energy, and a core electron is photoemitted. Then, the excited ion decays via the Auger process involving a 3p electron and a valence electron. The first electron fills the 2p hole, and the

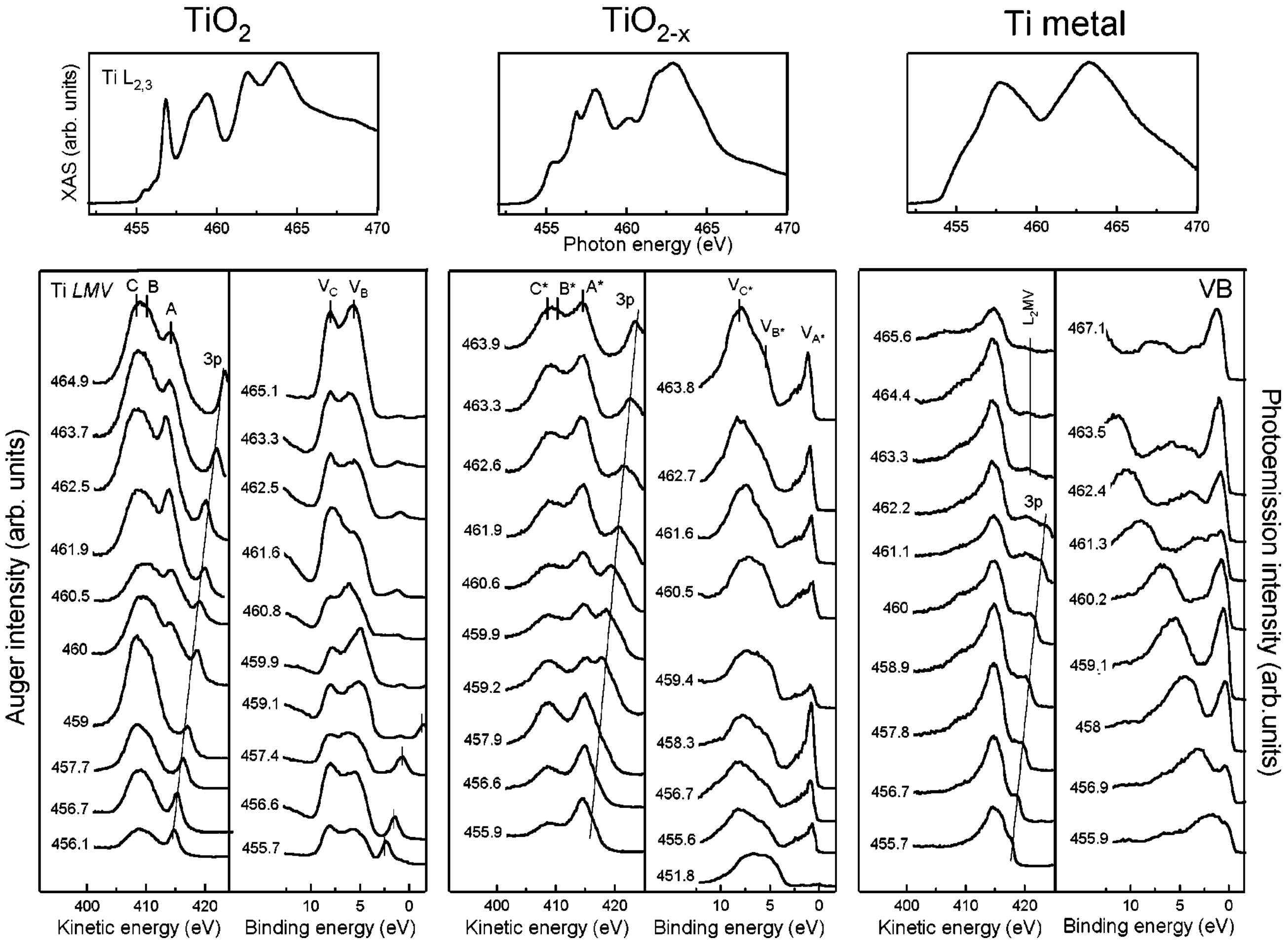

FIG. 2. Experimental resonant electron spectra obtained on stoichiometric TiO_2-rutile (left part), TiO_{2-x} (middle part) and metallic titanium (right part). The absorption spectrum (top), the resonant $L_{2,3}M_{2,3}V$ Auger spectra (bottom left), and the resonant valence-band spectra (bottom right), both recorded at the Ti-$L_{2,3}$ edges, are presented for each sample. For the resonant spectra, the excitative photon energy is given on the left of the spectrum. The slanting lines in the Auger panel indicate the position of the Ti-$3p$ photoemission lines, whose kinetic energy varies with photon energy. The strongly dispersive line observed in the valence-band spectra recorded on TiO_2, marked by a vertical stroke between 455 and 459.1 eV photon energy, is the Ti-$2p_{1/2}$ photoemission excited by the monochromator second-order reflection. The spectra recorded on metallic Ti, for photon energies above the Ti-L_2 edge show some contamination effects through the presence of carbon or oxygen valence states.

second one is emitted. In resonant conditions, when the photon energy is swept across the $L_{2,3}$ absorption edges, the Auger process can also be described, in a simplistic model, as a two-step process, in which, following the excitation of the $2p$ electron to an empty state above the Fermi level, the excited atom decays via a $L_{2,3}M_{2,3}V$ Auger process. When the photon energy corresponds to the maximum of the L_3 part of the XAS profile, only $2p_{3/2}$ core holes are created and only the $L_3M_{2,3}V$ part of the Auger decay is present in the resonant Auger spectra. At higher photon energies, in the L_2 part of the XAS profile, the creation of a $2p_{1/2}$ core hole is allowed. Then, in the resonant Auger spectra, the $L_2M_{2,3}V$ part of the Auger profile appears. Since at this higher photon energy the excited atom can also decay via a L_2L_3V Coster-Kronig process, some resonance of the $L_3M_{2,3}V$ can also occur at the L_2 XAS threshold through some kind of three-step process: creation of a $2p_{1/2}$ core hole, a Coster-Kronig decay with creation of a $2p_{3/2}$ hole, and then a $L_3M_{2,3}V$ Auger decay.

Finally, we have recorded resonant valence-band photoemission spectra. Since the LMV Auger process involves valence electronic states, the knowledge of the valence-band structure for the different samples is of major interest. At resonance, the direct photoemission of a valence-band electron interferes with the two-step autoionization process leading to the same final state. The incident photon induces the transition of a $2p$ electron to an empty $3d$ state above the Fermi level. Then, the excited atom decays, the photoelectron filling back the core hole and a valence electron being emitted.[12,13] The photon energy dependence of the valence-band spectra allows to emphasize the local density of states on the Ti atoms by the enhancement of its relative weight at the Ti-$2p \rightarrow 3d$ excitation threshold.

III. RESULTS

A. Stoichiometric TiO_2

Ti-$L_{2,3}M_{2,3}V$ Auger spectra recorded on stoichiometric TiO_2-rutile, TiO_{2-x} and metallic titanium at the Ti-$L_{2,3}$ absorption edges for different photon energies, are presented in Fig. 2, as well as resonant measurements of the valence band. For stoichiometric rutile, concerning the $L_{2,3}M_{2,3}V$ Auger decay, it is clear that, if the low-energy structure of the Auger spectra appears above the L_3 edge, the high kinetic energy structure only shows up near the L_2 edge, confirming the attribution of these lines to the L_3MV and L_2MV components of the Auger spectrum, respectively.[9] The valence-band spectra from the stoichiometric oxide can be compared to measurements by Prince *et al.*[12] (see also Thomas *et al.* for measurements on the anatase phase[13]), with a dominant structure due to the mixing of the O-$2p$ and Ti-$3d$ states[14,15,13] peaking between 5 and 10 eV binding energy. The small peak which shows up near the Fermi level (especially visible around a photon energy of 462 eV) is attributed to the filled $3d$ states of titanium associated to the presence on the surface of a small amount of defects. The much smaller intensity of this defects' peak in our measurements indicates that the surface of our sample was closer to the perfect TiO_2 stoichiometry than that used by Prince *et al.* in their experiment.[12] In a previous paper, the resonant Ti-$L_3M_{2,3}V$ Auger spectra on stoichiometric TiO_2 (Ref. 9) was modeled by two peaks labeled *B* and *C*, which were suggested to reflect the shape of the valence band.[12,14] Indeed, we confirm here that the splitting of roughly 1.7 eV between the two features V_B and V_C of the valence band is similar to the *B*-*C* energy separation in the Auger spectra (2.4 eV). Furthermore, in the decomposition of the resonant Auger spectra,[9] it is clear that the *C* structure is always more intense than *B*, except for photon excitations around the second peak of the Ti-L_3 edge which corresponds to the transition of the $2p$ photoelectron towards the $3d$ states of e_g-like symmetry.[16,17] Notably, it is also in this photon energy region that the component V_B is the most intense in the valence-band spectra.

B. TiO_{2-x}

The valence band of the TiO_{2-x} sample (Fig. 2) involves a broadband between 5 and 10 eV binding energy and a sharp feature peaking just below the Fermi level which exhibits a strong resonance behavior at the Ti-$L_{2,3}$ thresholds. This structure corresponds to valence-band states highly localized on the titanium sites. It is due to the filling of the Ti-$3d$ states in the vicinity of oxygen vacancies.[12,13] In contrast with the stoichiometric case, the Auger spectra show an almost constant profile, with two separated peaks, throughout the Ti-$L_{2,3}$ edges. In addition to the line centered around 409 eV kinetic energy, another L_3MV feature is peaking at 414.7 eV, at an energy position close to that of the L_2MV Auger decay in the stoichiometric sample. The obvious origin of the 414.7 eV L_3MV Auger component is the intense valence-band line observed below the Fermi level (Fig. 2), as evidenced by the 6.2 eV separation in energy between the two valence structures which nearly matches that between the two L_3MV lines ($\sim$5.7 eV). A complete interpretation of the Auger spectra in this reduced sample requires a more precise analysis which will be presented in Sec. IV.

C. Metallic Ti

As discussed in the introduction, there seems to be a gradual evolution in the $L_{2,3}M_{2,3}V$ Auger spectra from TiO_2 to metallic Ti. It is therefore relevant to analyze spectra from bulk titanium (see Fig. 2). The sharp feature of the valence-band spectra at the Fermi level is assigned to the Ti-$3d$ filled states. A L_3VV (L_2VV) Auger decay appears in the valence-band spectra at constant kinetic energy when the photon energy reaches the L_3 (L_2) ionization threshold. Associated with this valence-band profile, the Ti-$L_{2,3}M_{2,3}V$ Auger decay is dominated by a unique component. Unlike in the oxides, it appears first as a Raman line, at a fixed binding energy, with an asymmetrical line shape which can be explained by taking into account the density of empty *d* states above the Fermi level, as it was shown at the L_3 edge of silver.[18] Its kinetic energy becomes constant near the L_3 edge, where the process becomes a normal Auger decay. Apart from a weak feature at 420 eV kinetic energy appearing around the L_2 edge, these Auger spectra show very little differences between the L_2 and L_3 regions.

IV. DISCUSSION

A. Absorption

Changes in the oxygen concentration strongly affect the XAS spectrum at the Ti-$L_{2,3}$ absorption edges as shown by comparing the spectrum of TiO_{2-x} with that of the stoichiometric rutile (Fig. 3). In the rutile structure, titanium ions are surrounded by six oxygen ions forming a distorted octahedron which is stretched along one of its fourth-order axis (D_{4h} symmetry). Furthermore, in the plane perpendicular to this axis, the cell made of the titanium ion and of the four first nearest oxygen neighbors is not square but rectangular.[19] The Ti^{4+} $L_{2,3}$ edges in stoichiometric TiO_2 have been already calculated in the multiplet model, including crystal-field effects in the D_{4h} symmetry.[16,17] We have performed a similar calculation, which is compared to the experiment in Fig. 3 (curves *a* and *b*, respectively). In a perfect octahedral symmetry (belonging to the O_h group symmetry), the $3d$ levels are split into t_{2g} and e_g levels by the crystal field. The two main lines of the L_3 and L_2 edges correspond to transitions of the $2p$ photoelectron towards these two levels. A distortion of the octahedron along one of its axis has to be introduced to account for the splitting of the second structure of the L_3 edge. In the L_2 edge, larger broadenings of the multiplets (0.5 eV and 1.0 eV for the transitions towards t_{2g} and e_g orbitals, respectively, as compared to 0.15 eV and 0.6 eV for equivalent transitions at the L_3 edge) smooth out this splitting. These larger broadenings are justified by a $2p_{1/2}$ core hole lifetime reduced by Coster-Kronig (CK) decay, which will be discussed later. Further distortions of the octahedron have been neglected.

A calculation done with the same crystal-field parameters as for Ti^{4+}, but for a Ti^{3+} ion is also presented in Fig. 3 (curve d). A perfect agreement with the experimental spectrum is not expected, since the TiO_{2-x} sample contains Ti ions with various $3d$ fillings. However, this calculation gives a trend. At the L_3 edge, it reproduces the decrease of the

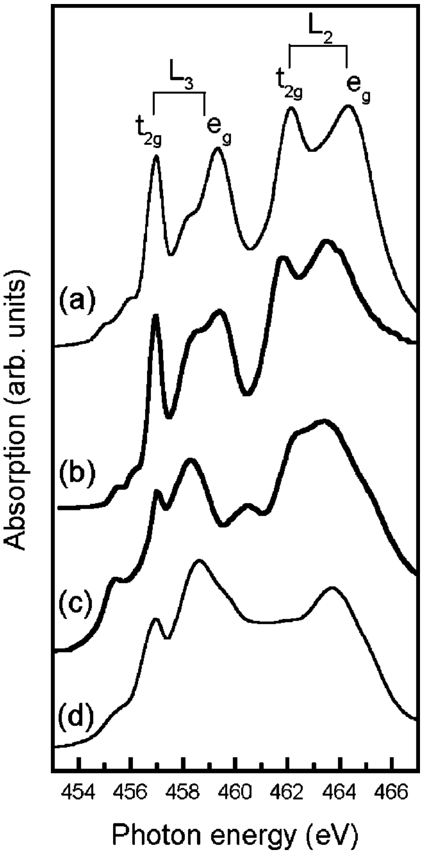

FIG. 3. Ti-$L_{2,3}$ absorption spectra: (a) $2p^63d^0 \rightarrow 2p^53d^1$ multiplet calculation for a Ti^{4+} ion in a D_{4h} crystal-field symmetry, with $10D\mathrm{q}=1.8$ eV, $D\mathrm{s}=-0.27$ eV, and $D\mathrm{t}=-0.05$ eV. The Slater integrals have been reduced to 80% of their atomic values. See text for the used energy widths. (b) experimental spectrum from stoichiometric $\mathrm{TiO_2}$-rutile and (c) reduced $\mathrm{TiO_2}$; (d) $2p^63d^1 \rightarrow 2p^53d^2$ multiplet calculation for a Ti^{3+} ion in the D_{4h} symmetry, with the same crystal-field parameters as *a*.

intensity of the $2p \rightarrow t_{2g}$-like structure at 457 eV, and the high intensity of the e_g-like structure around 458 eV. At the L_2 edge, the same tendency is observed, with a decrease of the $2p \rightarrow t_{2g}$-like structure, and a quite intense e_g-like structure around 464 eV. The measured structure at 462 eV is not reproduced by this calculation. The two main absorption lines for the Ti^{3+} ions are therefore two e_g-like features located around 458 and 464 eV, two photon energies where one can expect intense resonances of Ti local electronic states in XPS spectra.

B. Auger line shape and stoichiometry in titanium oxides

The resonant behavior of the Ti-$L_{2,3}M_{2,3}V$ Auger decay in a stoichiometric $\mathrm{TiO_2}$ sample has been precisely studied elsewhere.[9] The low kinetic energy structure, which appears from the L_3 edge was assigned to a $L_3M_{2,3}V$ Auger decay; the high kinetic energy structure was attributed to a $L_2M_{2,3}V$, since it appears only above the L_2 edge. This was confirmed by off-resonance coincidence measurements.[9] As a consequence, in stoichiometric $\mathrm{TiO_2}$, the interpretation of the Auger spectrum in terms of interatomic and intra-atomic processes[2] was ruled out, but the evolution of the Auger line shape with the degree of oxidation of titanium was still to be understood.

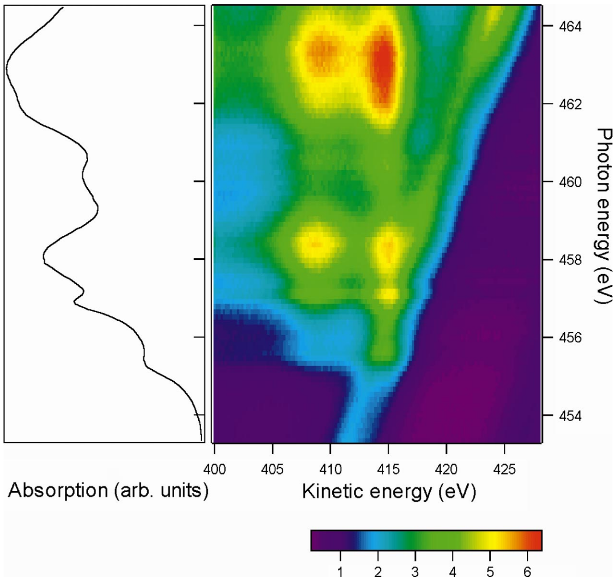

FIG. 4. (Color) Two-dimensional (2D) plot of the resonant Auger spectra recorded on the TiO_{2-x} sample. The spectra are plotted as a function of the electron kinetic energy (horizontal scale) and for the different photon energies across the Ti-$L_{2,3}$ edges (vertical scale), the colors indicating the Auger intensity for each of these two variables. The Ti-$L_{2,3}$ absorption edges in this sample are shown on the left side of the 2D Auger spectra plot.

Figure 4 gives a general view of the Auger data set collected on the TiO_{2-x} sample. The spectra are plotted as a function of the electron kinetic energy (horizontal scale) and for the different photon energies across the Ti-$L_{2,3}$ edges (vertical scale), the colors indicating the Auger intensity for each of these two variables. On the right side of the image, the slanting green line going from low kinetic energy at low photon energies to higher kinetic energy at higher photon energies is the Ti-$3p$ photoemission, which is mixed with the Ti-$L_{2,3}M_{2,3}V$ Auger spectra for photon energies around the L_3 edge.

Starting from the lowest photon energies, the first two yellow stains, around 407 and 414 eV kinetic energies are, respectively, the low and high kinetic energy structures of the Auger spectra visible in Fig. 2. The two structures always exists throughout the Ti-$L_{2,3}$ edges. At the L_3 edge, the low kinetic energy structure resonates mainly on the second part ($2p \rightarrow e_g$-like) of the edge (around 458 eV photon energy), while the high kinetic energy structure resonates both on the $2p \rightarrow t_{2g}$-like and $2p \rightarrow e_g$-like absorption lines. Same tendency is observed at the L_2 edge, the resonances being broader.

To obtain more quantitative results, the Ti-$L_{2,3}M_{2,3}V$ spectrum in TiO_{2-x} has been decomposed with the same procedure as in the study of the stoichiometric $\mathrm{TiO_2}$ sample.[9] To account for the changes in shape of the low kinetic energy line of the Auger spectra, this line has been decomposed into two components labeled C^* and B^*, at 408.3 eV and 410.7 eV kinetic energy, respectively (same as in the case of the

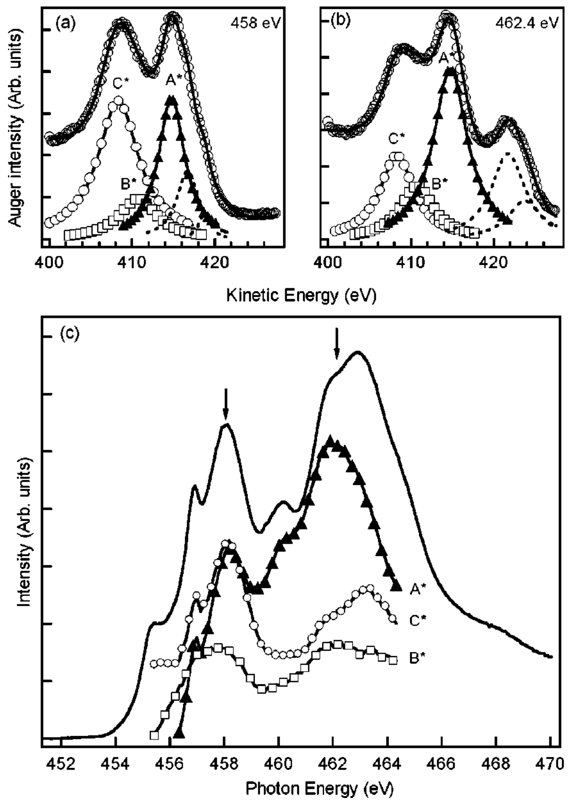

FIG. 5. Decomposition of the Ti-$L_{2,3}M_{2,3}V$ Auger spectra in TiO_{2-x}, recorded at photon energies of (a) 458 eV and (b) 462.4 eV [indicated by arrows in (c)], including the photoemission $3p$ lines (dashed line) and three Auger components at constant kinetic energies of 408.3 eV ($C*$: circles), 410.7 eV ($B*$: squares), and 414.75 eV ($A*$: triangles); (c) intensity of $A*$ (triangles), $B*$ (squares), and $C*$ (circles) through the Ti-$L_{2,3}$ thresholds (solid line).

stoichiometric sample[9]). The component labeled $A*$ at 414.75 eV stands for the high kinetic energy component of the Ti-$L_{2,3}M_{2,3}V$ spectrum (Fig. 2).

The resonance of these three lines (Fig. 5) in the L_3-edge region demonstrates that they all belong to the Ti-$L_3M_{2,3}V$ Auger transition. In particular, the $A*$ component, which appears at a kinetic energy very close to that of the $L_2M_{2,3}V$ component of the stoichiometric sample, has obviously another origin in the reduced sample. The valence-band measurements, presented in Fig. 2, allow to understand this $L_3M_{2,3}V$ Auger line shape. Together with the broad valence band, located between 4 and 10 eV binding energy (peaks V_{B*} and V_{C*}), which involves the O-$2p$ and Ti-$3d$ hybridized states, a sharp line (V_{A*}) is observed, close to the Fermi level. This line exhibits a strong resonance behavior both at the Ti-L_3 and L_2 absorption thresholds, and corresponds to the filling of the Ti-$3d$ states related to the presence of defects (see Fig. 6). The more intense resonance of this part of the valence band at the Ti-$L_{2,3}$ edges shows the higher degree of localization of these valence states on the Ti atoms. The shape of the Ti-$L_3M_{2,3}V$ Auger mimics the shape of the resonant valence band with a broad peak around 409 eV kinetic energy associated to the broad part of the valence band, and a sharper peak at a 6 eV higher kinetic energy corresponding to Ti-$3d$ defects states. Then, in this sample, the high kinetic energy component of the Auger spectrum originates at least partly, from a $L_3M_{2,3}V$(Ti) Auger decay related to the presence of oxygen vacancies.

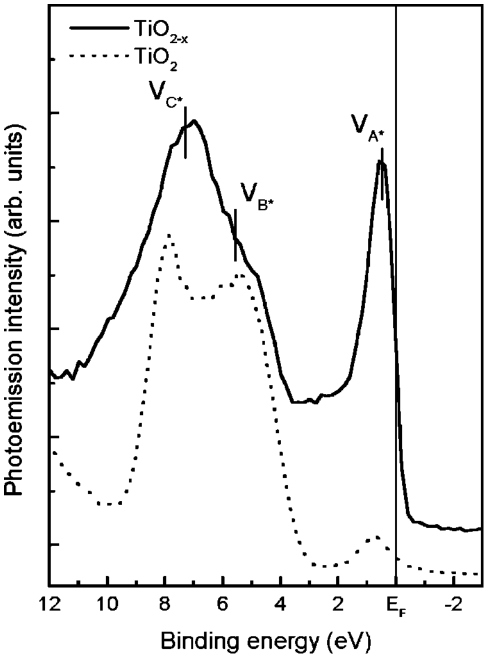

FIG. 6. Valence-band recorded at chosen photon energies in stoichiometric TiO_2 ($h\nu = 462.5$ eV, dashed line) and in TiO_{2-x} ($h\nu = 463.1$ eV, solid line).

The resonant behavior of the valence-band Ti-$3d$ feature of the reduced titanium oxide V_{A*} is displayed in Fig. 7. The intensity profile exhibits maxima at the same photon energy as the XAS spectrum, but with much higher enhancements both at 458 eV and 464 eV photon energy. This can be un-

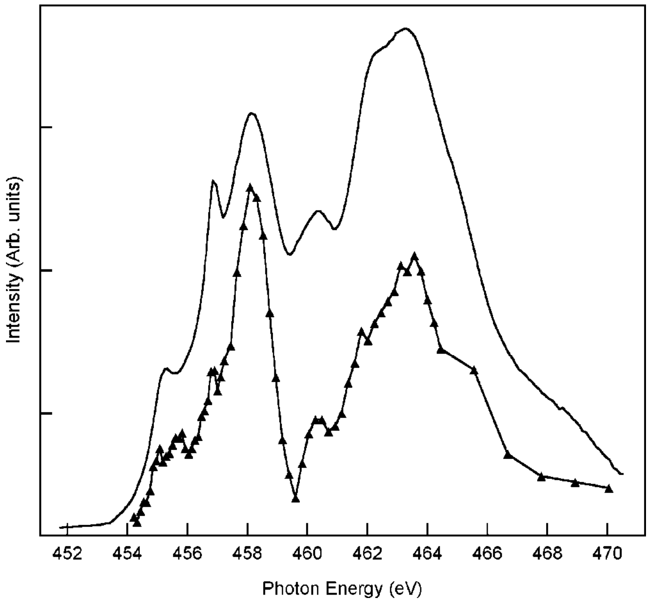

FIG. 7. Intensity of the Ti-$3d$ structure V_{A*} of the valence band (triangles) through the Ti-$L_{2,3}$ thresholds (solid line) in TiO_{2-x}.

derstood thanks to the XAS calculations presented on Fig. 3. Indeed, one of the main changes from the Ti^{4+} to the Ti^{3+} calculation is the relative increase of these two e_g-like structures, and the decrease in intensity of the t_{2g}-like components. This confirms that the resonant behavior of this peak, typically of Ti^{3+} origin, can give some indications on what would be a ‘‘site selective’’ XAS spectrum.[12]

The identification of the $L_2M_{2,3}V$ part of the Auger spectra is not straightforward. Indeed, in the L_2-edge region, the Ti-$L_{2,3}M_{2,3}V$ Auger decay can occur through three different routes. In addition to the resonant Ti-L_2MV and the nonresonant Ti-$L_3M_{2,3}V$ transition, a Ti-$L_3M_{2,3}V$ decay is expected to occur after the creation of a $2p_{3/2}$ core hole via a L_2L_3V CK process. This Ti-L_3MV transition will be labeled Ti-L_3MV(CK).

As in the case of stoichiometric TiO_2, the resonances of B^* and C^* in the L_2 region arise from Ti-L_3MV(CK) processes. Indeed, it is observed (Fig. 5) that the total intensity of B^* and C^* in the L_2 region [resonant Ti-L_3MV(CK) plus nonresonant direct Ti-L_3MV] is either equal or a little higher than that observed in the L_3 region (a similar intensity behavior has been observed in the stoichiometric rutile case[9]).

The component A^* is also expected to resonate in the L_2 region as a contribution to the Ti-L_3MV(CK) transition. In the absence of $L_2M_{2,3}V$ transitions, A^* should show a behavior similar to those of the B^* and C^* lines. The very high intensity of the A^* component [see Fig. 5(b)] suggests instead that it not only involves a Ti-L_3MV(CK) component but also, superimposed to it, a direct Ti-$L_2MV_{B^*,C^*}$ contribution, which corresponds to the V_{B^*} and V_{C^*} structures of the valence band (which are expected to appear at the same kinetic energy). Moreover, the L_2 resonant profile of A^* is much broader in energy than the B^* and C^* ones, a behavior which also supports a double origin of this resonance.

The present resonant Auger experiments clearly detect a unique L_2MV Auger line. Therefore, the triple line shape of the three-featured valence band in reduced sample should be present in the L_2MV Auger as in the L_3MV. The kinetic energy of the A^* peak, at about 414eV, corresponds to the $L_2MV_{B^*,C^*}$ line, as measured on the stoichiometric sample, and a $L_2MV_{A^*}$ line should be present at about 420 eV. However, it is not observed [see Fig. 5(b)]. Around the L_2 edge, the Ti-$3p$ photoemission peak appears at a similar kinetic energy with a quite high intensity. The presence of a $L_2M_{2,3}V_{A^*}$ component superimposed to it cannot be completely excluded. On Fig. 4, a photoemission peak shows up as a dispersive line, while an Auger peak has a nondispersive behavior. It is clear that, at the L_3 edge, at 414 eV kinetic energy, both a resonant $3p$ photoemission line and a resonant Auger structure are seen. But at the L_2 edge, at 420 eV kinetic energy, only the photoemission line seems to be present. This quasiabsence of the $L_2MV_{A^*}$ line even at resonance is observed also on metallic titanium (see next section). This demonstrates that, for titanium atoms with partially filled $3d$ levels, the very high probability of CK decay L_2L_3V transforms a $2p_{1/2}$ hole in a $2p_{3/2}$ one before the occurrence of the $L_2MV_{A^*}$ decay, so that only the $L_3MV_{A^*}$ decay is measurable.

Last, let us add two remarks on these Auger spectra recorded on the TiO_{2-x} sample. First, the Ti-L_3MV(CK) is not significantly shifted in energy with respect to the direct L_3MV transition. No screening effects are detectable in the normal Auger spectra, and this is also true in the resonant Auger spectra. The resonant lines always appear at the same kinetic energy as in the normal (off-resonance) Auger spectrum. Second, as in the stoichiometric sample, the two B^* and C^* peaks introduced in the decomposition of the Auger low kinetic energy structure reproduce the double-peak shape of the valence band. One sees clearly on Fig. 5 that C^* is always more intense than B^*, the two peaks having roughly the same intensity in the spectra recorded around 461 eV photon energy. The shape of the valence-band structure between 5 and 10 eV binding energy indicates the same intensity behavior for the corresponding V_{B^*} and V_{C^*} peaks. V_{C^*} is always more intense than V_{B^*}, which results in an asymmetric shape of the valence-band structure, except in the spectrum recorded around 461 eV photon energies (see Fig. 2) where it recovers a symmetric line shape. This more intense resonance of the high binding energy part of the valence bond is not surprising, since it was shown by calculations[20] and by recent site selective photoemission measurements[15] to be due to electronic states mostly localized on Ti atoms.

C. Auger *LMV*-Ti 2*p* coincidences in the reduced titanium oxide

To confirm these results out of the $L_{2,3}$ thresholds region, we measured the Ti-$L_{2,3}M_{2,3}V$ Auger spectrum in coincidence with Ti-$2p$ photoelectrons. This technique was already applied to stoichiometric TiO_2.[9] In this sample, the Auger electrons collected in coincidence with the $2p_{1/2}$ photoelectrons clearly contribute to the high kinetic energy part of the Auger spectrum, whereas the Auger electrons collected in coincidence with the $2p_{3/2}$ photoelectrons form the low kinetic energy part of the Auger spectrum. This confirms the attribution of these Auger structures to L_3MV and L_2MV Auger structures, respectively, as deduced from the resonant measurements.[9]

The Ti-$2p$ photoemission spectrum from the TiO_{2-x} sample is presented in Fig. 8(a). The $2p_{1/2}$ and $2p_{3/2}$ photoemission peaks are well separated. Although it is not visible with the resolution used in the coincidence experiments, the reduced titanium cations Ti^{3+} and Ti^{2+} produce an additional structure on high kinetic energy side of the main photoemission peaks which are associated to the Ti^{4+} ions.[7] The Auger-photoelectrons coincidences were first performed by setting the photoelectrons analyzers on the maximum of the $2p_{1/2}$ and $2p_{3/2}$ photoemission peaks. The results are presented on the panels 1 and 2 of Fig. 8(b), respectively. The $2p_{1/2}$ peak is superimposed to a large background arising from the $2p_{3/2}$ peak. A nonnegligible part of the signal is therefore due to coincidences with $2p_{3/2}$ photoelectrons, mixed together with the coincidences with $2p_{1/2}$. Last, the CK decay of the Ti-$2p_{1/2}$ core hole can lead to the Ti-L_3MV(CK) transition, which will be also collected in coincidence with the Ti-$2p_{1/2}$ photoemission peak. For these

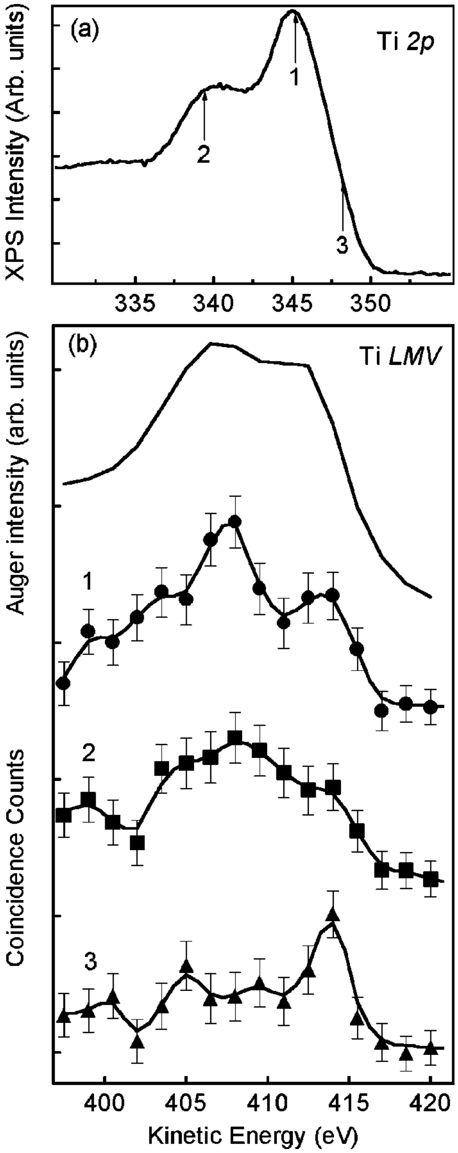

FIG. 8. (a) Ti-2p photoemission spectrum, recorded on TiO_{2-x} with the same resolution than the one used for the coincidences experiments. The arrows indicate the three kinetic energies (labeled 1, 2, and 3) chosen for these measurements. (b) (1) Auger spectrum recorded in coincidence with the $2p_{3/2}$ photoelectrons [kinetic energy 1 in (a)] (circles); (2) Auger spectrum recorded in coincidence with the $2p_{1/2}$ photoelectrons [kinetic energy 2 (a)] (squares); (3) Auger spectrum recorded in coincidence with the photoelectrons detected on the high kinetic energy side of the $2p_{3/2}$ peak [kinetic energy 3 in (a)] (triangles). All the coincidences measurements were done at a photon energy of 806 eV, far above the Ti-2p edges. The Auger spectrum recorded at the same photon energy is also shown (solid line).

reasons, the Auger spectrum recorded in coincidence with the Ti-$2p_{1/2}$ photoemission cannot be simply understood. On the contrary, the Auger spectrum collected in coincidence with the Ti-$2p_{3/2}$ emission can be safely interpreted as the Ti-L_3MV transition. Coherently with the conclusions drawn from the resonant experiments, it involves two main structures at 408 and 414 eV [Fig. 8(b)]. Next, we did another Auger measurement in coincidence with the high kinetic energy part of the $2p_{3/2}$ peak (labeled kinetic energy 3 on top of Fig. 8) which, as explained above, is due to cations with oxidation degrees of three and less. The coincidence spectrum is dominated by a unique decay structure around 414 eV which demonstrates that it mostly involves the Ti-3d states of the valence band.

D. Auger line shape in metallic titanium

The intensity of the main peak of the Ti-$L_{2,3}M_{2,3}V$ Auger decay recorded on the metallic titanium across the Ti-$L_{2,3}$ edges mostly follows the absorption edge profile, around both the L_3 and the L_2 edges (Fig. 2). When the photon energy reaches the L_2 edge, the only notable change in the Auger spectra is the appearance of a small peak at 420.4 eV kinetic energy, therefore attributed to the Ti-L_2MV decay (see Fig. 2). The very weak intensity of this L_2MV decay, which is only visible in resonance, is the most striking result of this metallic titanium study. It demonstrates the occurrence of a giant CK decay channel, which almost cancels the L_2MV Auger decay probabilities of the Ti-$2p_{1/2}$ core hole. This is, of course, of key importance to understand the off-resonance Ti-$L_{2,3}M_{2,3}V$ Auger profile which has to be seen only as a set of L_3MV Auger lines. As a matter of fact, the importance of CK decay channel certainly strongly varies with the filling of the d states through the 3d series. The width of the L_2 absorption thresholds gives an indication on the $2p_{1/2}$ core hole lifetime. Indeed, it increases notably from calcium to manganese (see, e.g., Fink *et al.*[21]), denoting a more and more shorter lifetime. Since the lifetime is limited by the fast CK process, this might be explained by an increasing CK probability while filling the 3d levels.

Hence, the Ti-$L_{2,3}M_{2,3}V$ Auger decay in metallic Ti consists in an apparently unique L_3MV line, appearing at the same kinetic energy position as the $L_2M_{2,3}V$ Auger decay in stoichiometric TiO_2. It has long been misinterpreted as the final state of a gradual evolution from a mostly interatomic to a completely intra-atomic Auger process. In fact, our comprehensive study on a complete set of samples shows that the explanation of this evolution is not as straightforfward. It should account for both the evolution of the valence band and CK processes.

V. CONCLUSION

Much information on the electronic structure can be found in Auger spectra. In this paper, we have presented a complete study of the Ti-LMV Auger decay in a series of Ti compounds with various degrees of oxidation of the Ti atoms. The evolution of this Auger decay with the chemical nature of Ti shows the richness of such spectroscopic fingerprint, especially when it involves the valence-band states. The two main lines of this Auger spectrum were previously assigned to $L_{2,3}M_{2,3}V(\mathrm{O})$ and $L_{2,3}M_{2,3}V(\mathrm{Ti})$ decay, where $V(\mathrm{O})$ and $V(\mathrm{Ti})$ refer, respectively, to O and Ti electronic states of the valence band. In stoichiometric TiO_2, this picture is not correct, and both our resonant Auger and Auger-photoelectrons coincidences measurements show that these lines should rather be attributed to $L_3M_{2,3}V$ and $L_2M_{2,3}V$ decays, respectively.

In a TiO$_{2-x}$ sample, some Ti-3d states are populated, and they appear in resonant valence-band spectra as an intense line below the Fermi level in addition to the main O$(2p)$-Ti $(3d)$ structure. Using the combined results of resonant Auger, resonant valence band and Auger-photoelectrons coincidence measurements, we have established that the Ti-$L_3M_{2,3}V$ is made up of two lines, reflecting the shape of the valence band with this additional 3d structure. A crucial observation is that the $L_2M_{2,3}V$ Auger lines are located at the same kinetic energy position as the high kinetic energy $L_3M_{2,3}V$ peak, since the Ti-2p spin-orbit splitting is nearly equal to the splitting between the two structures of the valence band. This explains that the apparently change in shape of the LMV Auger spectrum is in fact due to several independent phenomena. For these two samples, complete calculations are mandatory to explain the simple single line shape of the $L_2M_{2,3}V$, which, contrary to the $L_3M_{2,3}V$, seems not to mimic the structure of the valence band. Last, the metallic Ti conduction band is only constituted from the Ti-3d states at the Fermi level, and this gives rise to a single line in the Ti L_3MV Auger decay, located at the same kinetic energy position as the $L_3M_{2,3}V$ high energy peak in the TiO$_{2-x}$ sample. This is not surprising, since they involve exactly the same Ti electronic $2p$, $3p$ and $3d$ levels. In metallic Ti, the $L_2M_{2,3}V$ Auger decay is always very weak, and it is only hardly visible on-resonance, for photon energies around the maximum of the Ti-L_2 edge. In the normal off-resonance Auger spectrum, it is completely smoothed out by fast L_2L_3V CK processes.

The CK probability increases as the 3d states just below the Fermi level are filled, until having such drastic effects on the metallic Ti-$L_{2,3}M_{2,3}V$ Auger decay. It is necessary to introduce such processes to fully understand all the results obtained in the series of titanium oxides studied here. In metallic Ti, the absence of any $L_2M_{2,3}V$ line and the accidental occurrence of the $L_3M_{2,3}V$ Auger line at the same kinetic energy as the $L_2M_{2,3}V$ Auger decay in stoichiometric TiO$_2$ have led to an incorrect interpretation of the evolution of the $L_{2,3}M_{2,3}V$ Auger spectrum through the series of compounds. This could give the impression that the metallic Ti-LMV Auger spectrum is in line with an evolution started from TiO$_2$ and reduced TiO$_2$. Actually, it is not at all the result of a unique parameter which would vary continuously. These evolutions arise from (i) the change in the population of the valence band, especially the filling of the Ti-3d states, and (ii) the drastic increase of the probability of the L_2L_3V Coster-Kronig decay processes which leads to a parallel decrease in intensity of the $L_2M_{2,3}V$ transitions.

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