# Direct measurements of oxygen vacancy in $TiO_2$ single crystal by muon spin rotation spectroscopy

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## Abstract

Muon is a lighter isotope of hydrogen and muon spin rotation (μSR) can be a powerful probe to specify the behavior and local structure of hydrogen inside materials. Recently accelerator based strong pulse muon facilities have been developed and has opened the new feasibility for μSR measurements using strong spin polarized muons with various kinetic energies. Titanium dioxide ($TiO_2$) is the most widely used material as high efficiency photocatalysis.[1] One of the crucial and unrevealed issues are properties of defects, e.g. oxygen vacancies. Recently hydrogen dissolved in $TiO_2$ during preparation process [2,3] forms impurity states in the band gap to change electron excitation process and electron conductivity. We applied μSR measurement on the $TiO_2$ single crystal in order to understand the behavior and electronic properties of both defects and impurities.
The experiments were mainly carried out in the muon beam line at the J-PARC muon facility (MUSE). All the experiments are conducted under He atmosphere. $TiO_2$ single crystal was reduced by annealing in UHV.
In this contribution we will discuss the muon interaction with defect site of $TiO_2$ by zero-field, longitudinal and transverse external field μSR spectra. Figure 1 shows the time dependence of zero-external field μSR spectrum of unreduced and reduced $TiO_2$ at low temperature. The faster relaxation was found in the reduced $TiO_2$. We fitted the spectra with assumption that the magnetic field statistically distributed with Gaussian distribution (Kubo-Toyabe relaxation function). The spectrum of the stoichiometric $TiO_2$ is well fitted with the magnetic field of 0.22 mT, which is a typical value for nuclear spins. The relaxation of spectra for the reduced $TiO_2$ is fitted with the magnetic field of 0.28 mT. Those magnetic fields are not able to be explained only by nuclear magnetic moment of $TiO_2$, but are able to be explained with nuclear magnetic moment of Hydrogen, which H-μ distance was 1.1 nm. The origin of relaxation in reduced $TiO_2$ is muon interaction with Hydrogen in oxygen vacancies (fig. 1(c)).
We have also conducted μSR measurement with applying longitudinal and transverse external field. Those results show stable sites of muon (hydrogen) and electron distribution in the reduced $TiO_2$.

## References

[1] A. Fujishima, K. Honda, Nature **238** (1972) 37.
[2] X. Chen, L. Liu, P.Y. Yu, S.S. Mao, Science **331** (2011) 746.
[3] K. Shimomura, R. Kadono, A. Koda, K. Nishiyama, and M. Mihara, Phys. Rev. B **92** (2015) 075203.

## Figures

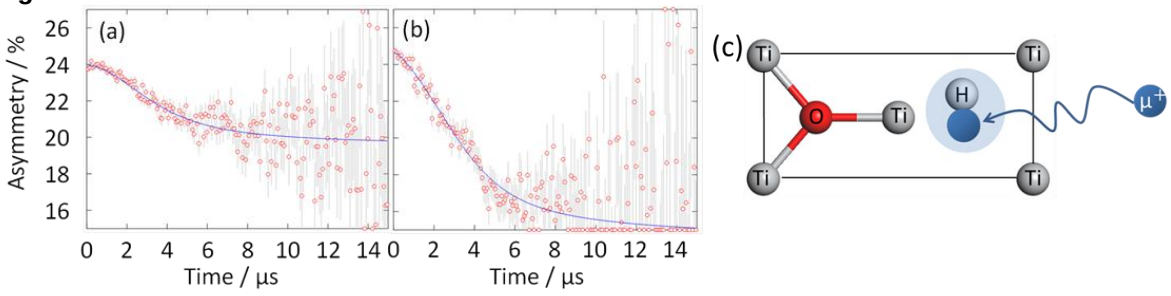


Figure 1. Zero field μSR spectrum of (a) stoichiometric and (b) reduced rutile $TiO_2$ at 15 K with error bar. Blue lines are fitting curve. (c) Structure model of muon stabilized site.