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Electronic structure of titania aerogels: Soft x-ray absorption study

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The electronic structure of TiO₂ aerogels is studied by soft x-ray absorption near-edge structure (XANES) spectroscopy. High-resolution O *K*-edge and Ti *L*_{2,3}-edge XANES spectra of aerogels are compared with those of rutile, anatase, and unrelaxed amorphous phases of full-density TiO₂. Results show that all the main spectroscopic features of aerogels, reflecting the element-specific partial density of empty electronic states and correlation effects, can be attributed to the absence of long-range order in stoichiometric amorphous TiO₂. Based on these results, we discuss the effects of short- and long-range order on the electronic structure of TiO₂.

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I. INTRODUCTION

Titanium dioxide (TiO₂) is currently the most studied single-crystal transition metal oxide in the field of surface science.¹ Significant research interest in TiO₂ has been fueled by its numerous technological applications, including heterogeneous catalysis, solar cells, optical and corrosion coatings, gas sensors, varistors, and pigments in paints and cosmetic products.¹ Several polymorphic forms of TiO₂ crystals can exist at ambient conditions, with tetragonal rutile and anatase being the most common phases. A stoichiometric amorphous phase of TiO₂ can also be stabilized at ambient conditions. Recently, various forms of nanostructured TiO₂, such as nanoparticles, xerogels, and aerogels, have been synthesized and have attracted significant research interest.^{1,2} Our interest in this work is focused on a somewhat extreme form of *nanoporous titania* — TiO₂ aerogels, which are open-cell solid foams derived from highly cross-linked gels by drying them under supercritical conditions.² Titania aerogels are typically characterized by a high degree of porosity, with ultrafine (nanometer size) cells/pores.²⁻⁴

Since many applications of TiO₂ are based on the specific surface and/or bulk electronic properties, numerous previous studies have been focused on understanding electronic structure of different forms of titania.¹ In particular, x-ray absorption near-edge structure (XANES) spectroscopy and electron energy loss spectroscopy (EELS) have been used to probe element-specific partial density of empty electronic states in different polymorphs of full-density TiO₂.¹ However, as will be discussed in detail below, physical mechanisms responsible for the difference in XANES spectra of different polymorphs of TiO₂ are still not well understood.

Recently, Ti *K*-edge XANES has also been applied to study TiO₂ xerogels.⁵⁻⁷ Such Ti *K*-edge studies of TiO₂ are typically focused on the analysis of relatively broad, low-intensity pre-edge peaks, which are assumed to be related to the crystal field symmetry around Ti atoms. There are still debates regarding assignment of these pre-edge features in Ti *K*-edge XANES spectra to particular core-level electron transitions.⁵⁻⁷ In contrast, the Ti

*L*_{2,3}-edge features (in the soft x-ray regime) are typically much better resolved and significantly more sensitive to the local bonding configurations (reflecting the valency of Ti and the geometry of its surroundings) than the Ti *K*-edge features.¹ However, we are not aware of previous Ti *L*_{2,3}-edge XANES studies of titania xerogels or any previous XANES studies of titania aerogels. Hence, in this paper, we present a high-resolution XANES study of titania aerogels and compare results with those for rutile, anatase, and amorphous phases of full-density TiO₂. We show that all the main spectroscopic features of aerogels can be attributed to the absence of long-range order in stoichiometric amorphous TiO₂ (*a*-TiO₂). We also show that some features of Ti *L*_{2,3}-edge XANES spectra which have previously been assigned to effects of oxide reduction^{1,8-10} can be attributed to the absence of long-range order in stoichiometric *a*-TiO₂ and are indicative of the presence of an amorphous phase.

II. EXPERIMENTAL

The following samples were investigated in this study: two titania aerogels with average densities of 180 and 370 mg/cm³ (i.e., ~ 4 and 9% of the full density); rutile, and anatase powders (with grain sizes $\gtrsim 5\mu\text{m}$) purchased from Sigma-Aldrich Corp.; and (001)-oriented rutile single crystals obtained from Princeton Scientific Corp.

A. Aerogel synthesis and structural characterization

The TiO₂ aerogels were prepared by a two-step sol-gel process that involved acid-catalyzed hydrolysis of titanium ethoxide [Ti(OEt)₄], followed by base-initiated gelation of the titania species. In a typical synthesis, titanium ethoxide (7.0 g, 31 mmol) was dissolved in absolute ethanol (25 mL), and the solution was chilled in an ice bath with vigorous stirring. When cool, the reaction solution was treated with hydrochloric acid (37%, 0.5 mL) and then distilled water (0.6 mL). After five min-

utes, propylene oxide (2.5 g, 43 mmol) was added to the solution. The reaction mixture was stirred for an additional five minutes, then transferred to glass molds, and, within 2 hours, translucent white alcogels formed. The titania alcogels were allowed to age at room temperature for 72 h, before being dried in a PolaronTM critical point extractor. The ethanol in the pores of the wet gels was exchanged with liquid CO₂ for 3–4 days, after which time, the temperature was ramped up to ~ 45 °C, while maintaining a pressure of ~ 100 bars. The autoclave was then depressurized at a rate of ~ 7 bar/h, affording the titania aerogels as opaque white monoliths.

The bulk densities of the aerogels were determined by measuring the dimensions and mass of monolithic samples. The microstructure of aerogels was studied by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (TEM). The TEM analysis was performed in a Philips CM300FEG transmission electron microscope operating at 300 kV using zero loss energy filtering with a Gatan energy imaging filter to remove inelastic scattering. The TEM images were taken under bright-field (BF) conditions and slightly defocussed to increase contrast.

B. Preparation of amorphous TiO₂

A sample of full-density *a*-TiO₂ was prepared by bombardment of a (001)-oriented rutile single crystal at 77 K with 340 keV ¹³²Xe²⁺ ions to a dose of 1.5×10^{15} cm⁻² with a beam flux of $\sim 2 \times 10^{12}$ cm⁻² s⁻¹. During bombardment, the sample was tilted by $\sim 7^\circ$ relative to the incident ion beam to minimize channeling. Previous studies^{11–13} have shown that bombardment under such conditions results in the formation of a continuous surface amorphous layer. Our Rutherford backscattering/channeling spectrometry analysis at LLNL (with 2 MeV ⁴He ions) suggested that the thickness of the surface amorphous layer in the implanted rutile sample was ~ 200 Å. The as-implanted sample was not subjected to any high-temperature processing, and stoichiometrical changes due to ion-beam-induced (preferential) sputtering were negligible for such a relatively low ion dose (1.5×10^{15} cm⁻²).^{14,15} Hence, the ~ 200 -Å-thick surface layer in this sample is composed of *unrelaxed stoichiometric a*-TiO₂.^{16,17}

C. X-ray absorption

The XANES experiments were performed at undulator beamline 8.0 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. Details of the beamline have been published elsewhere.¹⁸ Aerogels and TiO₂ powders were pressed into an indium metal foil and mounted on the sample holder. All spectra presented in this paper were obtained by measuring the total electron yield (TEY), by monitoring the total sample photocur-

rent, as a function of photon energy scanned through O *K*- and Ti *L*_{2,3}-edges. It should be noted that measurements in the total fluorescence yield (TFY) mode revealed the same spectral features for all the samples studied (but with the expected worse signal-to-noise ratio). All absorption measurements were performed at room temperature. The incoming radiation flux was monitored by the total photocurrent produced in a clean Au mesh inserted into the beam. The overall experimental resolution around the Ti *L*_{2,3}-edge was ~ 150 meV. The monochromator was calibrated by aligning the Ti *L*₃- and O *K*-edges of a rutile single crystal according to the EELS values reported by Brydson et al.¹⁹ After a background subtraction, all spectra were normalized to the post-edge step heights. To extract peak positions, each spectrum was fitted with a set of Lorentzian functions with a linear background.²⁰

III. RESULTS AND DISCUSSION

A. Microstructure of aerogels

Before the XANES study, the morphology of the two titania aerogels was studied by XRD and TEM. Our XRD analysis showed that both aerogels were fully amorphous, with no evidence for the presence of either rutile or anatase phase. The morphology of aerogels was further characterized by TEM. Figure 1(a) shows a BF TEM image illustrating how irregular TiO₂ particles of ~ 10 – 20 nm in size are interconnected to form a treelike structure of the aerogel. In agreement with XRD results, our selected-area diffraction analysis has confirmed that the aerogels are fully amorphous. The amorphous structure of the aerogel can also be seen in a high-resolution image in Fig. 1(b). It should be noted that the morphology of amorphous aerogels studied in this paper (see Fig. 1) is rather different from that reported previously in Ref. 3 and 4. Indeed, TiO₂ aerogels synthesized by Zhu et al.³ consisted of ~ 5 nm anatase particles closely packed into mesoaggregates ~ 30 nm in size, whereas those reported by Masson et al.⁴ were composed of faceted anatase particles ~ 30 nm in size. Such a difference in the structure and morphology (and, hence, the properties) of titania aerogels reported in different studies can be attributed to differences in conditions of aerogel synthesis.

B. Soft x-ray absorption

It should be noted that peak positions in both Ti and O edge XANES spectra were almost identical for the two aerogels studied. Likewise, no significant difference was found between peak positions in rutile spectra for powders and single crystals. Hence, for brevity, in this paper, we show spectra for only one aerogel (with a density of 370 mg/cm³) and single-crystal rutile.

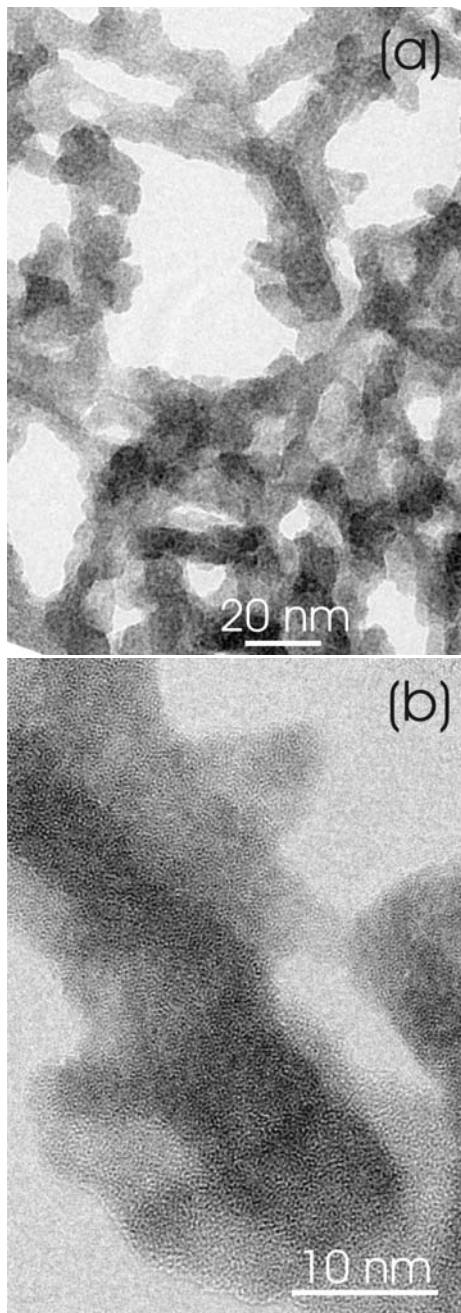


FIG. 1: High-resolution TEM images of a titania aerogel (with a density of 180 mg/cm^3) at different magnifications.

1. Oxygen *K*-edge

Figure 2 gives a comparison of O *K*-edge XANES spectra of rutile, anatase, *a*-TiO₂, and an aerogel. Spectra of rutile and anatase, shown in Fig. 2, are in general agreement with results of a number of previous XANES and EELS studies.^{1,8–10,19,21–24} It is seen from Fig. 2 that, for all the TiO₂ polymorphs studied, spectra exhibit two main peaks centered on ~ 531 and 534 eV (labelled C_O and E_O, whose positions are given in Table I) with an

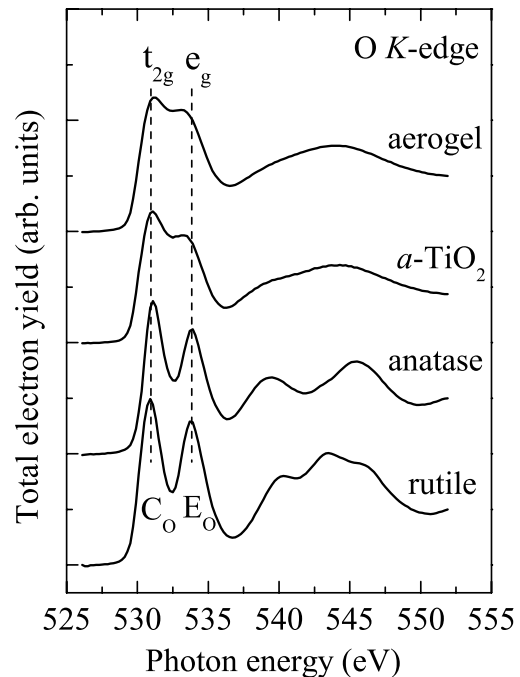


FIG. 2: Oxygen *K*-edge XANES spectra of rutile, anatase, amorphous TiO₂ (*a*-TiO₂), and a titania aerogel.

additional structure at higher energies. A slight shift of peak C_O to larger energies (by ~ 0.2 eV) in anatase as compared to the case of rutile can be seen from Fig. 2 and Table I, which could be attributed to a larger bandgap¹ of anatase (3.2 eV) as compared to that of rutile (3.0 eV).

Figure 2 and Table I also show that spectra of *a*-TiO₂ and an aerogel are very similar, suggesting that the (electronic) structure of the titania aerogels studied in this work is similar to that of stoichiometric *a*-TiO₂. All the peaks in spectra of an aerogel and *a*-TiO₂ are broadened as compared to the case of rutile (single-crystal and powder) and anatase (powder). Such an inhomogeneous broadening, due to slight variations in bond lengths and angles, is inherent to spectra from amorphous solids. A significant decrease in the distance between C_O and E_O peaks from ~ 3.0 to 2.3 eV upon amorphization can also be seen from Fig. 2 and Table I. Note that such a decrease is caused by the shift of peak E_O to lower energies, while, for both *a*-TiO₂ and an aerogel, peak C_O is at the same energy as for rutile.

Previous electronic band structure calculations have shown that O *K*-edge XANES and EELS spectra of rutile and anatase can be well explained with single-electron approximation models.²² These spectra essentially map the O 2p-projected density of empty states in TiO₂.²² Correlation effects appear to have a negligible influence

TABLE I: Peak positions (in eV) in O K -edge and Ti $L_{2,3}$ -edge XANES spectra, as labelled in Figs. 2–4.

	C _O	E _O	A	B	C ₃	D ₃	E ₃	C ₂	D ₂	E ₂	F ₃	G ₃	F ₂	G ₂
Rutile	530.9	533.9	456.6	457.3	458.2	460.0	461.1	463.8	465.7	466.5	471.4	473.3	477.0	479.2
Anatase	531.1	533.9	456.7	457.4	458.3	460.1	461.0	463.8	465.9	466.7	471.6	473.6	477.1	479.2
α -TiO ₂	530.9	533.2	456.6	457.4	458.2	459.8	460.6	463.7	465.6	466.3	471.0	472.7	476.8	478.6
Aerogel	530.9	533.1	456.6	457.4	458.2	459.8	460.6	463.7	465.6	466.6	471.1	472.9	476.7	478.5

on the O K -edge spectra since O 2p states are hybridized and relatively delocalized, resulting in their weak interaction with the O 1s core hole (i.e., a reduced screening of the electric field from the nucleus due to the absence of the electron at the core level).

In the molecular orbital (MO) picture of TiO₂,^{19,21,22,25} the bonding between Ti 4sp and O 2p orbitals forms the (mostly O 2p-derived) valence band. The conduction band, which is probed in XANES experiments, is formed by antibonding Ti 3d, 4s, and 4p and O 2p orbitals. In addition, the crystal field of the surrounding O atoms splits the Ti 3d band into t_{2g} (formed by d_{xy} , d_{xz} , and d_{yz} orbitals) and e_g (formed by $d_{x^2-y^2}$ and d_{z^2} orbitals) sub-bands. Since the Ti e_g orbitals point directly toward the 2p orbitals of the surrounding O atoms, the e_g band is very sensitive to the local environment. The e_g -related peaks are also expected to be broader than the t_{2g} peaks due to a larger degree of hybridization of the Ti e_g orbitals with O ligands and associated effects of solid-state broadening, which has been discussed in detail in Ref. 22.

Within the MO picture, the two main peaks C_O and E_O in Fig. 2 can be attributed to the excitation from the O 1s core level into the t_{2g} and e_g bands, respectively, and peaks at higher energies are due to transitions into antibonding O 2p and Ti 4sp-related bands.^{19,21,22,25} The ligand-field splitting can be estimated from the energy difference between the t_{2g} and e_g features in O K -edge spectra,²² giving ~ 3.0 and 2.8 eV for rutile and anatase, respectively. Table I also shows that the ligand-field splitting is further reduced to ~ 2.3 eV in α -TiO₂ and an aerogel, which is caused by a shift in the position of the e_g related peak E_O. This is consistent with the fact that the e_g orbitals are more sensitive to the local environment than the t_{2g} orbitals, and we will come back to this effect in the next section.

2. Titanium $L_{2,3}$ -edge

Figure 3 compares high-resolution Ti $L_{2,3}$ -edge XANES spectra of a titania aerogel and different TiO₂ polymorphs. In contrast to the O K -edge spectra discussed above, Ti $L_{2,3}$ -edge spectra, reflecting transitions of Ti 2p core electrons into Ti 3d states in the conduction band, show a considerably more complex behavior. Such complexity arises from correlation effects (which are described beyond the independent electron approximation).

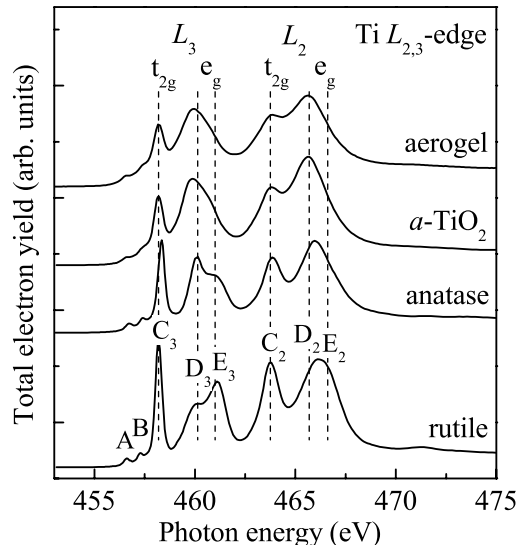


FIG. 3: Titanium $L_{2,3}$ -edge XANES spectra of rutile, anatase, amorphous TiO₂ (α -TiO₂), and a titania aerogel. See Table I for the positions of the peaks labelled.

Indeed, atomic multiplet calculations of de Groot et al.²⁶ have suggested that the multiplet structure, discussed below, is mainly due to strong Coulomb interactions between poorly screened Ti 3d electrons and the Ti 2p core hole.

In Fig. 3, peaks for all TiO₂ polymorphs are split into two groups, separated by ~ 5.5 eV, due to the spin-orbit coupling of Ti 2p core electrons, giving rise to L_2 and L_3 edges. The L_2 -edge features are broadened compared to those of the L_3 edge, owing to the increased Coster-Kronig Auger decay channel for the L_2 -edge (i.e., a shorter lifetime of the $2p_{1/2}$ core hole due to a radiationless electron transition from the $2p_{3/2}$ to the $2p_{1/2}$ level, accompanied by the promotion of a valence electron into the conduction band). For both L_2 and L_3 edges, the crystal field splits the 3d band into t_{2g} and e_g sub-bands, as discussed in Sec. III B 1. As in the case of O K -edge spectra in Fig. 2, the t_{2g} -related peaks C₂ and C₃ for anatase in Fig. 3 are slightly shifted to higher energies

as compared to cases of rutile, α -TiO₂, and an aerogel. Such a shift (which has often been overlooked in previous XANES and EELS studies due to insufficient experimental resolution) could be attributed to the difference in bandgaps of rutile and anatase. It should also be noted that, according to calculations of de Groot et al.,^{22,26} the distance between t_{2g} and e_g related peaks in Ti $L_{2,3}$ -edge spectra does not represent the crystal field splitting since these spectra are strongly affected by correlation effects.

Figure 3 also shows that, for all TiO₂ polymorphs, the e_g -related peak of the L_3 -edge is further split into two peaks, labelled D₃ and E₃. A similar splitting of the e_g band (into D₂ and E₂ peaks) also occurs for the L_2 -edge, although it is not well resolved due to the lifetime-related broadening of the L_2 -edge. Indeed, Fig. 3 clearly shows that an increase in the D₃/E₃ intensity ratio in transition from rutile to anatase to α -TiO₂/aerogel is followed by a shift of the broad L_2 -edge e_g peak to lower energies. This is consistent with the scenario when the e_g band of the L_2 -edge is composed of two peaks (D₂ and E₂), whose intensities follow the intensities of better resolved D₃ and E₃ peaks. This is also supported by results of our peak deconvolution/fitting (see Table I).

According to atomic multiplet calculations of de Groot et al.²⁶ for rutile and anatase, low-intensity peaks A and B in Fig. 3, mixed into the L_3 -edge and weakly affected by ligand field, are a result of the strong interaction between poorly screened 3d electrons and the 2p core hole. However, recent band structure calculations by Finkelstein et al.²⁸ suggest that these pre-edge peaks A and B can also be attributed to sharp features in the (one-electron) Ti 3d partial density of states, while the widths and intensities of these peaks are modified by correlation effects. Hence, additional theoretical studies are presently needed to better understand the origin of these pre-edge peaks A and B.

Figure 3 and Table I show that, as in the case of the O K -edge spectra discussed above, Ti $L_{2,3}$ -edge spectra of an aerogel and α -TiO₂ are very similar. It is also seen from Fig. 3 that, upon amorphization, in addition to the expected broadening of all peaks, the intensity of peaks E₂ and E₃ is largely reduced, and the e_g band for both L_2 and L_3 edges is dominated by D₂ and D₃ peaks, which are also slightly shifted to lower energies. This results in significant overall shifts of the broad L_2 -edge e_g -related peak to lower energies for α -TiO₂ and an aerogel. Figure 3 and Table I also show that the positions of t_{2g} -related peaks A, B, and C in an aerogel and α -TiO₂ are close to those in rutile rather than in anatase.

Figure 4 shows the higher-energy region of Ti $L_{2,3}$ -edge XANES spectra of different TiO₂ polymorphs after the subtraction of the contribution from Lorentzian D₂ and E₂ peaks.²⁹ Peaks in Fig. 4 are split into two groups (labelled F₃, G₃ and F₂, G₂ and given in Table I), separated by ~ 5.5 eV, suggesting that these are due to transitions from the 2p_{3/2} (L_3 -edge) and 2p_{1/2} (L_2 -edge) core levels. It is seen from Fig. 4 that, in the amorphous phase (spectra c and d), all four peaks appear to be present but are

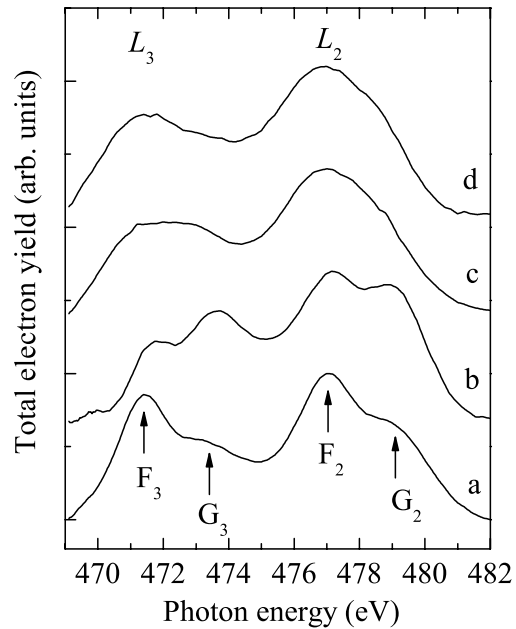


FIG. 4: High-energy region of Ti $L_{2,3}$ -edge XANES spectra of rutile (a), anatase (b), amorphous TiO₂ (c), and an aerogel (d). The curves were obtained by a background subtraction from $L_{2,3}$ -edge XANES spectra such as shown in Fig. 3.

broadened, which makes a more detailed peak analysis rather challenging. Within the MO approach,^{19,25} this higher-energy structure, which is ~ 13.3 eV above the first major peaks of the Ti $L_{2,3}$ -edge (peaks C₂ and C₃ in Fig. 3), can be attributed to a transition from the Ti 2p core levels to t_{1u} -type orbitals of rutile and anatase. One-electron calculations of Finkelstein et al.²⁸ for rutile have suggested (although not totally convincingly) that these peaks could be attributed to some features of the Ti 3d density of states. An alternative (and even more speculative) explanation, proposed over a decade ago by van der Laan,²⁴ is that these higher-energy peaks for rutile and anatase are a result of a polaronic-type transition of an electron from the valence band to the conduction band, accompanying the core-level x-ray absorption process. It is clear that, at present, additional theoretical work is needed to better understand the origin of these higher-energy $L_{2,3}$ -edge peaks in TiO₂ polymorphs.

Figure 3 and Table I have shown that the major difference between Ti $L_{2,3}$ -edge spectra of amorphous and crystalline phases of TiO₂ is a significant change in positions, intensities, and widths of e_g -related peaks D and E. Therefore, we discuss the splitting of the e_g -related band in more detail below. Different physical mechanisms have previously been proposed to explain the splitting of the

e_g band (into D and E peaks) in Ti $L_{2,3}$ -edge spectra of rutile and anatase. In atomic multiplet calculations of de Groot et al.,²⁶ this splitting has been produced by a distortion of the symmetry around Ti atoms from the perfect O_h (octahedral) to D_{2h} and D_{2d} by an amount to fit experimental XANES spectra for rutile and anatase, respectively. However, this concept has seriously been questioned by Crocombette and Jollet,³⁰ who, by taking into account the exact positions of O atoms in the first-neighbor shell of Ti, have demonstrated that the amount of lattice distortion used by de Groot et al.²⁶ is unrealistic.

In an alternative explanation proposed by Brydson et al.¹⁹, the splitting of the e_g band may be attributed to the *dynamic Jahn-Teller effect* (due to the coupling of the electronic and vibrational states). However, the actual values of the splitting observed in optical absorption experiments of Ti^{3+} ions in the octahedral environment in different systems and attributed to the Jahn-Teller effect are much smaller than the relatively large separation (~ 1 eV) of peaks D and E in Fig. 3. For example, the splitting of the e_g doublet measured by optical absorption in the $Al_2O_3:Ti^{3+}$ system is ~ 0.3 eV at 300 K.³¹ Moreover, the splitting due to the Jahn-Teller effect has a characteristic temperature dependence: it decreases with decreasing temperature. By analogy with the $Al_2O_3:Ti^{3+}$ system,³¹ the splitting of the e_g -related peak in XANES spectra would be expected to decrease by $\sim 50\%$ with decreasing sample temperature from 300 K to 77 K if it were due to the Jahn-Teller effect. In contrast, our XANES study of rutile (single-crystal) and anatase (powders) reveals a negligible change in positions of D and E peaks upon decreasing sample temperature to 77 K. This strongly suggests that the Jahn-Teller effect is not a major contributor to the splitting of the e_g -related band in Ti $L_{2,3}$ -edge XANES spectra of TiO_2 polymorphs.

Another explanation for the e_g band splitting has recently been given by Finkelstein et al.²⁸ based on their band structure calculations, suggesting that the splitting of the e_g band in rutile could simply be related to the particular shape of the Ti 3d partial density of states. This could also be inferred from the partial density of states related to the e_g subband of *rutile* calculated earlier by Munnix and Schmeits³² using a tight-binding method. However, only rutile has been studied in Refs. 28 and 32, and rather different densities of states for rutile (and anatase) have been predicted by other calculations (see, for example, Refs. 22,33–35). Hence, attributing difference in the e_g band splitting in different polymorphs of TiO_2 to variations in the (one-electron) partial density of states should currently await further theoretical studies.

Finally, the splitting of the e_g band can also be attributed to effects of long-range order, and in particular, to the influence of the interactions of Ti with the

second-neighbor shell.^{19,30} This mechanism seems to be supported by results of the present study, showing that significant changes occur to XANES spectra as a result of amorphization (i.e., loss of long-range order). It is also interesting to note that, although the Ti $L_{2,3}$ -edge spectra of *a-TiO₂/aerogel* are significantly different from those of both rutile and anatase, the e_g -related peaks in spectra of *a-TiO₂/aerogel* are more similar to those of anatase rather than rutile. This could be attributed to the fact that, according to previous extended x-ray absorption fine structure (EXAFS) studies,^{5–7,36,37} the local atomic arrangement in amorphous titania is similar to that in anatase rather than in rutile (particularly for the second coordination shell). Although this supports the importance of longer-range order in the interpretation of XANES spectra of TiO_2 polymorphs, additional (quantitative) theoretical studies are desirable to better understand the effect of long-range order on the electronic structure of titania.

IV. CONCLUSIONS

In conclusion, we have studied the electronic structure of amorphous TiO_2 aerogels by high-resolution soft x-ray absorption spectroscopy around O K - and Ti $L_{2,3}$ -edges. The main conclusions of this work can be summarized as follows.

(i) All the main spectroscopic features of amorphous aerogels are the same as those of full-density amorphous TiO_2 . Hence, these spectroscopic features are indicative of the absence of long-range order in TiO_2 . It is not necessary to invoke oxide reduction, as has previously been done to interpret similar features in XANES spectra of full-density titania.^{1,8–10}

(ii) The local order in amorphous TiO_2 , which can be conveniently probed by soft x-ray absorption, is more similar to that in anatase rather than in rutile.

(iii) The splitting of the e_g -related band in Ti $L_{2,3}$ -edge XANES spectra of TiO_2 polymorphs is attributed to effects of long-range order. However, additional (quantitative) theoretical studies are currently needed to support this assignment as well as to explain the appearance of high-energy peaks in Ti $L_{2,3}$ -edge XANES spectra of TiO_2 polymorphs.

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