Local chemical bonding and structural properties in Ti$_3$AlC$_2$ MAX phase and Ti$_3$C$_2T_x$ MXene probed by Ti 1s x-ray absorption spectroscopy

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The chemical bonding within the transition-metal carbide materials MAX phase Ti$_3$AlC$_2$ and MXene Ti$_3$C$_2T_x$ is investigated by x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine-structure (EXAFS) spectroscopies. MAX phases are inherently nanolaminated materials that consist of alternating layers of $M_{n+1}X_n$ and monolayers of an $A$-element from the IIIA or IVA group in the Periodic Table, where $M$ is a transition metal and $X$ is either carbon or nitrogen. Replacing the $A$-element with surface termination species $T_x$ will separate the $M_{n+1}X_n$-layers forming two-dimensional (2D) flakes of $M_{n+1}X_nT_x$. For Ti$_3$C$_2T_x$ the $T_x$ corresponds to fluorine (F) and oxygen (O) covering both sides of every single 2D $M_{n+1}X_n$-flake. The K-edge (1s) XANES of both Ti$_3$AlC$_2$ and Ti$_3$C$_2T_x$ exhibit characteristic preedge absorption regions of C 2p-Ti 3d hybridization with clear crystal-field splitting while the main-edge absorption features originate from the Ti 1s $\rightarrow$ 4p excitation, where only the latter shows sensitivity toward the fcc-site occupation of the termination species. The coordination numbers obtained from EXAFS show that Ti$_3$AlC$_2$ and Ti$_3$C$_2T_x$ are highly anisotropic with a strong in-plane contribution for Ti and with a dynamic out-of-plane contribution from the Al monolayers and termination species, respectively. As shown in the temperature-dependent measurements, the O contribution shifts to shorter bond length while the F diminishes as the temperature is raised from room temperature up to 750°C.

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I. INTRODUCTION

Despite the large interest in graphene [1], which lacks a natural band gap, it has been difficult to artificially produce graphene-based materials with suitable band gaps. This has encouraged researchers to explore other two-dimensional (2D) materials such as hexagonal boron nitride (h-BN), molybdenum disulfide (MoS$_2$), tungsten disulfide (WS$_2$), and MXenes ($M_{n+1}X_nT_x$). The last example is also the latest 2D material, developed in the past decade, and it consists of a family of 2D transition-metal carbides denoted $M_{n+1}X_nT_x$($n$ = 1, 2, 3), where $M$ is a transition metal, $X$ is either carbon or nitrogen, and $T_x$ denotes surface termination species [2–4]. The layered structures contain more than one element, thus they offer properties that may be useful for transistors and spintronic devices [5], 2D-based electronics and screens [6], in addition to energy storage systems such as supercapacitors [7], Li-ion batteries [8], fuel and solar cells [9], as well as transparent conductive electrodes [10] and composite materials with high strength [11].

The parent precursor compounds of MXenes are inherently nanolaminated materials known as MAX phases ($M_{n+1}AX_n$, $n$ = 1, 2, 3) [12] (space group $P6_3/mmc$), where A is a p-element that usually belongs to groups IIIA or IVA in the Periodic Table. These phases contain more than 150 variants [13], including Ti$_3$AlC$_2$, which is a precursor for the Ti$_3$C$_2T_x$ MXene. To make MXene from $M_{n+1}AX_n$, the weakly bound A-layers are etched away and replaced by surface termination groups ($T_x$) in the exfoliation process [2]. The delamination results in weakly bound stacks of 2D sheets with $M_{n+1}X_nT_x$ composition.

Generally, MXenes consist of a core of a few atoms thick 2D $M_{n+1}X_n$ conductive carbide layer that is crystalline in the basal plane and a transition-metal surface that can be functionalized for different material properties by changing the chemistry of the termination species. Layered structures like MXenes contain more than one element and can therefore offer better variations of physical properties than pure materials, such as graphene, since they can provide a larger number of compositional variables that can be tuned for specific properties. Figure 1 shows schematic side views of the Ti$_3$AlC$_2$, Ti$_3$C$_2T_x$, and TiC structures where the blue and black spheres are the Ti and C atoms, respectively, with strong covalent bonds in the conductive carbide core layer. The stacking of the Ti and C atoms forms three monolayers of Ti and two monolayers of C in an alternated sequence. In Ti$_3$AlC$_2$ the Ti$_3$C$_2$ layers are alternated with monolayers of Al, highlighted in Fig. 1 as yellow spheres, while Ti$_3$C$_2T_x$ shows purple and red spheres on both sides of the transition-metal carbide that are the F and O atoms, respectively, terminating the surfaces. Two alternatives for the F and O atoms to coordinate on the Ti$_3$C$_2$ surfaces are the threefold hollow face-centered-cubic (fcc) sites and the threefold hollow hexagonal-close-packed

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properties and interactions around the Ti atoms in Ti$_3$AlC$_2$ and Ti$_3$C$_2$Tx under the surfaces of the MX-(retermination) [20]. The different theoretical and experimental investigations find no obstacles regarding replacing the inherently formed termination species with others in the pursuit of tailoring the properties for specific applications. Yet there is no indisputably experimental evidence showing that the formation of the termination species can be replaced through synchrotron radiation-based Ti K-edge (1s) x-ray absorption spectroscopy, including both x-ray absorption fine structure (XANES) and extended x-ray absorption structure (EXAFS). XANES probes the unoccupied density of states of the absorbing atoms and is therefore an ideal technique for determining the chemical surroundings and local bonding structure around the transition metal. The 1s electron transition can, as a consequence of the selection rule, only occur to molecular orbitals with $p$-character (electric dipole transition) and $d$-character (electric quadrupole transition), although the probability of the $1s \rightarrow np$ transitions is about one-thousandth that of the $1s \rightarrow 3d$ transitions [21,22]. EXAFS provides information about the coordination numbers, atomic distances, and amount of atomic displacements and disorder around the probed element [23].

Ti 1s XANES and EXAFS spectra of Ti$_3$AlC$_2$ and Ti$_3$C$_2$Tx have been presented previously [24–26]. Yet a detailed analysis of the spectra remains to be performed. Instead of only comparing the Ti 1s XANES and EXAFS spectra of different compounds for similarities (or not) or a crude estimate of the Ti oxidation state, as in previous XANES and/or EXAFS studies of MAX-phases and MXenes [24–30], our aim in the present work is to learn more about the local bonding around the probed Ti atoms in both Ti$_3$AlC$_2$ and Ti$_3$C$_2$Tx through distinguished Ti 1s XAS features.

The Ti$_3$C$_2$Tx samples were fabricated as freestanding foils through wet etching, which leads to inherent F and O terminations [18]. Through heat treatments, the fcc site coordinated F will desorb and be replaced by O, which prefers the fcc sites when it is available [18]. The change of the fcc coordination will induce modifications in the XANES and EXAFS spectra, thus it will reveal local information on the bonding situation between the transition-metal atoms and termination species. Hence, the study demonstrates how x-ray absorption spectroscopy can be used to probe the MXene surfaces to shed more light on the local chemical interaction between F, O, and Ti atoms, which is relevant knowledge when designing MXenes for sought-after material properties.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Powders of Ti$_3$AlC$_2$ were produced starting with a mixture of TiC (Alfa Aesar, 98+%), Ti (Alfa Aesar, 98+%), and Al (Alfa Aesar, 98+%) in 1:1:2 molar ratios. The mixture was processed in a mortar with a pestle for 5 min and thereafter inserted in an alumina tube furnace. With a continuous stream of Ar gas, the furnace was heated at a rate of 5 °C min$^{-1}$ up to 1450 °C and held for 280 min before cooling down to room temperature. The resulting material is a lightly sintered Ti$_3$AlC$_2$ sample, which is then crushed to a powder with particle size $< 60 \mu$m using a mortar and pestle. A few mg of the Ti$_3$AlC$_2$ powder was mixed with polyethylene powder (Aldrich, 40–48 \mu;m particle size) and thereafter cold-pressed into an ~500-\mu;m-thick pellet for the x-ray absorption spectroscopy.

To convert the Ti$_3$AlC$_2$ to Ti$_3$C$_2$Tx flakes, half a gram of Ti$_3$AlC$_2$ powder was added to a premixed 10 mL aqueous solution of 12 M HCl (Fisher, technical grade) and 2.3 M LiF (Alfa Aesar, 98+%) in a Teflon bottle. Prior to adding the MAX powder to the HCl/LiF(aq) solution, the latter was
placed in an ice bath to avoid the initial overheating that otherwise can be a consequence of the exothermic reaction when the MAX power is added. After 0.5 h in the ice bath, the bottle was placed on a magnetic stirrer hot plate in an oil bath and held at 35 °C for 24 h. The mixture was thereafter washed, first through three cycles using 40 mL of 1 M HCl(aq) and thereafter three cycles using 40 mL of 1 M LiCl (Alfa Aesar, 98% purity). Then, the mixture was washed through cycles of 40 mL of deionized water until the supernatant reached a pH of approximately 6. In the end, 45 mL of deionized water was added, which was de-aerated by bubbling N2 gas through it and sonicated using an ultrasonic bath for 1 h. The resulting suspension was centrifuged for 1 h at 3500 rpm, which removed larger particles. The supernatant produced had a Ti3C2T1 concentration of 1 mg mL−1. To make freestanding films, 20 mL of the suspension was filtered through a nanopolypropylene membrane (3501 Coated PP, 0.064 μm pore size, Celgard, USA). The obtained Ti3C2T1 foil is described in detail in Ref. [7].

Moreover, to observe XANES and EXAFS features originating from termination species, the surfaces must be free from oxidized material, mainly TiO2 [31]. The newly made Ti3C2T1 foils were therefore stored in an argon (Ar) atmosphere and mounted on the sample holder in a glove-bag filled with nitrogen gas (N2). A continuous flow of N2 protected the sphere and mounted on the sample holder in a glove-bag filled with nitrogen gas (N2). A continuous flow of N2 protected the sample from oxidation during measurement. Hence, the obtained XANES and EXAFS spectra of the Ti3C2T1 foils have no detectable contribution from TiO2 impurities. The significant amount of TiO2 impurities and carbon-containing contamination in the Ti3C2T1 samples was confirmed through XPS. The XPS further showed a small amount of adsorbed Cl that desorbed completely at a moderate heat treatment. In addition, no indication of OH termination was observed, which agrees with the combined HRTEM/XPS study [18]. The Ti3AlC2 (and TiC), on the other hand, showed small amounts of TiO2 impurities in the XPS spectra. Contribution from TiO2 impurities in the Ti 1s XANES and EXAFS spectra of the Ti3AlC2 (and TiC), therefore, cannot be excluded. Nevertheless, the TiO2 contribution was shown to be at a negligible level.

B. XANES and EXAFS analysis

The XANES and EXAFS spectra were measured at the Ti 1s edge using an Si111 crystal in the monochromator at the wiggler beamline BALDER on the 3 GeV electron storage ring at MAX IV in Lund, Sweden. The x-ray absorption of the Ti3C2T1 MXene, the Ti3AlC2 MAX phase, a TiC reference, and a Ti metal reference foil were monitored in transmission mode with ionization chambers (I1 : 200 mbar N2 and He; I2 : 2 bar N2). The Ti3C2T1 sample was positioned in a water-cooled gas cell (Linkam Scientific Instruments) with a low N2 flow and a heating element that enabled measurements at different temperatures. The Ti 1s XANES spectra were obtained at room temperature (RT) and at 250 °C after 20 min heat treatments at 250, 550, and 750 °C. The energy resolution at the Ti 1s edge of the beamline monochromator was ~1.0 eV with 0.1 eV energy steps for XANES and 0.2 eV steps for EXAFS. The photon energy scale was calibrated using the first derivative of a Ti foil absorption spectrum, where the first inflection point was set to 4.9660 keV. The obtained spectra were normalized below the absorption edge before the background intensity subtraction and thereafter normalized above the absorption edge in the photon energy region of 5.045–5.145 keV. Self-absorption effects were found to be negligible in the normal incidence geometry for the Ti3C2T1 and the Ti foils. The spectra of the Ti3AlC2 and TiC pellets showed, on the other hand, some self-absorption effects甚至 at normal incidence, and they have therefore been corrected using the simple function A1(ε) [1–BI(ε)]−1, where A is a scaling factor, B is the self-absorption compensation factor, and I(ε) is the Ti 1s XANES spectrum of Ti3AlC2 and TiC, respectively. A and B are adjusted until the absorption features in the photon energy region of 5.045–5.145 keV have a similar appearance to the Ti 1s XANES spectrum of Ti3C2T1.

The Ti-Ti, Ti-C, Ti-O, and Ti-F scattering paths obtained from the effective scattering amplitudes (FEFF) [32–34] were included in the EXAFS fitting using the Visual Processing in EXAFS Researches (VIPER) software package [35]. The k2-weighted χ EXAFS oscillations were extracted from the raw absorption data, the average of 10 absorption spectra, after removing known monochromator-induced glitches and subsequent atomic background subtraction and normalization. The atomic distances (R), number of neighbors (N), and the σ2 consisting of a static and a vibrational part that was proportional to the difference of the mean-square atomic displacements [36–38].

III. RESULTS AND DISCUSSION

Figure 2 shows the obtained high-resolution Ti 1s XANES spectra of Ti-metal, TiC, Ti3AlC2, and Ti3C2T1. The absorption spectra consist of two regions: preedge and main edge. Features in the preedge region of Ti-metal, TiC, Ti3AlC2, and Ti3C2T1 are therefore in most cases assigned to transitions involving a mixing orbital (internal orbital mixing in the transition metal d orbitals) [21]. The sharp peak at 4.967 and 4.971 keV, respectively, are attributed to the 4d transition metal compounds assigned to electric dipole (1s → np) and quadrupole (1s → 3d) transitions. However, the intensity contribution of the latter is minor because of orbital symmetry restrictions [21,22,39], and preedge features are therefore in most cases assigned to 1s electron excitation into p-d hybridized orbitals, i.e., the transition into the p-component of the molecular orbitals that have both p- and d-character. The intensity of the preedge features depends mainly on coordination, symmetry, and bond angles [40].

The preedge features in the spectrum of the Ti metal reference, peaks A and B at 4.967 and 4.971 keV, respectively, are typical examples of 1s → p-d hybridized molecular orbital excitation near the Fermi energy (EF) [41]. The sharp peak A near the Fermi energy originates from 1s excitation into a local 3d-4p mixing orbital (local orbital mixing in the probed element), while peak B originates from 1s excitation into hybridized 3d-4p orbital where the 3d contribution...
The intensity of the preedge features is, however, reduced because of the sixfold coordination of the Ti atoms in the metal. The main-edge region consists of two broad features $C$ (white line) and $D$ that correspond to $1s \rightarrow 4p$ excitations. With the Ti 1s XANES spectrum of the Ti metal reference, it is possible to estimate the $E_F$ position, which is located close to the onset of peak $A$ at 4.9642 keV. The full width at half-maximum of peak $A$ of the Ti metal reference (1.3 eV) is also an indication of the good resolution at the Balder beamline.

The XANES spectra of TiC, Ti$_3$AlC$_2$, and Ti$_3$C$_2T_x$ display significantly different structures compared with the Ti metal reference spectrum (see Fig. 2). The preedge region consists of two features, which are highlighted in Fig. 3. The TiC and Ti$_3$AlC$_2$ spectra show a shoulder at 4.9679 keV and a peak at 4.9710 and 4.9709 keV, respectively, while the Ti$_3$C$_2T_x$ spectrum shows a shoulder at 4.9689 keV and a peak at 4.9711 keV. A basic density-of-states calculation obtained from a simple Ti$_3$C$_2T_x$ model with $T_x$ being F on the fcc sites and O on the bridge sites shows two C 2p peaks located at 4.2 and 7.1 eV above the $E_F$ and two Ti 3d peaks located at 4.0 and 6.9 eV above $E_F$. The orbital mixing provides the C 2p-Ti 3d hybridization and would correspond to $\sim$4.968 and $\sim$4.971 keV, respectively, in the Ti 1s XANES, which is close to the two preedge features obtained in the experimental spectra. Hence, the Ti 1s XANES preedge features of TiC, Ti$_3$AlC$_2$, and Ti$_3$C$_2T_x$ are assigned to Ti 1s $\rightarrow$ C 2p - Ti 3d hybridized molecular orbital excitations. The Ti$_3$C$_2T_x$ spectrum shows lower intensity in the preedge region.
region compared to TiC and Ti₃AlC₂, which suggests that the Ti 1s → C 2p − Ti 3d hybridized molecular orbital excitation is reduced for Ti₃C₂Tx compared with both TiC and Ti₃AlC₂. The energy difference between the two C 2p-Ti 3d peaks corresponds to the crystal-field splitting of the Ti 3d states into the t₂g and e₉ orbitals [43], thus it can be determined experimentally to be 3.1, 2.9, and 2.2 eV for TiC, Ti₃AlC₂, and Ti₃C₂Tx, respectively. The absence of a sharp peak near the 3p in the Ti 1s XANES of TiC, Ti₃AlC₂, and Ti₃C₂Tx indicates that there is no local unoccupied Ti 3d-4p hybridized orbital available for electron excitation.

The main-edge region shows two peaks, C and D in Fig. 2, which because of the 2D nature are relatively sharp for Ti₃C₂Tx. The peaks originate from Ti 1s → 4p excitations [43]. In addition, a closer look at the rising edge, i.e., the steep increase in intensity at the main edge, reveals a shoulder at 4.9780 keV. The shoulder is more noticeable in the Ti₃C₂Tx treatment of the Ti₃C₂Tx sample after it has been heated to 250, 550, and 750 °C, respectively. The absence of a sharp peak near the 3p in the Ti 1s XANES of TiC, Ti₃AlC₂, and Ti₃C₂Tx indicates that there is no local unoccupied Ti 3d-4p hybridized orbital available for electron excitation.

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oscillation intensity of the double peak at 7.55–7.95 Å$^{-1}$ also decreases with increasing temperature. More interestingly, the small features at 1.58 and 2.4–2.7 Å$^{-1}$ are also affected by the heat treatment. To analyze the detailed local structure and atomic distances in the films, Fourier transforms of the EXAFS data were performed.

Figure 5 shows the magnitude of the Fourier transform obtained from the $k^2$-weighted EXAFS oscillations $\chi (k)$ in Fig. 4 by the standard EXAFS procedure [34] related to the radial distribution function. The horizontal arrow at the top of Fig. 4 indicates the applied $k$-window. Table I shows the final results of the EXAFS fitting using the FEFF scattering paths of Ti$_3$AlC$_2$ and Ti$_3$C$_2T_x$ and hcp Ti metal as structure model systems. The obtained radius values are in comparison to atomic distances determined for lattice parameters from x-ray diffraction (XRD) in the literature, listed in parentheses in Table I. The initial crystal structure in the modelling assumes a Ti$_3$C$_2$F$_1$O$_2$ composition in line with previous quantitative core-level XPS results [18]. However, the obtained atomic distances have sources of errors such as photon energy calibration and dispersion, statistical noise, and inaccuracies in the ab initio calculations of scattering paths using FEFF.

The corresponding errors in XRD are in the same order of magnitude as for EXAFS.

In Ti metal with hcp structure, the main peak consists of the in-plane Ti-Ti scattering ($N = 6$) at 2.842 Å and ($N = 6$) of 2.966 Å, where the latter corresponds to the a-axis of the crystal. For comparison, the peak that consists of the out-of-plane Ti-Ti scattering path of the c-axis is located at 4.675 Å as a weak feature. The corresponding values obtained from XRD measurements are 2.897, 2.950, and 4.686 Å, respectively [47]. The more intense peak in Ti metal observed at ~4.7 Å in Fig. 4 is because of the superposition of the three longer direct Ti-Ti scattering paths with atomic distances 5.079–5.110 Å in the higher-order coordination shells.

For Ti$_3$AlC$_2$, shown in the middle in Fig. 5, there is a slight shift of the main Ti-Ti peak to larger atomic distance, and a new peak corresponding to Ti-C bonding appears at ~1.66 Å. In addition, there is a prominent peak at ~3.8 Å caused by Ti-Ti and Ti-Al scattering from the central Ti layer.

The main peak of the Ti$_3$C$_2T_x$, shown at the bottom in Fig. 5, is dominated ($N = 4.982$) by the in-plane Ti-Ti scattering at 3.016 Å; the in-plane Ti-Ti scattering corresponds to the c-axis unit-cell edge. The weaker out-of-plane scattering at 3.072 Å shows a significantly lower intensity ($N = 1.312$),
which is not surprising for a 2D material. As also observed in Fig. 5, the Ti-Ti distances of the in-plane and out-of-plane contributions of Ti$_3$C$_2$T$_x$ (3.016 and 3.072 Å) are located at slightly different distances compared to the Ti-Ti atomic distances in Ti$_3$AlC$_2$ (3.029 and 3.032 Å). The value of 3.016 Å for the in-plane Ti-Ti distance of Ti$_3$C$_2$T$_x$ is somewhat smaller than the calculated in-plane Ti-Ti atomic distance obtained from the XRD lattice parameter (α = 3.075 Å) [47].

The peak feature between 0 and 2 Å in the first coordination shell of Ti$_3$C$_2$T$_x$ is caused by superimposed Ti-O, Ti-F, and Ti-C scattering, where the Ti-C interaction has two different contributions: Ti for the inner Ti atoms that bond only to C, and a second Ti$_{II}$ contribution to the outer Ti atoms that bond both to C and to the termination species. The Ti-C bond length of the outer Ti atoms is 0.056 Å longer than that for the inner Ti atoms. Interestingly, the three peaks in the higher coordination shells between 3 and 6 Å also contain a large contribution of long inclined single Ti-O and Ti-F scattering paths from all surface Ti atoms to the termination species T$_x$, in addition to Ti-Ti scattering and superimposed multisattering paths, e.g., Ti-Ti-C, Ti-C-O, Ti-C-F, and Ti-F-Ti-F.

The Ti-T$_x$ scattering paths exhibit a significant temperature dependence as the data were measured at RT, 250, 550, and 750 °C. During heating, the peaks become significantly broadened and less intense as observed by the Debye-Waller factor, which increases with the temperature, as a consequence of more atomic vibrations. For the main Ti-Ti scattering, σ$^2$ increases linearly from 0.0066 at room temperature to 0.0082 at 750 °C. A similar trend has been observed in other systems using EXAFS [48]. The broadening is also observed as intensity increases between the peaks in the difference spectra. In addition to the broadening of the peaks, the vibrational behavior and peak broadening exhibit strong anisotropy of the Ti–Ti bonds. Therefore, before each measurement the elevated temperature was stabilized for 20 min and then decreased and stabilized at 250 °C after which the spectra were recorded.

Figure 6 shows the Fourier transform obtained from the $k^2$-weighted EXAFS oscillations $χ(k)$ of Ti$_3$C$_2$T$_x$ and the effect of the heat treatment, where arrows indicate the general trends. Difference spectra that highlight the temperature-induced changes are shown in the bottom. In the low-radius region of the first coordination shell of the probed Ti (between 1 and 2 Å), including the bonding of the O and F elements, an intensity shift is observed corresponding to an ∼0.2 Å shorter bond distance. In particular, the F-related intensity decreases indicating desorption of the F upon heating to 750 °C.

### Table I. Structural parameters for Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$ in comparison to Ti metal reference obtained from fitting of calculated scattering paths in the first coordination shell. N is the coordination number, R is the atomic distance (in Å) for the Ti-Ti and Ti-C scattering paths, respectively, σ is the corresponding Debye-Waller factor representing the amount of atomic displacement and disorder, reduced $χ^2$ is the squared area of the residual, $N_{ind}$ is the number of independent points, $P$ is the number of fitting parameters, and $v$ is the degrees of freedom. Atomic distances obtained from lattice parameters in XRD are given in parentheses [39].

| System          | Shell        | R (Å)$^a$ | N$^b$  | σ (Å$^2$)$^c$ | Statistics               |
|-----------------|--------------|-----------|--------|--------------|--------------------------|
| Ti metal (at RT)| 6*Ti-Ti      | 2.842     | 5.535  | 0.0042       | $χ_{20}^{0.95} = 8.44$   |
|                 |              | (2.897)   |        |              | $N_{ind} = 28, P = 8$    |
|                 | 6*Ti-Ti: LP$^d$-α | 2.966     | 2.237  | 0.0014       | $v = N_{ind} - P = 20$  |
|                 |              | (2.950)   |        |              |                          |
|                 | 6*Ti-Ti: LP$^d$-c | 4.675     | 2.005  | 0.0077       |                          |
|                 |              | (4.686)   |        |              |                          |
| Ti$_3$AlC$_2$ (at RT) | 3 * Ti$_{II}$-C | 2.160     | 2.764  | 0.0025       | $χ_{20}^{0.95} = 9.487$ |
|                 |              | (2.120)   |        |              | $N_{ind} = 24, P = 20$  |
|                 | 6 * Ti$_{II}$-C | 2.220     | 1.560  | 0.0025       | $v = N_{ind} - P = 4$   |
|                 |              | (2.227)   |        |              |                          |
|                 | 3 * Ti$_{II}$-Al | 2.708     | 1.299  | 0.0015       |                          |
|                 |              | (2.781)   |        |              |                          |
|                 | 3*Ti-Ti oop$^c$ | 3.029     | 1.164  | 0.0011       |                          |
|                 |              | (3.069)   |        |              |                          |
|                 | 6*Ti-Ti: LP$^d$-α | 3.032     | 5.735  | 0.0066       |                          |
|                 |              | (3.075)   |        |              |                          |
| Ti$_3$C$_2$T$_x$ (at RT) | 1 * Ti$_{II}$-O$_A$ | 1.707     | 0.199  | 0.0045       | $χ_{10}^{0.95} = 8.307$ |
|                 | 1 * Ti$_{II}$-O$_B$ | 1.952     | 0.292  | 0.0030       | $N_{ind} = 36, P = 26$  |
|                 | 1 * Ti$_{II}$-F | 2.115     | 0.245  | 0.0029       | $v = N_{ind} - P = 10$  |
|                 | 6 * Ti$_{II}$-C | 2.139     | 1.992  | 0.0012       |                          |
|                 | 3 * Ti$_{II}$-C | 2.234     | 2.057  | 0.0079       |                          |
|                 | 6*Ti-Ti: LP$^d$-α | 3.016     | 4.982  | 0.0056       |                          |
|                 |              | (3.075)   |        |              |                          |
|                 | 3*Ti-Ti oop$^c$ | 3.072     | 1.312  | 0.0021       |                          |
|                 |              | (3.135)   |        |              |                          |

$^a$The errors in the atomic distances are estimated to be ±0.01 Å.
$^b$The errors in the coordination numbers are estimated to be ±0.01.
$^c$The errors in the Debye-Waller factors are estimated to be ±0.001 Å$^2$.
$^d$Out-of-plane parameter.
$^e$Out-of-plane.
FIG. 6. Temperature-dependent Fourier transforms obtained from Ti 1s EXAFS oscillations \(\chi(k)\) of \(\text{Ti}_3\text{C}_2\text{T}_x\). Difference spectra (x3.5) are shown at the bottom.

Contrary to F, the intensity related to O-bonding slightly increases and shifts to shorter bond lengths. This behavior is consistent with previous temperature-dependent core-level XPS results [18] that showed desorption of F and a change of bond site for O in this temperature region.

The three peaks observed between 3 and 6 Å in \(\text{Ti}_3\text{C}_2\text{T}_x\) also occur in EXAFS data of cubic TiC [45,46]. The first peak at \(\sim 3.5\) Å is mainly ascribed to Ti-Ti and Ti-C scattering in the second coordination shell. The second peak at 4.5–5 Å mainly consists of Ti-C-Ti and Ti-Ti-O/F scattering, while the third peak 5.5–6 Å contain many multiscattering paths such as Ti-Ti-Ti (5.30 Å) and Ti-Ti-Ti-C (5.31 Å), etc. However, the intensity of the three peaks in the higher coordination shell also contains a significant contribution of long inclined single Ti-O (3.62, 3.73, 4.28, 4.75, 4.79, and 5.04 Å) and Ti-F (3.76, 4.58 Å, 4.78, and 4.86 Å) scattering paths. As observed in the difference spectra, the contributions of these paths decrease as the temperature is increased. This is consistent with the fitting results showing that the Ti-O bond length in the first coordination shell seems to shorten as the temperature increases to \(750^\circ\)C.

Yet, after a decade of extensive research activities, there is new knowledge to gain about MAX phases and MXenes. In the present study, there are several interesting observations. For example, through XANES we find that the C 2p-Ti 3d hybridization is altered when the \(\text{Ti}_3\text{AlC}_2\) transforms into \(\text{Ti}_3\text{C}_2\text{T}_x\), leading to a smaller crystal-field splitting of the \(t_{2g}\) and \(e_g\) orbitals, which suggests slightly weaker Ti-C bonds in \(\text{Ti}_3\text{C}_2\text{T}_x\) compared to \(\text{Ti}_3\text{AlC}_2\). Another observation is the 1.4 eV energy shift of the main absorption edge for the \(\text{Ti}_3\text{C}_2\text{T}_x\) compared to \(\text{Ti}_3\text{AlC}_2\). A main-edge shift is often an indication of a charge redistribution, and when the shift is toward higher energies, the charge transfer is away from the probed atoms. Hence, replacing the weak interacting Al layers in \(\text{Ti}_3\text{AlC}_2\) with chemisorbed F and O in \(\text{Ti}_3\text{C}_2\text{T}_x\) will withdraw charge from the Ti toward the termination species.

The additional main-edge energy shift caused by the heat treatment, however, cannot be a consequence of a further withdrawal of charge from the Ti atoms, because that would contradict the previous temperature-programmed XPS study [18]; the intensity at the high-binding-energy side of the Ti 2p\(^{3/2}\) XPS spectra decreases while F desorbs, indicating that Ti in \(\text{Ti}_3\text{C}_2\text{T}_x\) chemically reduces in a heat treatment. In addition, the electronegativity of O is lower compared to F (Pauling scale 3.44 and 3.98, respectively). The Ti 1s XANES main-edge shift toward higher energy must therefore be caused by something else. It can, for example, be a response to the stronger bonding of the O in the fcc site compared to F that pushes the unoccupied Ti 4p orbitals toward higher energy. Regardless of the reason, the Ti 1s XANES shows that orbitals with Ti 4p character are sensitive to changes of the termination species on the fcc sites.

From the EXAFS we learn that the in-plane Ti-Ti distances decrease while the out-of-plane Ti-Ti distances increase when the \(\text{Ti}_3\text{AlC}_2\) is converted into \(\text{Ti}_3\text{C}_2\text{T}_x\). Concerning EXAFS, it probes the local short-order atomic distances between the absorber atom and the neighboring scatterers using the constructive and destructive interference in the unoccupied electronic structure. Since the EXAFS photoelectrons travel much faster than the speed of the thermal motion of the atoms, the obtained atom distances are an average of “snapshots” that in most cases correspond to the distance between the average atomic positions as obtained with XRD and neutron diffraction, which are considered to be long-order probes. However, if adjacent atoms are moving in an anticorrelated motion, the distance between them will be the same as the atomic positions distance only when both atoms are in-plane, while it will become larger when the atoms are moving in the opposite direction out-of-plane. The atom distances obtained from EXAFS will then be larger than if they would be obtained from XRD and neutron diffraction.

The surface Ti atoms and the termination species F and O are expected to move in an anticorrelated motion, and the obtained TiII-OA, TiII-Oe, and TiII-F distances are probably larger than the true atomic positions. This discrepancy between the average atom distances between the \(T_x\) atoms and the surface Ti atoms will become larger with increasing temperature.

IV. CONCLUSIONS

Through a combination of XANES and EXAFS we have investigated the MAX phase material \(\text{Ti}_3\text{AlC}_2\) and the MXene material \(\text{Ti}_3\text{C}_2\text{T}_x\), where the latter was examined before and after a series of heat treatments. The preedge absorption region of both \(\text{Ti}_3\text{AlC}_2\) and \(\text{Ti}_3\text{C}_2\text{T}_x\) shows mainly Ti 1s excitations into two C 2p-Ti 3d hybridized molecular orbitals corresponding to the Ti 3d\(^{2p}\) and \(\varepsilon_g\) orbitals. The crystal-field splitting is determined to be 2.9 and 2.2 eV for \(\text{Ti}_3\text{AlC}_2\) and \(\text{Ti}_3\text{C}_2\text{T}_x\), respectively. The main-edge absorption features originate from the Ti 1s \(\rightarrow 4p\) excitation and appear to be sensitive toward the fcc-site occupation, which led to a 1.4 eV
shift when the Al layers in Ti3AlC2 were replaced with the termination species F and O. The local chemical bonding structure and structural properties with atomic distances in Ti3C2Tx MXene show a significant temperature dependence. Heat treatment up to 750 °C removed F and made the fcc sites available for O occupation, which is manifested as a 0.5 eV high-energy shift of the peaks in the main-edge absorption region.

EXAFS shows that the shortest inplane Ti-Ti atomic distances in Ti3AlC2 and Ti3C2Tx are 3.032 and 3.016 Å, respectively, which are longer and shorter than the out-of-plane distance of 3.029 Å in Ti3AlC2 and the corresponding atomic distance in Ti3C2T6 of 3.072 Å. The TiI-C and TiII-C bond lengths in Ti3AlC2 are 2.220 and 2.160 Å, respectively, while the TiI-C and TiII-C bond lengths in Ti3C2T6 are 2.139 and 2.234 Å, respectively. Significant changes in the Ti-O/F coordination are observed with increasing temperature in the heat treatment. The TiII-O bond lengths becomes shorter because of a change in coordination from bridge to fcc facilitated through the desorption of the F as the F contribution is found to diminish when the temperature is raised from room temperature up to 750 °C. The significant contribution of long inclined single Ti-O and Ti-F scattering paths decreases as the temperature increases.

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