



	<b>Experiment title:</b> <b>Local coordination and electronic structure of doped nanostructured TiO<sub>2</sub></b>	<b>Experiment number:</b> HE 2317
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### **Preliminary Report:**

The change of electronic structure in semiconductors upon doping is a central question in materials science. TiO<sub>2</sub> takes an prominent role because of its importance in photochemistry. The goal of the beamtime was to explore the potential of X-ray emission detection with lifetime resolution (XES) in the study of local electronic changes and to apply new spectroscopic techniques to study doped TiO<sub>2</sub>. We focused on (non-)resonant XES on rutile and anatase TiO<sub>2</sub> doped with W and Zr. Using a Si(311) reflection for the incident energy and a Ge 331 (R=1000 mm) analyzer crystal for Ti XES we achieved a combined energy bandwidth of 1.0 eV, mainly limited by geometrical contributions. The W X-ray L $\alpha$  and L $\gamma$  emission could be measured using the same analyzer crystal orientation Si(111) (R=500 mm) and by observing either the 444 or 555 reflection. Furthermore, a Si(111) monochromator was used for the incident energy. The overall experimental energy bandwidth for the W experiments around the Fermi level was 3.3 eV. In terms of experimental feasibility we achieved remarkable results. All attempted X-ray emission techniques showed sufficient contrast:

- 1) Resonant X-ray emission (resonant inelastic X-ray scattering) spectroscopy at small energy transfers (< 10 eV) after resonant 1s to 3d excitation (first pre-edge feature) in TiO<sub>2</sub> gave 400 cts/sec. This opens up the possibility of measuring low energy (optical) excitations in Ti(IV) systems and, using the resonance effect, to disentangle O 2p from Ti 3d contributions in the valence band electronic structure.
- 2) Using RIXS and angular dependence on TiO<sub>2</sub> rutile single crystals we were able to unequivocally identify 4 contributions to the TiO<sub>2</sub> pre-edge. This has been suggested before mainly by calculations.[1] However, by observing a similar pre-edge structure in TiO(acac)<sub>2</sub> as in TiO<sub>2</sub> we tend to reject the idea of strong Ti-Ti orbital hybridization in order to explain the four pre-edge peaks.
- 3) High-energy resolution fluorescence detected (HERFD) XANES spectra of W using the L $\alpha_1$  emission line reveal the orbital splitting in the 5d shell.

- 4) We recorded, to our knowledge for the first time, XES spectra of a 5d element just below the Fermi level. This opens up a realm of new applications for 5d systems. Spectra were taken on W oxides as well as on W in TiO<sub>2</sub>.

The 1s3p RIXS planes of TiO<sub>2</sub> in anatase and rutile form are shown in Figure 1. Three strong structures can be seen. The center structure shows a pronounced shoulder toward larger energy transfer. We can thus identify two pairs of excitations. These pairs turn out to gain their spectral intensity mainly from quadrupole and dipole transition matrix elements, respectively. This is in agreement with theoretical models.[2] Energy position and spectral strength of this shoulder changes depending on the crystal structure. Scans at constant emission energy move along diagonal lines in the RIXS plane. By changing the emission energy one can emphasize either the first or the second pair pre-edge excitations.

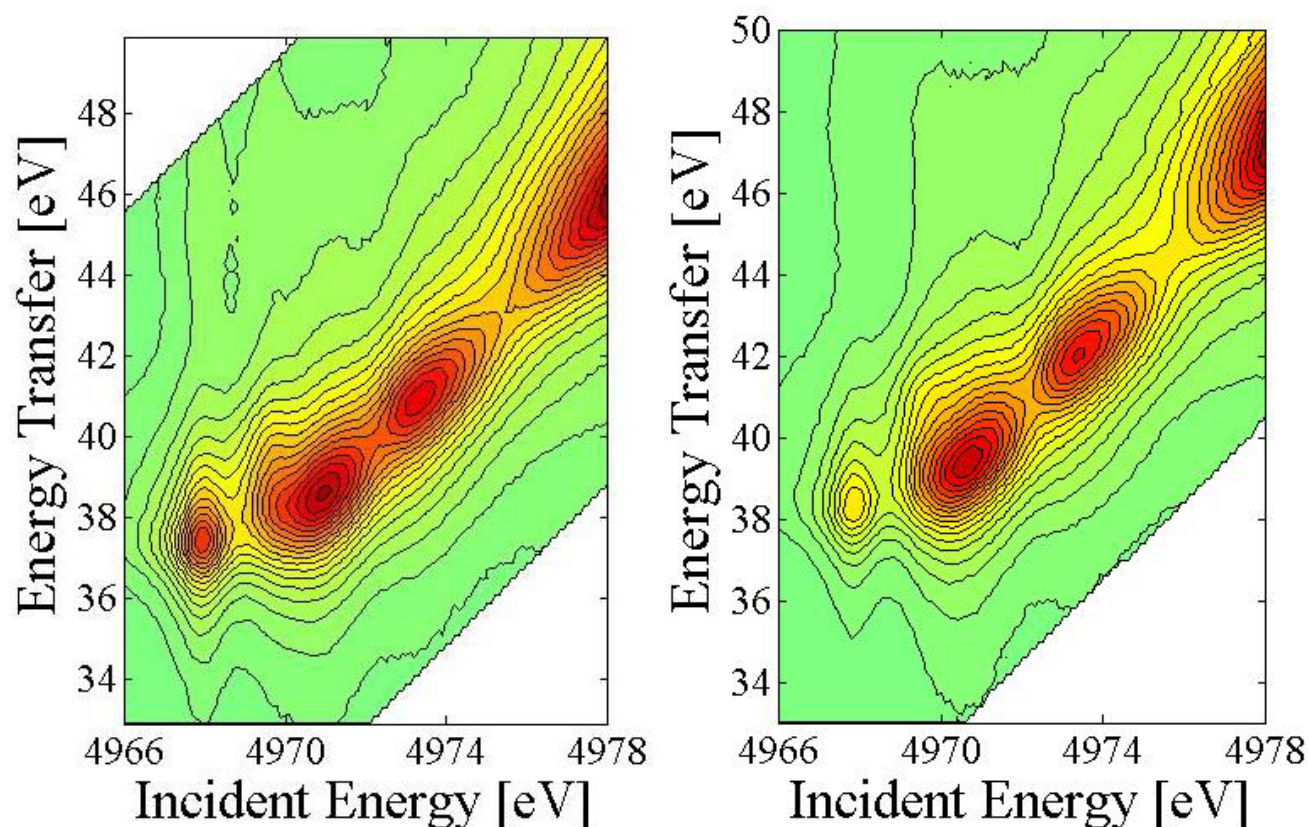


Figure1: 1s3p RIXS planes of TiO<sub>2</sub> in anatase (left) and rutile (right) from.

Figures 2 and 3 show the pre-edges in TiO<sub>2</sub> anatase and rutile as well as TiO(acac)<sub>2</sub>. Figure 3 shows how the low energy quadrupole excitations into the 3d orbitals can be emphasized by choosing appropriate emission energies. All compounds show four excitations at similar energies however with changing relative intensities. This indicates the same origin for all peaks (two local and two non-local excitations) but with changing hybridization strengths between the 3d and the ligand orbitals. Ti-Ti interactions are expected to be considerably weaker in TiO(acac)<sub>2</sub> because of the large ligands. However, the dipole excitations show similar strength as in TiO<sub>2</sub> and we thus assume that Ti-Ti interactions only contribute weakly to the pre-edge spectral intensity.

It is noteworthy that the peak positions hardly change between the different compounds. Also upon doping with W (Figure 4) the peak positions remain invariant while the relative peak intensities do change. In particular the second quadrupole resonance grows in intensity as compared to the dipole transitions. A similar series as in Figure 4 was recorded for different Zr dopings in anatase TiO<sub>2</sub>.

Theoretical interpretation of TM pre-edges still present a challenge to the theory. In order to obtain more experimental input, we recorded the X-ray emission spectra just below the Fermi level after resonant and non-resonant excitations. While the latter represents the density of occupied electronic states with p-symmetry around the Ti atoms, the resonant excitations show low energy (optical) excitations. The energy of the low energy excitation is given by the energy transfer, i.e. the difference between excitation and emission energy. Figures 5 and 6 show the 1sValenceBand RIXS plane in anatase TiO<sub>2</sub> as well as doped with W and a comparison between the resonant and non-resonant emission lines, respectively. At the time this report was

written, we do not have an explanation for the structure. It is interesting to note that while the non-resonant emission lines do not change with different W doping levels, the resonant lines do show a broadening towards larger energy transfer. This should be correlated with the decrease in the optical band gap with higher doping levels of W in  $\text{TiO}_2$ . [3] Also, the scattering at 0 eV energy transfer gains considerably in intensity with doping level.

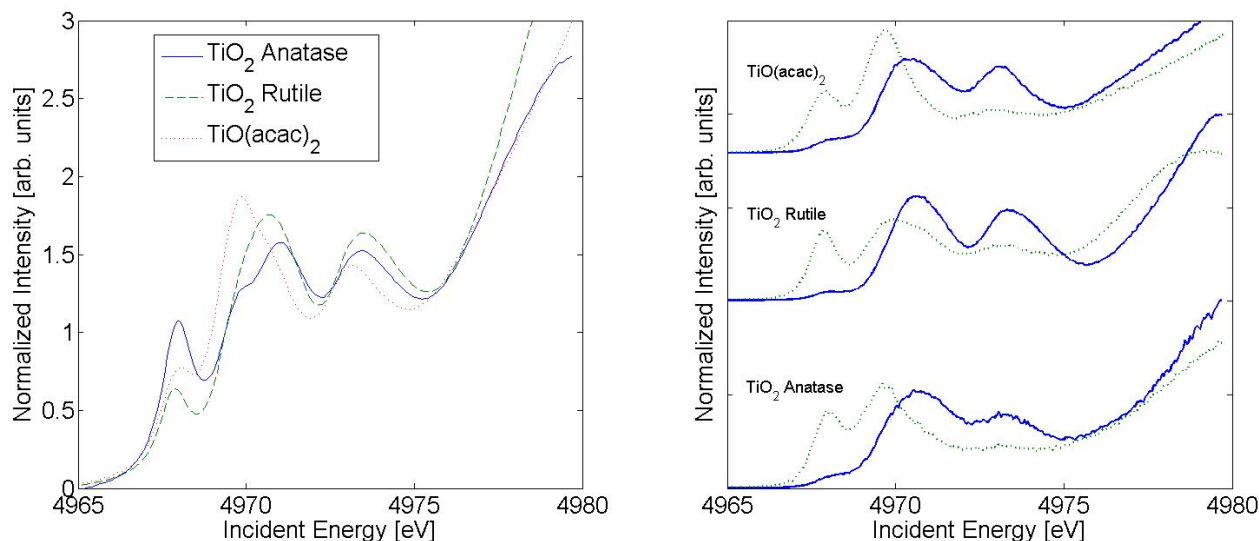


Figure 2 (left) : Pre-edges in Ti compounds recorded in total fluorescence yield.

Figure 3 (right): Pre-edges recorded on the maximum of the  $\text{K}\beta_{1,3}$  emission line (solid) and shifted by 1.8 eV to lower emission energies (dotted).

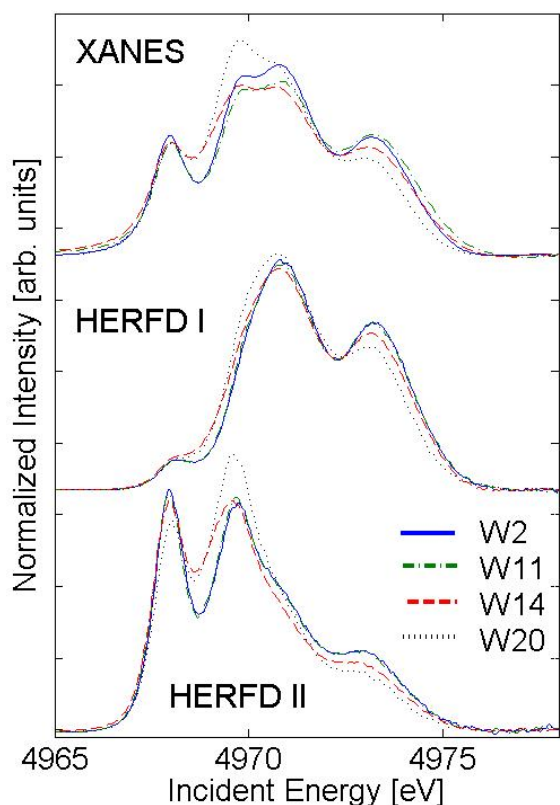


Figure 4: Pre-edges of  $\text{TiO}_2$  doped with W for different concentrations of W (2, 11, 14, 20 weight%) after subtraction of the main edge. The edges are shown recorded in total fluorescence yield (XANES), on the maximum of the  $\text{K}\beta_{1,3}$  emission line (HERFD I) and shifted by 1.8 eV to lower emission energies (HERFD II). This corresponds to emphasizing either the pair of quadrupole resonances at low incident energies or the pair of dipole resonances at higher energies. (cf. Figure 1). A similar series was recorded for different Zr

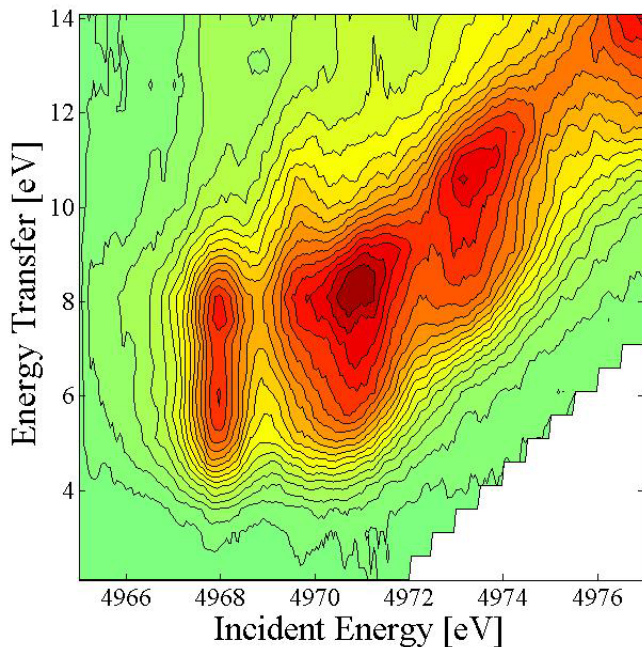


Figure 5 (left): 1sValenceBand RIXS in TiO<sub>2</sub> anatase.

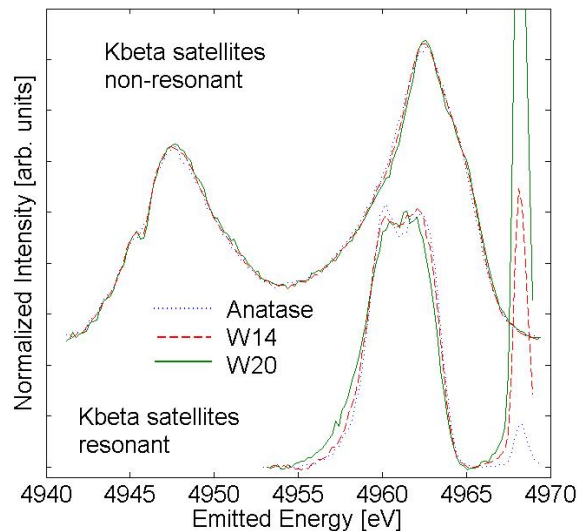


Figure 6 (right): Resonant and non-resonant X-ray emission in TiO<sub>2</sub>.

### W XAS-XES:

The spectral sharpening for W is shown in Figures 7 and 8. The 5d orbital splitting becomes clearly visible. The spectra for W in TiO<sub>2</sub> show a similar behaviour as the Ti pre-edges for the same compounds: The orbital splitting does not change. The spectra have not yet been corrected for self-absorption effects so the absolute intensities cannot be compared. The x-ray emission lines after resonant excitations do not differ in shape. However, like for the Ti RIXS spectra the relative intensities change.

A problem occurred for the HERFD W XAS data: The setup with R=500 mm at ~ 70.5 degrees Bragg angle for the emission detection is very sensitive to the beam position. Due to a software problem, the second monochromator crystal piezo was not always set to the correct position resulting in a slightly shifted beam position on the sample. This makes it very difficult to compare the intensities in the W XAS spectra.

We note that a save way is to always record the full RIXS plane because beam drifts can be easily detected and correct HERFD spectra can be extracted from the RIXS plane.

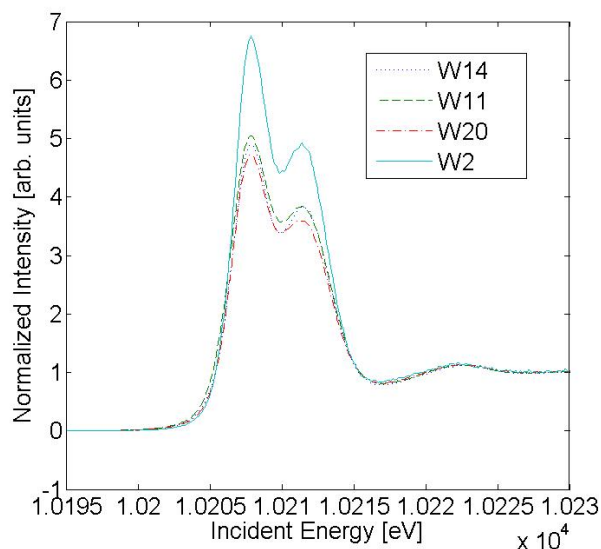
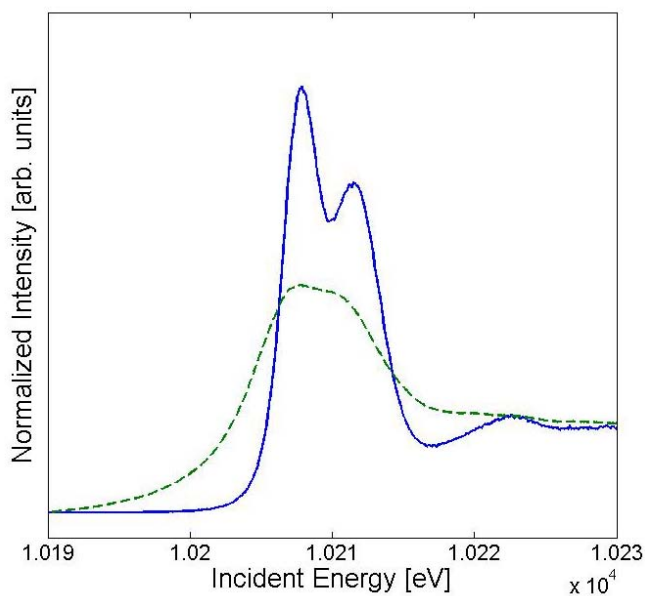


Figure 7 (left): Conventional and HERFD XANES of 2 weight% of W in TiO<sub>2</sub>.

Figure 8 (right): HERFD XANES of W in TiO<sub>2</sub> with different doping levels.

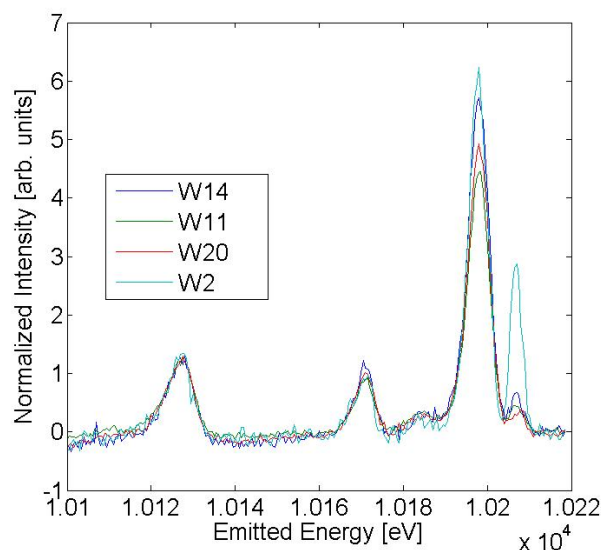


Figure 8: W XES in TiO<sub>2</sub> with different doping levels. The peak at highest energies is the (pseudo-)elastic peak.

Figure 8 shows that XES at the Fermi level of W is possible. We observe changes in the relative peak intensities for different W dopings. The resolution of 3.2 eV does not suffice to detect the small changes as observe in the Ti RIXS in Figure 6.

### Conclusions:

A number of new spectroscopic techniques was successfully tried. While some spectral features show strong changes with the degree of W and Zr doping in anatase TiO<sub>2</sub> (Ti XAS and RIXS intensities, W and Zr to be redone) other remain invariant (peak positions, non-resonant XES). The most important results are:

- We add experimental evidence for 4 pre-edge structures in Ti(IV). The information obtained during this beamtime will serve to re-evaluate the interpretation of the Ti(IV) pre-edges.
- Resonant XES just below the Fermi level (1sValenceBand RIXS) after excitation into the lowest unoccupied electronic states is feasible for Ti(IV) and W.
- The Ti pre-edges show a strong dependence on W doping. While the peak positions remain unchanged, the relative intensities vary. This indicates changes in electron orbital populations.
- The Ti 1sValencBand RIXS shows broader structures with increasing W doping.
- The W 2pValenceBand RIXS show changes in relative peak intensities.

### To be improved:

- The full RIXS planes should be recorded for all systems under investigation. This will considerably facilitate interpretation of the spectra and prevent artefacts.[4]
- The instrumental energy bandwidth for the W experiments can be improved by using a Si(311) monochromator crystal for the incident energy and an R=1000mm analyzer crystal.
- The study should be extended to anionic dopants (N,C).

### References:

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- 3 M. Fernandez-Garcia, A. Martinez-Arias, A. Fuente, et al., *J. Phys. Chem. B* **109**, 6075 (2005).
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