I. Introduction

Since the successful separation of graphene from graphite, interest in other two-dimensional (2D) materials such as hexagonal boron nitride (h-BN), transition metal dichalcogenides (TMDs) and, more recently, transition metal carbides and carbonitride labelled MXenes has increased significantly. MXenes are a new family of 2D materials that are synthesized via selective etching of the “A”-layers by HF, or other fluorine containing salts, from the MAX phases (M_{n+1}AX_{n}, where n = 1, 2, or 3). The latter are layered ternary carbides and nitrides, where M represents a transition metal, A is typically a IIIA or IVA element (e.g. Al, Si, etc.); and X is C and/or N. When the A-layers are selectively etched, they are replaced with surface terminations. Thus the correct formula for MXenes is M_{n+1}X_{n}T_{x}, where T_{x} represents various surface termination functional groups, including O, OH, and F.

MXenes exhibit unusual characteristics and properties. For example, they combine hydrophilicity and metallic-like conductivity. This unique combination can be further tuned by manipulating their composition and/or surface chemistries, which is one reason they have attracted wide interest.

Another important reason is that they are seriously being considered in a large and diverse host of applications. The number of papers published and number of citations referring to these materials are both growing exponentially. The same is true for theoretical studies on their properties and potential applications since their discovery in 2011. The gist of many of these theoretical papers is that it is possible to dramatically alter the properties. For example, it has been predicted that some non-terminated MXenes would be magnetic. Concomitantly, all studies predict MXenes, with surface terminations, to be non-magnetic. However, since it is almost impossible to maintain un-terminated nanosheets – especially under ambient atmospheres – due to their reactivity, other approaches must be found to change/control their terminations and structures.

One obvious approach is to reduce the MXene flakes. In one of the earliest attempts, Mashtalir et al. exposed Ti_{3}C_{2}T_{x} multilayers, MLs, to nitrogen-containing organic molecules.
including hydrazine (N_2H_4), urea, and dimethylsulfoxide (DMSO).\textsuperscript{15} The original purpose of that effort was to reduce the surfaces as is done for reduced graphene oxides (rGOs).\textsuperscript{16} Instead of reducing the surfaces, however, the hydrazine, and other small organic molecules are simply intercalated between the layers. And while this approach allows for the delamination of the MXene layers, whether it also reduced the Ti–C sheets was not investigated.\textsuperscript{15}

Herein we reduced Ti_{3}C_{2} and to understand what occurs upon reduction it is instructive to review what is known about reduced titanias, r-TiO_2. By now it is reasonably well established that reducing TiO_2 results in the formation of oxygen vacancies, V_{O}.\textsuperscript{17,18} For example, heating TiO_2 in the presence of urea reduced some of the Ti^{4+} ions to Ti^{3+} and created oxygen vacancies.\textsuperscript{19,20} Over the years there have been multiple approaches to reduce TiO_2, which ranged from using metals such as Al, Zn, Fe, etc., to heating under reducing atmospheres, or exposure to hydrazine hydrate, urea, etc.\textsuperscript{18} Two decades ago, Diebold and co-workers used atomic-resolution scanning tunnelling microscopy (STM) to directly evidence oxygen vacancies, V_{O}, generated under vacuum on a TiO_2 (110) surface.\textsuperscript{21,22} Early on, DFT calculations have shown that the removal of neutral, bridging oxygen atoms from rutile TiO_2 (110) surfaces generated two unpaired electrons that were localized at the 3d orbitals of neighbouring 5-coordinated Ti atoms.\textsuperscript{23} Note that in this work we adopt the Kroger–Vink notation in which oxygen vacancies with two, one and no localized electrons are denoted as V_{O}^2, V_{O}^1, and V_{O}^0, respectively. Furthermore, if the electrons are localized on a Ti^{4+} site, the latter becomes Ti^{3+}, that – in the Kroger–Vink notation – is described as Ti^{3+}_{V}. There is a quite recent comprehensive review on reduced TiO_{2}\textsuperscript{18} in which the fundamental role of V_{O} in reduced TiO_{2} is outlined and documented in much more detail. For our purposes, what is important is that reducing TiO_{2} results in oxygen vacancies.

Herein, we present a new synthetic route to reduce 2D Ti_{3}C_{2}T_{x} MXenes – henceforth referred to as r-Ti_{3}C_{2}T_{x} – via a facile, low temperature solution process. The resulting material is Pauli paramagnetic, which constitutes in turn, the first evidence of magnetism of any kind in a MXene. For the reduction, we chose the “super-base”, lithium-ethylene diamine (Li-EDA). This solution-based process is facile and amenable to mass production. In addition, since the parent MAX phases are Pauli paramagnets,\textsuperscript{7} we expect that the chemically reduced Ti_{3}C_{2}T_{x} would provide a strong paramagnetic signal. In addition, we show that by controlling the reduction temperature, we can “dial in” the density of states, DOS, at the Fermi level, E_F.

This paper is structured as follows: First, we describe the process make and reduce Ti_{3}C_{2}T_{x} flakes in the presence of Li-EDA. We then characterize the resulting material after washing with water and ethanol using a number of techniques including X-ray diffraction, XRD, Raman spectroscopy, electron spin resonance, ESR, magnetization measurements as a function of temperature, scanning and transmission electron microscopy and X-ray photoemission spectroscopy (XPS). XPS spectra provide strong evidence for the formation of Ti^{3+} ions and, by extension, oxygen vacancies. The ESR and magnetization measurements show the r-Ti_{3}C_{2}T_{x} to be Pauli paramagnetic. Finally, we show that our results are consistent with what would be expected for a disordered metal, close to a metallic to insulator, M-I, transition, where E_F is near the mobility edge.

II. Experimental
A. Sample preparation

To prepare Ti_{3}AlC_{2}, Ti_{3}AlC (Kantanl) and TiC (>99%, Alfa Aesar) were mixed using a ball mill for 24 h at a molar ratio of 1 : 1 (after adjusting ~34 wt% Ti_{3}AlC_{2} present in the commercial powder).\textsuperscript{4} The mixed powders were then heated to 1350 °C for 2 h under argon and were held at temperature for 0.3 h resulting in lightly sintered brick. Finally, the Ti_{3}AlC_{2} was crushed into powder by ball milling for further reactions and characterization. To synthesize the Ti_{3}C_{2}T_{x}, we carefully followed previous reaction conditions described elsewhere.\textsuperscript{4} In short, the Ti_{3}AlC_{2} powders are immersed in a 50% concentrated HF solution at room temperature, RT, for 2 h. The resulting suspension was then washed more than 5 times with DI water, and centrifuged to separate the supernatant and obtain Ti_{3}C_{2}T_{x} powders.

Synthesis of r-Ti_{3}C_{2}T_{x} from Ti_{3}C_{2}T_{y} by lithium ethylenediamine. Because Li and EDA are quite sensitive to moisture, every piece of glassware used was fully dried in a drying oven to remove residual water molecules. Then, 100 mg of Ti_{3}C_{2}T_{y} and 70 mg of Li metal (Sigma Aldrich) were carefully placed in a flask under a N_2 atmosphere in a glovebox. Then, 100 mg of EDA (Sigma Aldrich) was injected slowly over 20–30 min. During this stage, the mixture was sonicated to produce a homogeneous solution and to ensure that the Li metal dissolved in the EDA solution. Once the Li metal was well dissolved, the reaction solution turned dark blue. This change in colour was taken as evidence for the formation of electrode salts. Subsequently, the reaction solution was stirred for 24 h under an inert N_2 atmosphere at 25, 40, 80 or 120 °C. After the reaction was complete, deionized, DI, water and ethanol were carefully added to the reacted solution to neutralize it and remove the Li ions intercalated between the Ti_{3}C_{2}T_{x} nanosheets. This process was repeated several times. The resulting ML samples were dried and stored under vacuum in an oven at 60 °C for further characterization and use.

Delamination of r-Ti_{3}C_{2}T_{x} by lithium ethylenediamine. This procedure is identical to the synthesis described above except that the r-Ti_{3}C_{2}T_{y} MLs were delaminated after the reaction was complete. In this case, only DI water was added to the solution. The solution was sonicated for 6 h and centrifuged, and the supernatant was decanted. The product was washed with DI water several times to remove any Li or EDA residues. Finally, the supernatant, containing mostly delaminated MXene flakes, was filtered through a 200 nm anodisk to prepare free-standing r-Ti_{3}C_{2}T_{x} films.
B. Chemical and physical characterization

The samples’ microstructures were observed using a field emission scanning electron microscope (FE-SEM, JSM-6701F/INCA Energy, JEOL) and a transmission electron microscope (JEOL JEM 3010). Atomic force microscopy, AFM, was performed using a SPA400 instrument with an SPI-3800 controller (Seiko Instrument Industry Co.) at RT. XRD patterns were obtained using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation at a scanning rate of 5° min⁻¹. All XPS measurements were performed on a Thermo VG Microtech ESCA 2000 with a monochromatic Al KR X-ray source at 100 W. Raman spectroscopy measurements were obtained using a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (514 nm). The thermal properties of the materials were characterized by thermogravimetric analysis, TGA (Polymer laboratory, TGA 1000 plus).

The magnetic properties were measured using: (i) ESR spectroscopy (CW-EPR, Bruker EMX plus 6/1 spectrometer) at RT with a microwave power of 0.94 mW, a microwave frequency of 9.64 GHz, a modulation frequency of 100 kHz, and a modulation amplitude of 10 G and (ii) a superconducting quantum interference device (SQUID) and a vibrating sample magnetometer (VSM). The magnetization, M, vs. magnetic field, H, measurement was carried out at RT under 30 Oe.

III. Results and discussion

The details of the operative reaction mechanisms can be found in the ESI.† Fig. 1 schematically summarizes the steps to produce r-Ti₃C₂Tₓ using Li-EDA that is a well-known intercalant as a reducing agent and an exfoliator for 2D materials.15,24–26 Besides forming free standing films, this treatment also creates defects (oxygen and/or carbon vacancies) in the MXene layers, as well as, increases the DOS at the Fermi level (see below).

The SEM images of as-etched Ti₃C₂Tₓ, r-Ti₃C₂Tₓ and r-Ti₃C₂Tₓ after delamination are presented in Fig. 2A, B, and C, respectively. These micrographs are typical of MXenes after etching of Al from the parent MAX phase using HF. Note that the layers are retained after Li-EDA treatment (Fig. 2B), which implies that the reduction process has no significant effect on the overall MXene morphology. This conclusion is further confirmed by SEM images of freestanding filtered films (Fig. 2D and E) that are typical of such MXene films. The films produced were ≈2 µm thick measured by SEM and with a flexibility (Fig. 2F) comparable to that of graphene oxide16,26 and other MXene filtered films.25,27,34

The 2D nature of the flakes and their purity were further elucidated by TEM. As shown in Fig. 2G and Fig. S1A and S1B† the as-reduced and the delaminated MXene nanosheets exist as single or few stacked layers. The high-resolution (HRTEM) analysis shows clear lattice fringes of ca. 0.26 nm that are identified for the (1010) (Fig. 2H) and the corresponding selected area electron diffraction, SAED, (inset in Fig. 2H) confirms that the hexagonal structure of the parent MAX phase is maintained after reduction. In particular, the space parameters of r-Ti₃C₂Tₓ attributed to (2110), (1100) and (1010) planes are displayed clearly in the SAED.

AFM of flakes deposited on SiO₂ substrates (Fig. 2I) shows that, at least, some of the ML flakes have lateral dimension of the order of a few micrometres, while being a few nm thick.

Recent XPS results28 have shown that the Ti oxidation states in multilayered Ti₃C₂Tₓ are far from simple. Peaks in the range of 454.9 eV to 458.6 eV were identified and assigned Ti, Ti²⁺, Ti³⁺ and Ti⁴⁺. The Ti-peak – located at the same position as the Ti peak in Ti₃AlC₂ – viz. 455 eV – was assigned to Ti bonded to C atoms.28 The Ti²⁺ and Ti⁴⁺ peaks are located at 457.9 eV and 458.9 eV, respectively.28,29 Herein we unambiguously show that...
the Ti$^{3+}$ peak in r-Ti$_3$C$_2$Tx occurs at 458.0 ± 0.2 eV and the Ti$^{4+}$ peak at 459 ± 0.2 eV. It should be noted that the slight differences of the peak positions of Ti$^{3+}$ and Ti$^{4+}$ in Ref. 28, 29 and our work are most probably due to the sputtering. Halim et al. showed that sputtering can slightly shift the peak positions. The overall XPS spectra, over the full range of energy, are shown in Fig. S2A†. The spectra of the Ti 2p-region of Ti$_3$AlC$_2$, Ti$_3$C$_2$Tx and r-Ti$_3$C$_2$Tx, reduced at 25 °C, 40 °C, 80 °C and 120 °C, are shown in Fig. 3A. The intensities are normalized to the Ti–C peak, labeled on the left. A perusal of these results clearly shows that: (1) there are three main peaks labelled from left to right as Ti–C, Ti$^{3+}$ and Ti$^{4+}$. A shoulder between the Ti–C peak which is almost at the same energy as that of Ti$_3$AlC$_2$ and the Ti$^{3+}$ peak presumably due to the introduction of defects. (2) The Ti$^{4+}$ peak for Ti$_3$AlC$_2$ is due to a surface oxide layer. It is also present for Ti$_3$C$_2$Tx but conspicuously absent from samples reduced at 25, 40 and 80 °C. That peak, however, is prominent for the sample reduced at 120 °C. (3) The Ti$^{3+}$ peak, on the other hand, increases monotonically with increasing reduction temperature. (4) Peaks at 461 eV and higher – denoted by arrows – belong to 2p$_{1/2}$. It follows that all major peaks and prominent shoulders can be assigned to Ti–C, Ti$^{3+}$ and/or Ti$^{4+}$.

Most of our peak assignments agree with previous work on Ti$_3$C$_2$Tx. In previous work, however, a Ti$^{3+}$ peak was not directly observable; it was deduced via deconvolution of a much wider peak and thus subject to some subjective interpretation. It follows that an important result obtained here is the clear and unambiguous assignment of Ti$^{3+}$ in Ti$_3$C$_2$Tx to 458.0 ± 0.2 eV. As discussed below, the correlation between the intensity of this peak – that increases monotonically with increasing reduction temperature – and the paramagnetism is good. More specifically, the ratio of the intensities of the Ti$^{3+}$ and Ti–C peaks (Ti$^{3+}$/Ti–C) after reduction at 25 °C, 40 °C and 80 °C was 0.5 ± 0.2, 0.6 ± 0.2 and 0.9 ± 0.2 (see Fig. S3A, B and C†). The results after reduction at 120 °C were more scattered (Fig. S3D†). The exact reason for the scatter is unclear at this time, but as discussed below, the samples reduced at 120 °C were more prone to oxidation and indeed the increase in the peak intensities of Ti$^{3+}$ at 459 eV is evidence for oxidation. Furthermore, it is obviously seen in Fig. S4B† that the peak intensities Ti$^{3+}$ between Ti–C and Ti$^{3+}$ gradually decreased as the reduction temperature increased. More specifically, the Ti$^{2+}$ concentration percentage for r-Ti$_3$C$_2$Tx reduced at RT, 40, 80 and 120 °C samples is calculated to be 17.7 at%, 11.8 at%, 10.0 at% and 8.5 at%, respectively. Note that the oxidation does not occur during the reduction process, but later when the samples are exposed to air. This comment notwithstanding, in all cases, the intensities of the peaks or shoulder at 458 eV, corresponding to Ti$^{3+}$, are significantly higher than the Ti–C peaks or the shoulder at ≈455 eV. Note that the ESR signals of the three samples measured in XPS were quite comparable and strong (Fig. S3E†) and thus the oxidation observed most probably only affected the outermost layers probed by the XPS.

To sum up the Ti XPS results: a strong correlation was found between the reduction temperature and the intensities of the Ti$^{3+}$ peaks. The simplest interpretation is that the Li-EDA treatment reduces some Ti$^{4+}$ into Ti$^{3+}$. It is important to note in this context that for there to be something to reduce, Ti$^{4+}$ must have been incorporated into the etched MXenes to begin with and/or C-vacancies are formed (see below). When the O 1s spectra for the MXenes tested herein are compared (Fig. 3B) it is obvious that increasing the reduction temperature shifts the center of gravity of the spectra to higher energy, confirming the fact that Li-EDA treatment indeed reduces Ti$_3$C$_2$Tx. However, the shoulder for the samples reduced at 120 °C is consistent with our conjecture that this sample was partially oxidized. Fig. S2B† plots the C 1s XPS spectra as a function of etching and reduction temperature, from which it is clear that the peak intensity ratio of the C atoms associated with Ti$_3$C$_2$Tx (viz. 282 eV) and all other C components such as C–C (248.8 ± 0.2 eV), CH (285.5 ± 0.2 eV), C–O (286.8 ± 0.2 eV) and COOH (289.0 ± 0.2 eV) decreases – from about 1.8 to 0.9 – with increasing reduction temperatures (see Table S1†). Also noteworthy is the gradual increase in the intensity of the graphitic C–C peak. The intensity of the CH, peak first increases up to a reduction temperature of 80 °C before ultimately decreasing after reduction at 120 °C (Fig. S2B†). In contrast, the intensities of the C–O (286.8 ± 0.2 eV) and COOH (289.0 ± 0.2 eV) peaks remain more or less constant. In summary, it is reasonable to assume that during the reduction process, C atoms – that subsequently react with oxygen to form hydrocarbons, or react with other C atoms to form graphitic sheets – are produced. It is currently well established, and confirmed herein, that etching of Ti$_3$AlC$_2$ in HF results in a mixture of O,
OH and F-terminations as shown in Fig. S2A.\textsuperscript{†}\textsuperscript{6,9,15,28}
Increasing the reduction temperature, however, replaces F-terminations with O or OH terminations. This is best seen in Fig. S2C\textsuperscript{†} that shows that after reduction at 120 °C, the F 1s signal almost disappears. This result is not too surprising since it is established that the F-terminations are less stable than the O and/or the OH terminations.\textsuperscript{8} A small N 1s peak also appeared around 400 eV due to EDA molecules intercalated after Li-EDA treatment as shown in Fig. S2A.\textsuperscript{†}\textsuperscript{15,35}

Raman spectra of Ti\textsubscript{3}AlC\textsubscript{2}, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, and r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} are compared in Fig. 3C. The three main Raman peaks located at ca. 260, 400, and 605 cm\textsuperscript{-1} can be assigned to the E\textsubscript{g(1)}; A\textsubscript{1g} and E\textsubscript{g(2)} vibration modes of in-plane vibration of carbon and oxygen bonds and Ti–C vibrations, respectively.\textsuperscript{4,45} The Raman spectra of Ti\textsubscript{3}AlC\textsubscript{2} and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} are comparable, showing almost no changes in the peak position. But, the peak intensities of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} (as compared with Ti\textsubscript{3}AlC\textsubscript{2} at 400 and 605 cm\textsuperscript{-1}) were weaker and noisier as a result of etching.\textsuperscript{4}

More interestingly, compared to Ti\textsubscript{3}AlC\textsubscript{2}, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} the Raman peak of r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} at around 145 cm\textsuperscript{-1} is new, and can possibly be attributed to the vibration of anatase, indicating that r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} are prone more to oxidation than Ti\textsubscript{3}AlC\textsubscript{2} or Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}.\textsuperscript{45,46} Furthermore, the peak at around 400 cm\textsuperscript{-1} was shifted to ∼430 cm\textsuperscript{-1} which can be attributed to the thickness of nanosheets during reduction.\textsuperscript{33,47} The two broad peaks at ∼1390 cm\textsuperscript{-1} and ∼1590 cm\textsuperscript{-1} are characteristic of the D- and G-modes of graphitic carbon. The ratio of the D- and G-band intensities, I\textsubscript{D}/I\textsubscript{G}, was ∼1.12. The broadening of G- and D-bands and the fact that the I\textsubscript{D}/I\textsubscript{G} ratio >1 (Fig. S2D\textsuperscript{†}) are evidence for highly disordered or oxidized C, similar to what has been reported for graphene oxide.\textsuperscript{16}

Fig. S4A\textsuperscript{†} compares the weight losses when the various powders were heated to 800 °C under a N\textsubscript{2} atmosphere. The HF-etched Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} exhibited a small (∼3%) weight loss, attributed to the elimination of interlamellar water and possibly the loss of some F associated with the terminations. The weight losses of the r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} films gradually increased as the reduction temperature increased up to ∼600 °C, before increasing again. The initial weight losses in the r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} samples are higher than those in the unreduced material suggesting that the inter-lamellar water is less tightly bound in the former than the latter. The weight gain is mostly probably associated with the reaction of the powders with residual O\textsubscript{2} or N\textsubscript{2}, and is consistent with the notion that the reduced powders are more reactive than their un-reduced counterparts.\textsuperscript{35,44}

We now shift our attention to what occurs to the MXene structure as a result of Li-EDA treatment followed by washing with water. The effect of the latter is best seen in Fig. 3D, where the XRD patterns of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{y}, r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, ML and filtered delaminated films are compared. After HF etching, the typical XRD peaks ((002), (006), (008), (010), (012) and (110)) of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{y} pattern are obtained, wherein the diffraction peaks in the 35–45° range broaden significantly. More importantly, the 0002 peak shifts downward to a 2θ = 9.02°, and broadens.\textsuperscript{3,5,15} The latter signifies a c-lattice parameter, c-LP, of about 19.5 ± 0.1 Å which is typical of HF-etched Ti\textsubscript{3}AlC\textsubscript{2}.\textsuperscript{4,15} After the Li-EDA treatment (middle pattern in Fig. 3D), the (0002) peak shifts down further to 2θ = 6.5° that corresponds to a c-LP of 27.1 ± 0.1 Å, more typical of Ti\textsubscript{3}AlC\textsubscript{2} etched in the presence of Li.\textsuperscript{32} In the XRD patterns of the films, composed of mostly delaminated flakes, the (0002) peak downshifts further to 2θ = 6.28°, corresponding to a c-LP of 28.1 ± 0.3 Å. It follows that exposing HF-etched Ti\textsubscript{3}AlC\textsubscript{2} to Li-EDA followed by washing in water results in the intercalation of, at least Li\textsuperscript{+} ions and their water of hydration, between the layers. Note the disappearance of the peak at 61°2θ, in the free-standing films. Previously, it was assumed that the loss of this peak signified complete delamination and the formation of a turbostratic MXene.\textsuperscript{15} More recent work\textsuperscript{16} has shown that not to be the case; the loss of this peak simply reflects a better alignment of the basal planes on the substrate as a result of the filtration process. XPS in the Li 1s region confirmed that Li was intercalated between the layers (bottom spectrum in Fig. S2E\textsuperscript{†}). Two peaks, one at 54.2 ± 0.2 eV (red curve) and the other at 55.9 ± 0.2 eV (blue curve), were fitted. The first we assign to Li cations between the layers, and the second is due to LiF salts that are left over from the etching process.\textsuperscript{32} Note that when these films are washed, the Li peaks disappeared (top spectrum in Fig. S2E\textsuperscript{†}). It follows that simply washing the MLs, in excess water, replaces Li by, presumably, hydronium ions.

Finally we turn to the most important result obtained herein, which is the appearance of a paramagnetic signal as a result of the reduction. EPR is a highly sensitive technique that allows for the investigation of paramagnetic species having one, or more, unpaired electrons either in bulk or solutions.\textsuperscript{37} Fig. 4A compares the RT EPR spectra – observed at a magnetic field of 3447 ± 1 G – of Ti\textsubscript{3}AlC\textsubscript{2}, HF-etched Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, and r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} films as a function of reduction temperature. Why the Ti\textsubscript{3}AlC\textsubscript{2} sample did not show an EPR signal is unclear, since it is well established that most MAX phases are Pauli-paramagnets.\textsuperscript{7} For example, the magnetic susceptibility, χ\textsubscript{m} of Ti\textsubscript{3}SiC\textsubscript{2} was found to be ∼4 × 10\textsuperscript{-6} and temperature independent. In contrast, the EPR signal of the HF-etched Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} was weak, but measurable (inset in Fig. 4A). In addition, as the reduction temperature increased from 25 to 120 °C, the EPR peaks became stronger, sharper and more symmetric (Fig. 4A). Sharp EPR spectra of all r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} were observed at a resonance field of B\textsubscript{res} = 3447 ± 1 G, with a peak-to-peak line width of ∆B\textsubscript{pp} = 10 G. The EPR spectra of r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} reduced at 40, 80 and 120 °C showed a signal at g = 1.9998, 1.9993 and 1.9981, respectively. The fact that g is essentially 2 is important in this context because it is the value expected for free electrons. Said otherwise, as discussed in more detail below, the magnetism does not originate from the Ti\textsuperscript{4+} ions – for which g ranges from 1.99 to 1.988\textsuperscript{17} – but rather from delocalized electrons.

Before proceeding further, it is important to describe what structural changes occur when r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} are exposed to different solutions and drying protocols. Fig. S5\textsuperscript{†} shows the XRD results of various treatments carried out on the r-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} films. As shown in Fig. 3D and Fig. S5A\textsuperscript{†} after HF etching, the (0002) peak is found at around 2θ ≈ 9°, (peak labeled i in Fig. S5A\textsuperscript{†}) that corresponds to a c-LP ≈ 19.5 Å, typical of HF
etched Ti$_3$C$_2$Tx. After treatment in EDA, 2θ decreases to ≈6.5°, or a c-LP ≈ 27.1 Å (curve labeled ii in Fig. S5A†). When the latter is dried at 25 °C for 24 h, 2θ increases slightly to ≈6.6°, or a c-LP ≈ 26.7 Å (curve labeled iii in Fig. S5A†). Further drying at 80° for 48 h shifts the peak to ≈7.3°, c-LP ≈ 24.2 Å (curve labeled iv in Fig. S5A†). Finally, drying at 150 °C for 72 h returns the peak position to almost the initial value of ≈9°, with a c-LP ≈ 20.0 Å (curve labeled v in Fig. S5A†). Fig. S5B† shows that after Li intercalation, but prior to washing, the (0002) peak is located at 2θ ≈ 6.5°, or a c-LP ≈ 27.1 Å (curve labeled ii in Fig. S5B†). However, after washing the MLs in ethanol and a 5 wt% HCl solution, during which the Li$^+$ ions are presumably exchanged by protons, the (0002) peak is located at 2θ ≈ 8.5°, or a c-LP ≈ 20.8 Å (curve labeled iii in Fig. S5B†). In other words, by drying or simply washing the intercalated MLs, it is possible to de-intercalate either the EDA or Li ions. The effect of these treatments on the ESR signal is significant. When Li or EDA intercalates between the layers, the paramagnetism vanishes (Fig. 4B); when they are de-intercalated, by washing for e.g., the ESR signal is recovered (Fig. 4B).

To assess the general stability of our r-Ti$_3$C$_2$Tx we stored powders made from the material reduced at 40 °C, either in water or in air. Like most aqueous Ti$_3$C$_2$Tx colloidal suspensions, they started off black (Fig. S6A†). After 2–3 days in water, however, the color of the solution changed to sky blue (Fig. S6B†) indicating that r-Ti$_3$C$_2$Tx is not stable in aerated water. Storing the dried powder in air for 30 days, however, did not alter its color (inset in Fig. S6C†). Most importantly, the ESR signal after storing the samples in air for 30 d was almost identical to that of fresh powders (compare Fig. S5C† and Fig. 4A). It follows that the paramagnetism observed in r-Ti$_3$C$_2$Tx films is robust vis-a-vis atmospheric oxygen if samples are stored in air. These observations are in general agreement with previous work on the oxidation of Ti$_3$C$_2$Tx that has shown that indeed Ti$_3$C$_2$Tx powders are prone to oxidation in oxygen containing water, but much more stable if stored as dried powders.8,15,38

To complement the ESR measurements we carried out magnetization, M, measurements as a function of temperature. As shown in Fig. 4C, the M at 300 K increased with increasing reduction temperatures. The total magnetic susceptibility, $\chi_T$, given by the slope of the M–H plots near the origin – also increased with increasing reduction temperatures. When these measurements were repeated as a function of temperature, $\chi_T$ was found to be more or less constant over the 300 to 20 K temperature range (Fig. 4D). At $T < 20$ K, $\chi_T$ increased.

We can now suggest the following scenario – shown schematically in Fig. 1 – for what occurs when Ti$_3$AlC$_2$ is first etched in HF, reduced with Li-EDA and finally washed. Any
model put forward has to explain a number of important observations, chief amongst them: (i) upon reduction, the Ti$^{4+}$ concentration increases at the expense of the Ti$^{3+}$, (ii) some of the Ti atoms in the Ti$_3$C$_2$T$_x$ are in a +4 oxidation state and (iii) the average oxidation states of the Ti and C in Ti$_3$C$_2$T$_x$ are, respectively, +2.4 and −2.6. For the sake of simplicity, they will henceforth both be assumed to be 2.5; (iv) C atoms are released during the etching step.

We propose the following simplified scheme to model our system. In previous work, the Ti$^{4+}$ signal was ascribed to TiO$_2$ particles generated during the etching process. This work shows that it may not be the case. We will assume that after etching the Ti$_3$C$_2$T$_x$ chemistry is Ti$_3$C$_2$O(OH). If we now replace one of the C atoms with O, the final chemistry is Ti$_3$CO$_2$(OH). This replacement changes the atomic arrangement from O-Ti C-TiO-Ti to O$^{2−}$-Ti$^{4+}$-O$^{2−}$-Ti$^{1.75+}$-C$^{2.5−}$-Ti$^{1.75+}$-(OH)$^{1−}$. The oxidation states chosen are consistent with the fact that the average oxidation states of the Ti and C of +2.5 and −2.5, respectively, and as importantly account for clear evidence for peaks belonging to “TiO$_2$” in Ti$_3$C$_2$T$_x$ (Fig. 3B). Said otherwise, as shown in Fig. 1B, the replacement of a C atom by an O atom creates regions where the Ti ion carries an oxidation state of +4 because it is now surrounded solely by O$^{2−}$ ions.

When the MLs are exposed to Li-EDA, it is reasonable to assume that oxygen vacancies are created according to the following reaction:

$$\text{Ti}_3\text{Ti}^x + \text{O}_c^x = \text{Ti}^y_3 + \text{V}^x_O + \frac{1}{2} \text{O}_2$$  \hspace{1cm} (1)

Said otherwise, as shown in Fig. 1c, exposure to Li-EDA removes a near surface O and one of the electrons released converts one Ti$^{4+}$ ion to Ti$^{3+}$. The second electron most likely is localized on the vacant oxygen sites, forming V$_O^x$. The latter are most probably the localized states near $E_F$ that are responsible for the Curie-type component of the Pauli paramagnetic behaviour observed at $T < 10$ K discussed below.

The density of electronic carriers in the MAX phase and their MXene is quite large (of the order of $10^{27}$ m$^{-3}$). Consequently, as noted above, most MAX phases are Pauli paramagnets, wherein the magnetic susceptibility, $\chi_{P}$, is independent of temperature and given by:

$$\chi_P = \mu_0 \mu_B^2 N(E_F)$$  \hspace{1cm} (2)

where $\mu_0$ is the permeability of free space, $\mu_B$ is the Bohr magneton and $N(E_F)$ is the DOS at $E_F$, per energy per unit volume. Knowing $\chi_P$, $N(E_F)$ can be calculated from eqn (2). These results are listed in Table 1.

Fig. 4F reproduces the DOS for Ti$_3$C$_2$O$_2$ calculated by Yu and Kent. Here the DOS at $E_F$ is $\approx 0.5$ eV per formula unit. Assuming that the thickness of a Ti$_3$C$_2$O$_2$ flake is 1 nm – a value slightly higher than $\frac{1}{2}$ the c-LP of Ti$_3$AlC$_2$ and the value measured by AFM on single flakes$^{41}$ – the theoretical DOS at $E_F$ is $3.9 \times 10^{46}$ J$^{-1}$ m$^{-3}$. Coincidentally or not, this value is in excellent agreement with the value, $5.3 \times 10^{46}$ J$^{-1}$ m$^{-3}$, obtained here for Ti$_3$C$_2$T$_x$ (Table 1). This agreement is even more impressive when it is appreciated that the chemistry of our MXene is not Ti$_3$C$_2$O$_2$ and is defective. Note that the values for the MXene samples reduced at 80 °C and 120 °C are significantly higher than the theoretical values, which can be attributed at least partially to defects and the fact that our chemistry is relatively far from Ti$_3$C$_2$O$_2$.

The results shown in Fig. 4D suggest that at $T < 10$ K, a temperature dependent Curie-like term, $\chi_C$, given by:

$$\chi_C = \frac{\mu_B \mu_B^2 N_s}{k_B T} = \frac{C}{T}$$  \hspace{1cm} (3)

comes into play. Here, $T$ is the absolute temperature, $k_B$ is Boltzmann’s constant and $N_s$ is the number of singly occupied states, with spin $\frac{1}{2}$ per unit volume. The total susceptibility, $\chi_T$, is thus given by:

$$\chi_T = \chi_C + \chi_P$$  \hspace{1cm} (4)

To check the validity of eqn (3) and (4), $1/(\chi_T - \chi_P)$ vs. $T$ was plotted (Fig. 4E) and indeed straight lines – mostly passing through the origin, with $\chi^2$ values $>0.99$ – were obtained. To make sense of these results, we assume our system is that of a disordered metal, close to a metallic to insulator, M-I, transition, and where $E_F$ is near the mobility edge. In that case, the susceptibility is given by:

$$\chi(T) = \frac{2\mu_B \mu_B^2 \beta}{k_B T} \sum_{i} \frac{1}{2 + e^{\beta(\epsilon_i - U)}} + e^{-\beta(\epsilon_i - U)}$$  \hspace{1cm} (5)

where $\beta = 1/k_B T$, $\mu$ is the chemical potential, $\epsilon_i$ are the energies of the localized states and $U$ is the average intrasite electron-electron Coulomb interaction energy. At high temperatures, eqn (2) is recovered. However, at temperatures sufficiently low that $k_B T < U$, states near $E_F$ become singly occupied and $C$ is given by eqn (3). Kamimura et al$^{43}$ called the transition between a temperature independent Pauli type behavior and a Curie-law type a cross-over temperature, $T_C$, for which $k_B T_C \approx U$. It
follows that the number of sites that are singly occupied, \(N_p\), per unit volume is given by:\(^{42}\)

\[
N_p \approx UN(E_F) \approx k_B T_C N(E_F)
\]

(6)

where \(T_C\) is the temperature at which the electron–electron interactions are comparable to the thermal energy in this disordered metal near the boundary of the M–I transition. From Fig. S7, \(T_C\) can be estimated as the temperature at which the intersection of the \(T\) dependent and temperature independent portions of \(\chi\) intersect. Based on this, admittedly, crude analysis, \(T_C\) ranges from 5 to 10 K (see column 5 in Table 1). It follows that at \(\approx 0.4\) to 0.7 meV, the \(U\) values are thus quite small presumably because of the metallic screening of the high concentration of mobile electrons. For comparison, Sariciftci et al.\(^{42}\) have shown that in some conductive polymers, \(T_C\) is of the order of 50 K and \(U \approx 4–5\) meV.

The value of \(N_0\) obtained from Curie’s law should be equal to \(N_p\) calculated from eqn (6). A comparison of columns 6 and 7 shows that the maximum discrepancy is a factor of \(\approx 4\). This agreement – from totally independent measurements – has to be considered good considering the many simplifying assumptions made in deriving eqn (2) and (3), the most egregious of which is the assumption of a spherical Fermi surface, totally free electrons, etc.

The Curie-like contributions to the susceptibility arise from single occupancy of localized states near \(E_F\).\(^{42}\) Based on the totality of our results, it is reasonable to assume that these localized states are locations where C atoms were first replaced by \(\text{O}^{2-}\) ions during the etching process. The reduction process removes these ions and replaces them with oxygen/carbon vacancies. Again assuming the thickness of a single Ti\(_3\)C\(_2\)O\(_2\) flake to be 1 nm, then the total number of C-sites is \(\approx 2.5 \times 10^{28}\) m\(^{-3}\). The fraction of vacant sites, \(f_v\), is thus of the order of \(\approx 10^{25}/2.5 \times 10^{28}\), or \(\approx 0.0004\). This value is quite low and suggests that there is quite a bit of room to further enhance \(\chi\) with say more aggressive or longer reduction protocols. The corresponding value reported by Sariciftci et al.\(^{42}\) for conductive polymers is 0.001.

The last piece of the puzzle that needs to be addressed is why when \(\text{Li}\) or \(\text{EDA}\) intercalates between the layers, the paramagnetism vanishes (Fig. 4B). If indeed the system is poised between a M–I transition, then it would be reasonable to assume that upon intercalation and the transfer of electrons from the MXene sheets to the intercalant, the system is pushed into an insulating state. This important conclusion is backed by DFT calculations on Ti\(_3\)C\(_2\)O\(_2\) reproduced in Fig. 4F, from which it is obvious that \(E_F\) – given by the solid vertical line – is clearly at the upper edge of a pseudogap. When Ti\(_3\)C\(_2\)O\(_2\) is reduced, \(E_F\) moves presumably to the right and the DOS at \(E_F\) increases accordingly. When, on the other hand, those same electrons are transferred to the intercalant, \(E_F\) can easily shift into the pseudogap, where the DOS is significantly reduced. This interpretation would thus explain the loss of the ESR signal upon intercalation. In other words, the results and conclusions are totally consistent with the assumption that the system is close to an M–I transition. In such a system an increase in electrical conductivity upon reduction should be observed and indeed one was found. The average resistivity of 40 \(\mu\)m thick filtered films before reduction was about \(40 \pm 3\) \(\Omega\) cm\(^{-1}\); after reduction, at \(28 \pm 2.5\) \(\Omega\) cm\(^{-1}\), i.e. the average resistivities were reduced by a third. We note in passing that when the EDA or \(\text{Li}^+\) ions are de-intercalated they are replaced by protons. Why the latter do not reduce the EPR signal is an open question at this time and beyond the scope of this paper.

IV. Conclusions

We developed a new, facile, solution-based synthetic method to reduce 2D Ti\(_3\)C\(_2\)T\(_x\) multilayers by immersing them in the strong reducing agent, Li-EDA. XPS spectra provided strong evidence for the formation of Ti\(^{3+}\) ions and by extension oxygen vacancies. The chemically reduced Ti\(_3\)C\(_2\)T\(_x\) films are Pauli paramagnetic in that the magnetization is not a function of temperature in the 20 to 300 K temperature range. The magnetism, however, does not stem from the defects, but from changes in the DOS at \(E_F\). This allowed us to experimentally determine, for the first time, the DOS at \(E_F\). The latter are in reasonable agreement with theoretical predictions, lending credence to both. The fact that the paramagnetism disappears when the layers are intercalated is strong evidence that the paramagnetism is related to the MXene layers and is not, for example, emanating from reduced TiO\(_2\) nanoparticles. In the reduced TiO\(_2\) literature, Ti\(^{3+}\) is sometimes found to be the origin of the ESR signal. The fact that herein \(g \approx 2\) eliminates Ti\(^{3+}\) as the magnetism’s source.

Reducing Ti\(_3\)C\(_2\)T\(_x\) flakes in the super base Li-EDA – at temperatures between 25 °C and 120 °C – resulted in a significant increase in their Pauli paramagnetism and concomitantly the concentration of Ti\(^{3+}\) ions. At temperatures <10 K, a Curie-like contribution is observed, indicative of interacting, singly occupied states at \(E_F\). The latter are presumed to be C/O vacancies. To explain these results, we assume MXenes to be a disordered metal near a metal–insulator transition. Making this assumption we can not only explain why the DOS at \(E_F\) increases substantially with increased reduction temperatures, but also the disappearance of a magnetic signature upon intercalation with \(\text{Li}\) or EDA. At temperatures below about 10 K, the singly occupied states near \(E_F\) presumably interact with each other with a coulombic energy of the order of \(\approx 0.4\) to 0.7 meV.

To conclude, by successfully reducing Ti\(_3\)C\(_2\)T\(_x\) we greatly enhanced its paramagnetic properties and indirectly shed light on the nature of DOS near \(E_F\). This technique is thus a powerful, relatively straightforward technique to shed important light on conduction in these new, and potentially quite useful, 2D materials. The as-reduced MXenes can be easily further applied to various applications such as photo and electrocatalysts, solar cells and magnetic and electronic devices.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

H. L. and T. A. L. acknowledge support from the Institute for Basic Science (IBS-R011-D1). Y. Y. acknowledges support from the National Research Foundation of Korea (NRF) under grant no. NRF-2017R1A6A3A11033347. MWB acknowledges the support of the Swedish Research Council [Grant # 621-2014-4890].

Notes and references


