The $c$-axis dimer and its electronic break-up: the insulator-to-metal transition in Ti$_2$O$_3$

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We report on our investigation of the electronic structure of Ti$_2$O$_3$ using (hard) x-ray photoelectron and soft x-ray absorption spectroscopy. From the distinct satellite structures in the spectra we have been able to establish unambiguously that the Ti-Ti $c$-axis dimer in the corundum crystal structure is electronically present and forms an $a_{1g}$-$a_{1g}$ molecular singlet in the low temperature insulating phase. Upon heating we observed a considerable spectral weight transfer to lower energies with orbital reconstruction. The insulator-metal transition may be viewed as a transition from a solid of isolated Ti-Ti molecules into a solid of electronically partially broken dimers where the Ti ions acquire additional hopping in the $a$-$b$ plane via the $e_g^0$ channel, the opening of which requires the consideration of the multiplet structure of the on-site Coulomb interaction.

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The role of ion pair formation for the metal-insulator transition (MIT) in early transition metal oxides with the octahedra sharing either a common face or a common edge has been a matter of debate in the past several decades. Based on the presence of the $c$-axis V–V dimers in the corundum crystal structure of V$_2$O$_3$, C. Castellani et al.

proposed a molecular singlet model for the $a_{1g}$ orbitals, projecting the system effectively onto a solid with $S = 1/2$ entities which then should carry the essential physics for the MIT and the magnetic structure in the antiferromagnetic insulating phase. However, soft x-ray absorption spectroscopy (XAS) experiments

showed that the two $d$ electrons on each V are in the high-spin $S = 1$ state, implying that the atomic Hund’s rule coupling is much stronger than the intra-dimer hopping integrals. Furthermore, using band structure calculations

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found that the intra-dimer hopping integral is not the most important one, rather that the hopping integrals between second, third and fourth nearest V neighbors are at least equally important: in other words, the $c$-axis dimers need not to be present electronically although structurally they are there.

Ti$_2$O$_3$ shares much of the fascination as V$_2$O$_3$. It has also the corundum crystal structure (see the inset in Fig. 1) and exhibits upon lowering the temperature a MIT. The earliest models explained the low-temperature insulating phase of Ti$_2$O$_3$ by assuming a band splitting caused by an antiferromagnetic long-range order. However, different from V$_2$O$_3$, the transition is gradual and is not accompanied by a structural transition nor magnetic ordering. It was also proposed by Goodenough and van-Zandt et al. that the short $c$-axis pair bond length, which is with 2.578 Å at 300 K much shorter than in V$_2$O$_3$ at 300 K, increases the trigonal crystal field splitting so that the conductivity gap is opened. This model is, however, contradicted by band structure calculations which showed that the overlap of the $a_{1g}$ and $e_g^0$ orbitals can only be suppressed for an unrealistically short bond length, i.e. Ti$_2$O$_3$ is a metal at all temperatures with mixed $a_{1g}$-$e_g^0$ states for the $c$-axis dimer from the point of view of band theory. Correlation effects have to be included in one way or another to explain the insulating ground state in Ti$_2$O$_3$.

Here we report on our spectroscopic study of the electronic structure of Ti$_2$O$_3$ with the goal to determine whether and how correlation effects and the $c$-axis dimer play a role for the formation of the low-temperature insulating phase. Moreover, we would like to identify the key factors in the electronic structure that can transform the compound from an insulator into a metal. We found in our spectra direct evidence that Ti$_2$O$_3$ is a strongly correlated system in which the $c$-axis Ti-Ti dimers form isolated $a_{1g}$-$a_{1g}$ molecular singlets at low temperatures, and
that at high temperatures the dimers partially break-up electronically with the Ti ions gaining hopping in the a-b plane via the $e^g_\pi$ channel. Crucial is that the orbital switching from $a_{1g}$ towards $e^g_\pi$ is possible only if the multiplet aspect of the on-site Coulomb interaction is another decisive element in the electronic structure of Ti$_2$O$_3$.

X-ray photoelectron spectroscopy (XPS) measurements with $h\nu = 1486.6$ eV were performed in Cologne using a Vacuum Generators twin crystal monochromatized Al-K$\alpha$ source and a Scienta SES-100 electron energy analyzer. The overall energy resolution was set to 0.4 eV. Hard x-ray photoelectron spectroscopy (HAX-PES) experiments were carried out at the ID16 beamline of the ESRF using the VOLPE spectrometer with $h\nu = 5931$ eV and an overall resolution of 0.4 eV, as well as at the Taiwan beamline BL12XU at SPring-8 using the Max-Planck-NSRRC end-station equipped with a MB Scientific A-1 HE hemispherical analyzer employing $h\nu \approx 6.5$ keV and an overall resolution of 0.2 eV. Soft-x-ray absorption spectra (XAS) were collected at the Dragon beam line at the NSRRC in Taiwan in the total electron yield mode with a photon energy resolution of 0.25 eV and degree of linear polarization of 98%. All spectra were collected from freshly in vacuo cleaved Ti$_2$O$_3$ single crystals. Ti$_2$O$_3$ single crystals were grown by using the floating zone method. The purity and structure of crystals were verified as a single phase crystal by using EDX, powder diffraction measurements, Laue and polarization microscopy. The stoichiometry of the crystals has been characterized by thermogravimetric analysis.

Figure 1 shows the valence band XPS spectrum of Ti$_2$O$_3$ taken at 300 K, i.e. in the insulating phase. The group of peaks at 4–11 eV binding energies is mainly the contribution of O 2p states. The lower binding energy region from the Fermi level up to 4 eV consists of mainly the Ti 3d. This part of the spectrum is characterized by two distinct spectral features. The main line (M) is a quite symmetric peak centered at about 0.68 eV with a width of $\approx 0.8$ eV (FWHM). The semiconducting or insulating nature of Ti$_2$O$_3$ at room temperature [2, 28, 29] is reflected by the fact that the spectral weight vanishes at the Fermi level, in agreement with earlier photoemission reports [30, 31] and the observation of a 0.2 eV gap in the optical conductivity [18, 30].

The second feature is a somewhat broader but clearly noticeable satellite (S) at around 2.43 eV binding energy. The origin of this peak has so far been disputed. Ultraviolet photoelectron spectroscopy (UPS) studies had speculated that it was a surface state with a considerable 3d band character [30, 31]. However, an angle-resolved UPS study was not able to confirm this speculation [32]. We claim here that our spectrum is representative for the bulk material, i.e. that both features M and S belong to the photoemission spectrum of bulk Ti$_2$O$_3$. This relies on the fact that our spectrum was taken on a cleaved single crystal at normal emission with a photon energy of 1486.6 eV, thereby obtaining larger probing depths [37-39]. Below we will also provide more spectroscopic evidence that all our spectra are representative for the bulk.

The absence of any spectral weight at the Fermi level in the low temperature phase of Ti$_2$O$_3$ invalidates the predictions of band structure calculations [3, 6, 13] which always display a finite density of states at the Fermi level. This is a strong sign that correlation effects play a crucial role. Indeed, using hybrid functionals, non-local exchange, or dynamical mean field approaches (DMFT), one can recover a band gap in the calculations [12, 25-27]. Interestingly, all calculations except the two-site cluster DMFT [12] did not produce a satellite structure like the feature S we observe at 2.43 eV binding energy. Somewhat puzzling is yet that the two-site cluster DMFT calculation did produce a satellite structure, but with a much too low intensity.

In order to unveil the origin of the satellite structure S, we now resort to configuration interaction cluster calculations with full atomic multiplet theory, an approach which is very successful to explain quantitatively the basic features in many photoelectron and x-ray absorption spectra of 3d transition metal oxides [10, 13]. We start with the standard single transition metal site cluster, i.e. a TiO$_6$ octahedral cluster with the Ti ion in the center [34], and use model parameters typical for titanium oxides [12, 41, 44, 45]. We find that the Ti 3d one-electron removal spectrum near the Fermi level consists of a single peak, see the blue curve in Fig. 1. Satellite S is not re-
produced in a single-site cluster. Next, motivated by the presence of the Ti-Ti c-axis dimer in the crystal structure, we calculate the spectrum of a Ti$_9$O$_9$ cluster consisting of two face-shared TiO$_6$ octahedral units along the c-axis, using the same parameters as for the TiO$_6$ cluster, but with the addition of a parameter describing the inter-Ti hopping \cite{4}. The result is given by the red curve in Fig. 1 and we can observe that both the satellite structure S and the main peak M can be reproduced very well.

To interpret this result, we can use the following schematic model. The relevant orbital in this Ti-Ti dimer is the one pointing along the bond, namely the $a_{1g}$. With each Ti ion having the 3+ valence, we then consider the following singlet configurations forming the ground state: $a_{1g}Aa_{1g}B$, $a_{1g}Aa_{1g}A$, and $a_{1g}Ba_{1g}B$, where A and B denotes the two Ti sites. The configurations with the double occupation on one site have the extra energy Hubbard $U$, and the hopping integral between the $a_{1g}A$ and $a_{1g}B$ orbitals is denoted by $t$ \cite{40}. The photoemission final states, in which one electron has been removed, are given by the following two configurations, namely $a_{1g}A$ and $a_{1g}B$, which are degenerate in energy and form bonding and anti-bonding states with energies $-t$ and $+t$. Their energy separation, $2t$, can then be read directly from the energy separation between feature M and S, i.e. $2t \approx 1.75$ eV ($t = 0.88$ eV). The intensity ratio between M and S is determined by $U/t$. For $U/t = 0$, the intensity of the satellite S vanishes and we are back in a one-electron approximation. In the limit of $U/t \to \infty$, M and S will have equal intensities. From the experimental intensity ratios, we estimate that $U/t$ is about 3–4, i.e. $U \approx 2.5–3.5$ eV. The essential outcome of the Ti$_9$O$_9$ cluster calculation is thus that the inter-site Ti hopping together with the on-site Coulomb interaction produces a main line M with a satellite structure S, and that the presence of M and S shows that there is a strong electronic bond between the two Ti ions of the dimer.

In order to collect more evidence for the presence of the strong electronic bond within the Ti-Ti c-axis dimer we now investigate the Ti 2p core level spectrum. Fig. 2 shows the Ti 2p core level spectrum of Ti$_2$O$_3$ taken at 300 K with $h\nu = 1486.6$ eV (black line, XPS), with $h\nu = 5931$ eV (red circle, HAXPES ESRF), and with $h\nu \approx 6500$ eV (dark green triangle symbol, HAXPES SPring-8), and experimental Ti 2p core-level photoemission spectra of YTiO$_3$ taken at 300 K (navy circle) and of LaTiO$_3$ taken at 200 K (green line) with $h\nu \approx 6500$ eV (HAXPES SPring-8). Also shown are the theoretical configuration interaction calculations using a TiO$_6$ (blue line) and a Ti$_2$O$_9$ (red line) cluster, see text.

![Graph showing Ti 2p core-level photoemission spectra](image)

**FIG. 2:** Experimental Ti 2p core-level photoemission spectra of Ti$_2$O$_3$ taken at 300 K with $h\nu = 1486.6$ eV (black line, XPS), with $h\nu = 5931$ eV (red circle, HAXPES ESRF), and with $h\nu \approx 6500$ eV (dark green triangle symbol, HAXPES SPring-8), and experimental Ti 2p core-level photoemission spectra of YTiO$_3$ taken at 300 K (navy circle) and of LaTiO$_3$ taken at 200 K (green line) with $h\nu \approx 6500$ eV (HAXPES SPring-8). Also shown are the theoretical configuration interaction calculations using a TiO$_6$ (blue line) and a Ti$_2$O$_9$ (red line) cluster, see text.

To quantify the observations, we calculate the Ti 2p electron removal spectrum using the single-site Ti cluster, i.e. TiO$_6$, and the two-site Ti cluster, i.e. Ti$_2$O$_9$, as described above. The result for the TiO$_6$ cluster is shown by the blue line in Fig. 2 the calculated spectrum is essentially similar to the one reported in Ref. \cite{59}, and it reproduces excellently the YTiO$_3$ and LaTiO$_3$ spectra. The result for the Ti$_2$O$_9$ cluster is quite different from that of the TiO$_6$ cluster, and matches very well the experimental Ti$_2$O$_3$ spectra including the high intensity satellite features S1 and S2. These findings show that the Ti ions in YTiO$_3$ and LaTiO$_3$ are relatively isolated, while in Ti$_2$O$_3$ they form electronically very strongly bonded pairs, fully consistent with the analysis for the valence band spectrum discussed above.

Having established the electronic presence of the c-axis dimers, we need to determine or to verify that different batches of Ti$_2$O$_3$ samples, and using the XPS in our home laboratory as well as the more bulk sensitive HAXPES at two different experimental stations (ESRF and SPring8), all to verify that the spectra we were collecting are indeed reproducible. The second aspect to notice, is that the Ti$_2$O$_3$ spectra are very different from those of YTiO$_3$ and LaTiO$_3$, despite the fact that all are Ti$^{3+}$ 3$d^5$ compounds. The satellites marked as S1 and S2 have truly massive intensities, indicative of essential differences in the local electronic structure between Ti$_2$O$_3$ and YTiO$_3$/LaTiO$_3$. 

![Graph showing binding energy vs intensity](image)
FIG. 3: Panel (a): Experimental polarization-dependent Ti-\(L_{2,3}\) XAS spectra of Ti_2O_3 taken at 150 K, 300 K, 458 K, 500 K and 575 K. Panel (b): Calculated polarization-dependent Ti-\(L_{2,3}\) XAS spectra for the corresponding temperatures using a TiO_6 cluster. Panel (c): Close up of the experimental linear dichroic (LD) spectrum in the low temperature phase (blue and black circles) and the simulation using a TiO_6 (green line: \(a_1g\)) and a Ti_2O_9 (red line: \(a_1g a_1g\)) cluster. Panel (d): temperature dependence of the Ti 2p core level spectrum.

the relevant orbitals which form the bond are the Ti \(a_{1g}\). We need also to investigate how this orbital occupation may evolve as a function of temperature across the insulator-metal transition. The panel (a) of Fig. 3 shows the polarization-dependent Ti \(L_{2,3}\) XAS spectra of Ti_2O_3 taken at 150 K, 300 K, 458 K, 500 K and 575 K, i.e. from deep in the insulating low temperature phase, across the gradual insulator-metal transition, and well into the metallic high temperature phase. We can observe a strong polarization dependence indicative of a distinct orbital occupation of the Ti 3d shell. We can also notice that the polarization dependence decreases across the transition. In order to quantitatively extract the orbital occupation of the Ti 3d states from these Ti \(L_{2,3}\) XAS spectra, we simulated the spectra using the Ti_2O_9 cluster. The results are shown in the panel (b) of Fig. 3. We can clearly observe the excellent overall match between experiment and theory for all temperatures.

Focusing first on the low temperature phase, we find that the 150 K and 300 K spectra can be very well described by a Ti-Ti \(c\)-axis dimer in an essentially pure \(a_{1g} a_{1g}\) singlet ground state. Also a close-up look at the dichroic spectrum, i.e. the difference between the spectrum taken with E \(\parallel\) c and the spectrum with E \(\perp\) c spectra, where E denotes the electric field vector of the incoming light, shows that the \(a_{1g} a_{1g}\) ground state reproduces the experiment to a great detail, see panel (c) of Fig. 3 (experiment: blue and black dots; simulation: red line). By contrast, a single-site TiO_6 cluster with a \(a_{1g}\) initial state produces a significantly poorer fit (green line). The low temperature XAS spectra thus not only confirm fully the findings from the photoemission experiments shown above about the strong intra-dimer electronic bond but also that this bond is formed by the \(a_{1g} a_{1g}\) singlet.

With this finding we in fact restore the presumptions of the early model by Goodenough and van-Zandt et al. [1, 2] for the insulating state, namely that the ground state is given by the dimer in the \(a_{1g} a_{1g}\) singlet. This model has been rejected for decades by band structure calculations [3, 6, 13] on the basis that these calculations found a heavily mixed orbital occupation. We also validate completely the starting point of the Mott-Hubbard model by Tanaka [11], thereby correcting the numbers found in an earlier polarization dependent Ti \(L_{2,3}\) XAS experiment [17]: by extending our experiment to lower temperatures, we ensure that our low temperature spectrum is taken from deep inside the insulating phase, and by including the O 2p ligands in our analysis, we were able to obtain a better match between the simulation and experiment as shown in panel (c) of Fig. 3.

Concerning the temperature evolution, the decrease in the polarization dependence of the XAS spectra across the gradual insulator-metal transition can be ascribed to
a re-population of the Ti 3d orbitals. Our simulations find that the occupation of the $a_{1g}$-$a_{1g}$ singlet state is reduced to 78%, 72%, and 49% for $T = 458$ K, 500 K and 575 K, respectively. The $e_g$ orbitals of the Ti $t_2g$ shell get more and more occupied. The Ti ion thus becomes electronically less anisotropic, thereby also weakening and eventually, breaking-up the electronic bond of the $c$-axis dimer. This is mirrored by the strong changes in the Ti core-level spectrum and in particular in the reduction of the satellites S1 and S2 intensities, see panel (d) of Fig. 3. Also the lengthening of the $c$-axis dimer bond distance across the gradual insulator-metal transition can be viewed as a weakening of the bond.

The partial break-up of the dimer and the orbital reconstruction with temperature have consequences for the states closest to the chemical potential. In the left panel of Fig. 4 we display a close-up of the valence band collected with the bulk-sensitive HAXPES method and in the right panel we show the threshold region of the O K edge XAS as an indicator for the unoccupied states. We can clearly observe the gradual closing of the band gap. Perhaps more striking is the fact that spectral weight is transferred over an energy range of 0.3 eV on both sides of the chemical potential. Similar effects can also be seen in the optical conductivity. One may try to explain these changes in terms of large shifts in the energies of the relevant orbitals, or perhaps also in terms of large changes in the strength of the intra-dimer hopping integrals, but the density of states from band structure calculations show only modest changes with temperature.

We therefore have to take strong electron correlation effects explicitly into account in the explanation, so that small changes in the one-electron band width and in the strength of the effective Coulomb interaction $U_{eff}$ can lead to large changes in the electronic structure, e.g., a MIT with a large transfer of spectral weight. The key issue for $\text{Ti}_2\text{O}_3$ is the orbital reoccupation away from a pure $a_{1g}$-$a_{1g}$ dimer singlet state at low temperatures. Those dimers are electronically isolated from each other in the solid: the hopping in the $a$-$b$ plane for electrons in the $a_{1g}$ orbital (oriented along the $c$-axis) is small ($\lesssim 1$ eV) compared to the Coulomb energy $U_{eff}=U$, where $U$ ($\approx 3$ eV, see above) is the energy repulsion between two electrons doubly occupying the same $a_{1g}$ orbital of one particular Ti site after such a hopping process in the plane.

If on the other hand, the electrons are also allowed to occupy the $e_g$ orbitals, then the hopping in the $a$-$b$ plane will be greatly enhanced, simply because the $e_g$ orbitals are much more directed in this plane. Moreover, after such a hopping the doubly occupied state can be a triplet (high spin) $a_{1g}e_g^\pi$. The effective Coulomb energy $U_{eff}$ then will be given by $U'-J_H$, where $J_H$ denotes the gain in Hund’s rule exchange energy for pairs of spin-parallel electrons, and where $U'$ is the energy repulsion between electrons in different orbitals, to be distinguished from $U$ which is for electrons in the same orbital. $U'$ is smaller than $U$ by about $2J_H$, so that $U_{eff}$ for the $a_{1g}e_g^\pi$ situation is smaller by an amount of $3J_H$ than the $U_{eff}$ for the $a_{1g}$-$a_{1g}$. Considering that $J_H$ is typically 0.7 eV, $U_{eff}$ for the $a_{1g}e_g^\pi$ can be 2.1 eV smaller than that for the $a_{1g}$-$a_{1g}$. So for the $a_{1g}e_g^\pi$ situation the $e_g^\pi$ band width in the $a$-$b$ plane ($\approx 1.5$ eV) can overcome $U_{eff}$ ($\approx 0.9$ eV) as to stabilize a metallic state.

To justify that converting a dimer in the singlet $a_{1g}$-$a_{1g}$ situation into a dimer with the triplet $a_{1g}e_g^\pi$ requires only a modest amount of energy, we need to estimate the dimer’s total energy in each situation. For the $a_{1g}$-$a_{1g}$, the hopping between the state with one electron on each Ti and the state with one of the Ti doubly occupied and the other empty is given by $\sqrt{2}t_{a_{1g}}$ (there are two ways to make the latter state, thus the $\sqrt{2}$ factor). The $U_{eff}$ is given by $U$, see above. For the $a_{1g}e_g^\pi$, the hopping between the state with one electron on each Ti and the state with one of the Ti doubly occupied and the other empty is given by $t_{a_{1g}}$ (here we neglect the hopping of the $e_g^\pi$ along the $c$-axis completely). The $U_{eff}$ is $U'-J_H$, see above. Thus, whereas for the $a_{1g}$-$a_{1g}$ both the hopping and $U_{eff}$ are large, for the $a_{1g}e_g^\pi$ both the hopping and $U_{eff}$ are small. One can therefore argue that together with lattice effects one can find physically reasonable parameters as to keep the total energy difference between the two situations within 0.1 eV. These findings provide strong experimental support for the theoretical model proposed by Tanaka to explain the MIT in $\text{Ti}_2\text{O}_3$.

To summarize, using a combination of photoelectron and polarized x-ray absorption spectroscopy we were able to establish that the low temperature phase of $\text{Ti}_2\text{O}_3$ can be viewed as a collection of isolated $c$-axis Ti-Ti dimers in the singlet $a_{1g}$-$a_{1g}$ configuration. Upon heating and crossing the gradual insulator-metal transition, the dimers start to break-up with a reoccupation of the orbitals. The availability of the $e_g^\pi$ channel increases the hopping
within the $a$-$b$ plane. The smaller effective Coulomb interaction for the triplet $a_{1g}e_g^3$ configuration facilitates the orbital reconstruction and the stabilization of the metallic state at high temperatures.

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