# Doping effects on electronic structure of TiO$_2$

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## Introduction

Catalysis is a key thechnology in chemical and pharmaceutical industries but also extremely important for the production of clean energy and environmental protection. Photocatalysis is an emerging strategy that can help solve the energy crisis by converting solar radiation into chemical bonds. TiO$_2$ is the most commonly used photocatalyst but it requires excitation with UV light due to its wide band gap (3.2 eV). A common strategy to improve visible light absorption is to reduce the band gap energy by doping with 3d elements, which shifts the conduction band downwards in energy and/or light elements such as N, C and S able to shift the valence band upwards in energy.

In this poster we present experimental results for the measurement of Resonant X-ray Emission and X-ray Absorption spectroscopy for chromium and nitrogen doped titanium dioxide. The results were compared with theoretical calculations for densities of states using FEFF program. The study aimed to assess the impact of the effect of doping on the electronic structure of TiO$_2$ [1].
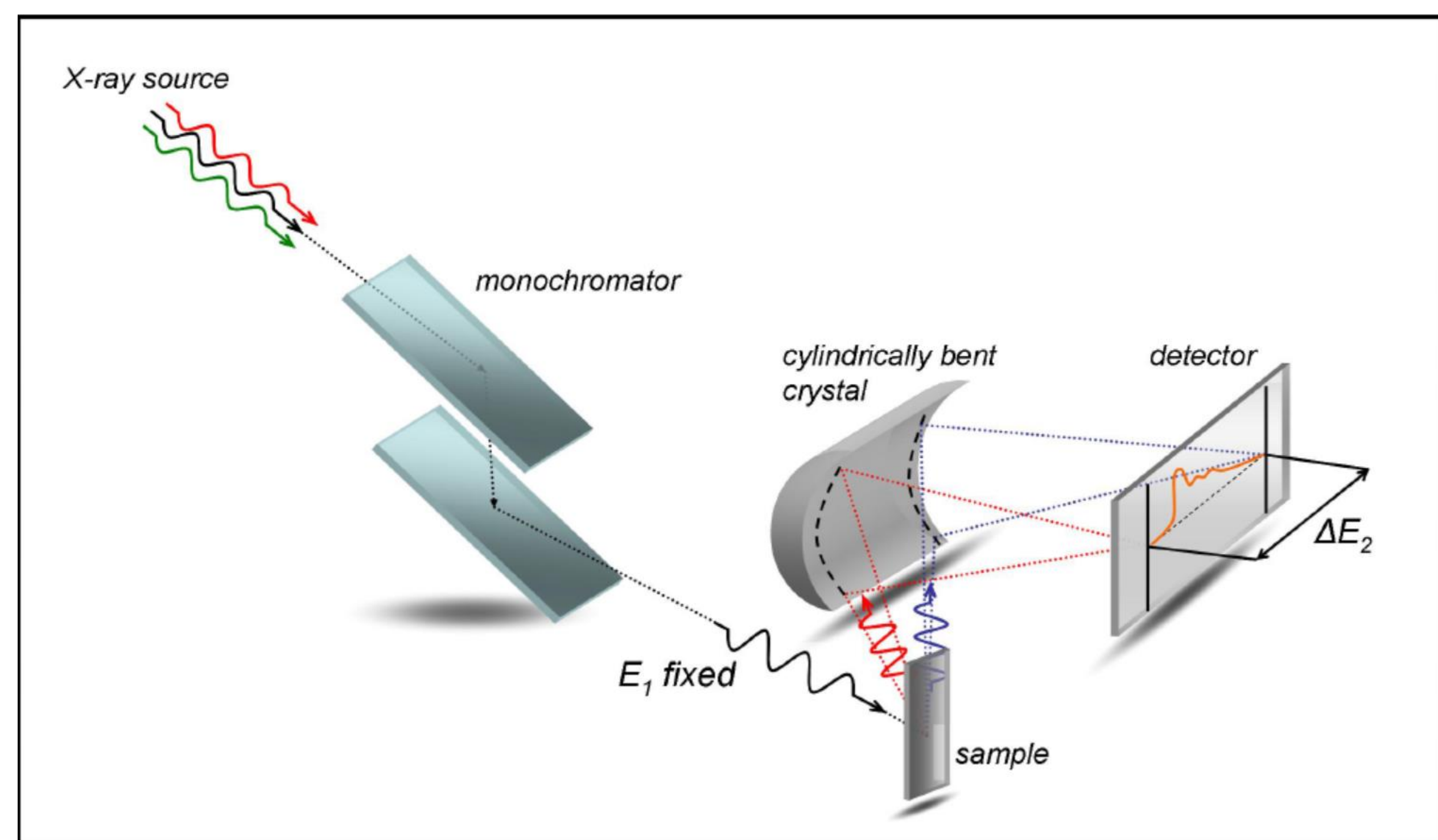
## Experimental setup



The resonant X-ray emission spectroscopy experiment was performed at SuperXAS beamline of Swiss Light Source, Switzerland. The beamline delivers X-rays by means of bending magnet source. The X-rays are collimated by Si-mirror that provides high energy cut-off at 10 keV. The monochromatization is performed with double crystal Si(111) monochromator providing relative energy resolution $\Delta E/E$ of 2 x 10$^{-4}$ that at Ti K-edge gives 1eV bandwidth. X-ray beam is focused down to 100 x 100 $\mu m^2$ spot with Pt-toroidal mirror placed downstream of monochromator.

The experiment was conducted around the Ti K-edge (1s$\rightarrow$3p transition) at 4966 eV, with incidence X-ray flux of 10$^{11}$ photons/s. The K$\beta$ X-ray emission from the sample was measured by means of von Hamos-type X-ray spectrometer equipped with Ge(400) crystal for X-ray dispersion at central Bragg angle of 61º. Within the setup, we could measure X-ray emission spectra in the range of over few tens of eV without necessity of moving any spectrometer components [3].

*The experimental setup with double crystal Si(111) monochromator and spectrometer setup in the geometry of von Hamos [2].*

## RXES measurement for chromium doped TiO$_2$
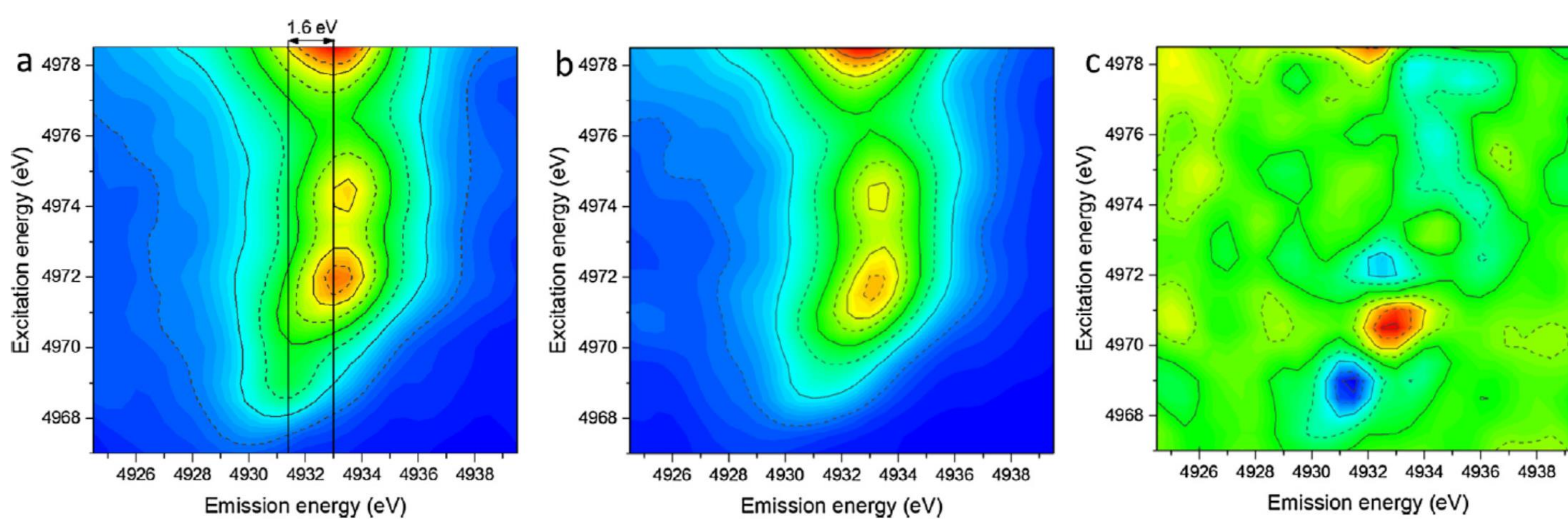


*(a) Pre-edge K$\beta$ RXES plane for anatase TiO$_2$, (b) pre-edge K$\beta$ RXES plane for Cr-doped anatase TiO$_2$, (c) pre-edge K$\beta$ RXES plane difference (doped minus un-doped anatase TiO$_2$) [3].*

The pre-edge K$\beta$ RXES data for TiO$_2$ and Cr-doped TiO$_2$ samples are plotted in Fig. 2a and b, respectively; while in Fig. 2c we show the difference RXES plane (Cr-doped TiO$_2$ minus un-doped TiO$_2$). The pre-edge structure of TiO$_2$ is characterized by three main features located at incidence energies of 4969 eV, 4972 eV and 4974.5 eV, respectively [3], that composed of unoccupied d-orbital of Ti. As shown in Fig. 2a, the first pre-edge resonance is located at X-ray emission energy lower by about 1.6 eV than the two resonances observed at higher incidence X-ray energies. This effect relates to the excitation of 1s electron into the localized d-orbital that in consequence leads to the energy shift of the initial and final atomic configurations. In case of the two remaining resonances at higher excitation energies, the 1s electron is promoted into the delocalized d-orbital and therefore its influence on electronic Ti configuration is being negligible. Therefore, these resonances do not show any energy shifts and are recorded with maximum intensities peaking at X-ray emission energy corresponding to non-resonant K$\beta$ (3p$\rightarrow$1s) electronic transition at emission X-ray energy of 4933 eV [3].

## Density of states calculations for chromium doped TiO$_2$



The calculated density of states for Cr-doped TiO$_2$ reveals twofold influence on electronic state composition. First the Ti 3d-band is slightly damped in intensity by about 5%, but keep the doublet d-band structure as in case of pure TiO$_2$. Secondly, a new electronic orbital is introduced on the low energy side of unoccupied electronic states that corresponds to Cr d-band.

Based on density of states functions, we calculated pre-edge absorption spectra, which takes into account the excitation probabilities of 1s core-electron. The result is plotted in Fig. 4 and shows good agreement with measured XAS data [3].

*Comparison of measured (top) and calculated (bottom) X-ray absorption signals for anatase TiO$_2$ and Cr-doped anatase TiO$_2$ samples [3].*
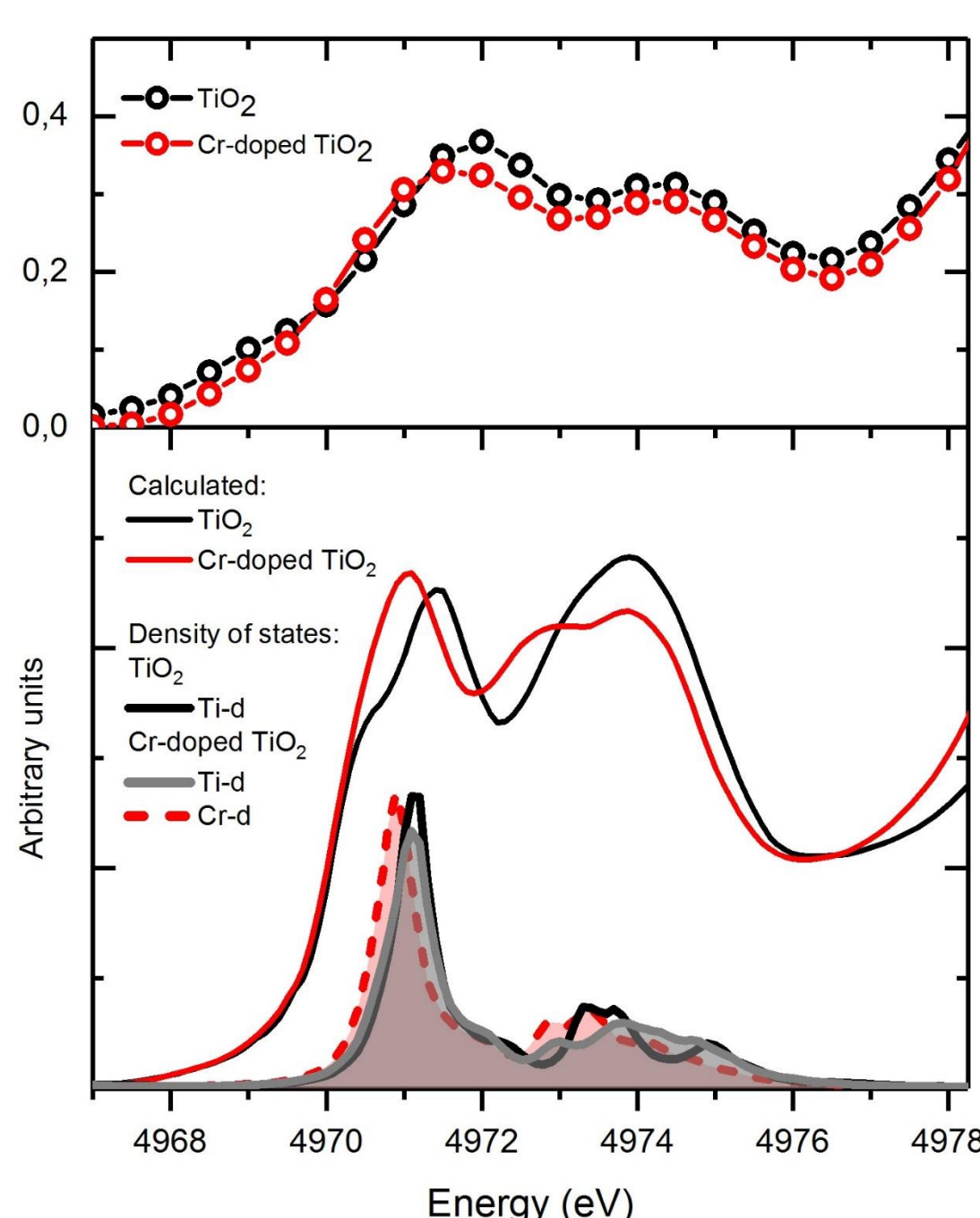
## XES and XAS spectroscopy on nitrogen doped TiO$_2$.

Combination of XAS/XES spectroscopy allows the determination of the electronic band structure including occupied (XES) and unoccupied (XAS) states. This allows to determine the structure of the electron conduction band and valence band of any semiconductor. [1]
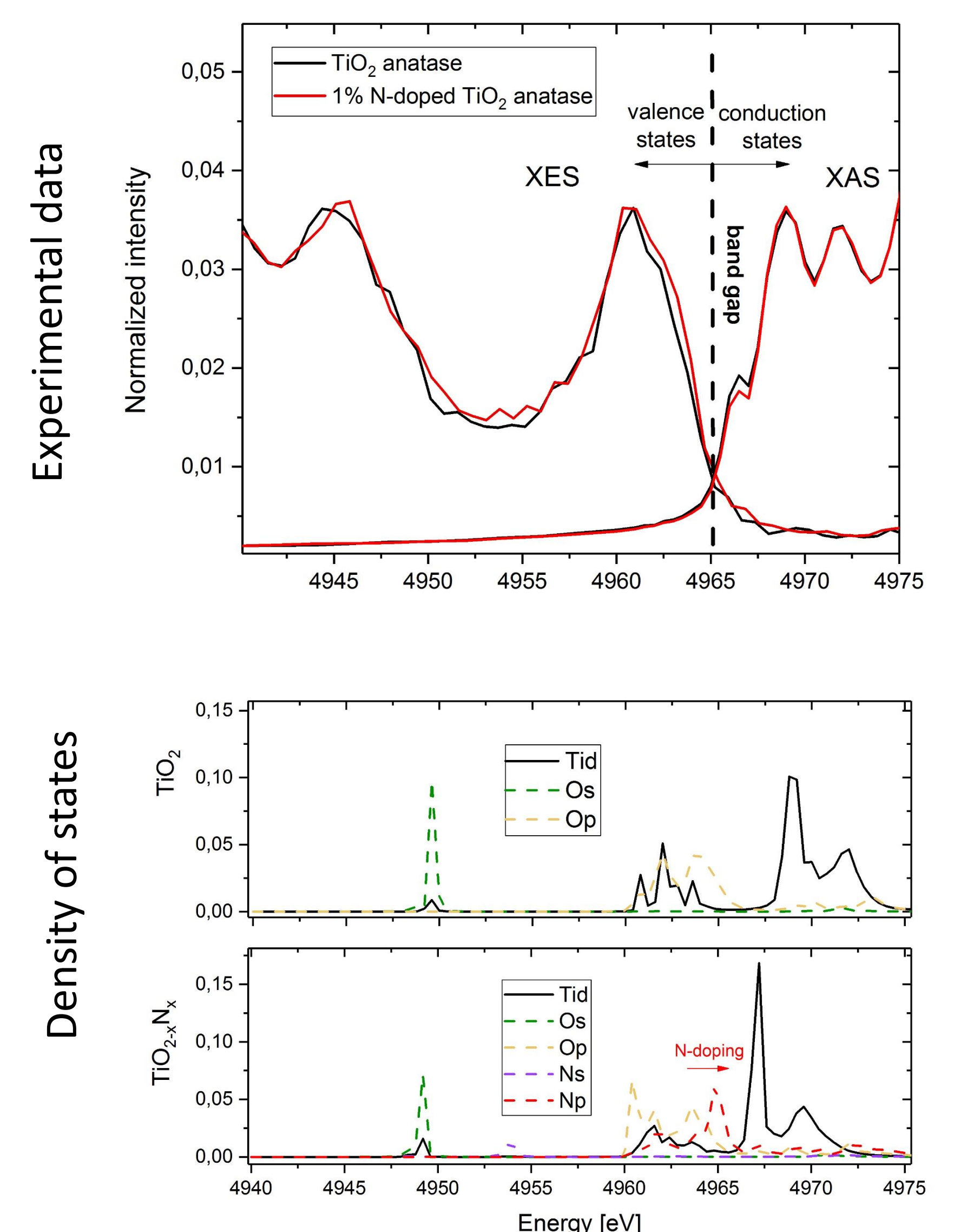


*Experimental results of XAS/XES experiment for TiO$_2$ and N-doped TiO$_2$ samples. The results are compared to density of states calculations.*

The experimental data shows two-fold effect induced by N-doping. XAS spectrum exhibits slight dumping of first pre-edge structure at energy of 4966eV, but no shift on band positions is detected. For XES measurements, we observe shift of valence-to-core feature to higher energies indicating band gap narrowing. In order to confirm this observation, we calculate N-doping effects on density of states of TiO$_2$. The computations, shows that indeed N-2p band is introduced on high energy side of valence states of TiO$_2$ structure.

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