Investigations of defects in TiO_2 rutile crystal by muon and muonium

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Metal oxides play a key role in the field of environmental science, heterogeneous catalysis, electrochemistry, biology, chemical sensors, magnetism, and other chemical processes. It is well known that the existence of defect sites drastically changes the chemical and physical properties of metal oxides. TiO_2 is the one of the most studied material among metal oxides. The defect sites in TiO_2 affect the catalytic and photocatalytic properties. The structure of defect site on surface is well known by scanning probe microscope (STM, AFM and so on) observations. The major defect on the surface is oxygen vacancy. However, the microscopic insight of bulk defect sites has not been established yet. Although oxygen vacancy is believed to be a typical defect site in TiO_2, no direct evidence has been reported to characterize the defect structure, and its properties have not been revealed because of the difficulty in detecting defects directly. In order to establish a charge balance, Ti^{3+} is assumed in the nearest neighbor of the bulk oxygen vacancy. Thus, oxygen vacancy has been discussed by measuring Ti^{3+} species, which have one d electron and are characterized with ESR or NMR techniques. However, since Ti^{3+} species do not only exist next to the oxygen vacancies but also at other sites such as interstitial Ti, planar defects, CS planes and so on, it is necessary to obtain information including the adjacent morphology of Ti^{3+}. It is suggested that hydrogen stabilizes at an oxygen vacancy as hydrid (H^-) in TiO_2 through density functional calculations. As Muon is regarded as an isotope of hydrogen, μSR has potential to be the probe of oxygen vacancy.

Our recent preliminary TF μSR measurements at the RIKEN-RAL suggested the existence of a large fraction of a diamagnetic component ($\mu^+ or Mu^-$) and some normal muonium at room temperature in TiO_2 with an oxygen vacancy. The purpose of the present work is to clarify whether negative muonium ions exist in TiO_2 with an oxygen vacancy by laser irradiation and also to determine a further detailed state of μ^+.

We have performed both zero-field (ZF) measurements and "Pump and probe" measurements by laser irradiation at various temperatures. The μSR measurements were performed at the RIKEN-RAL Muon Facility. The mirror-polished rutile TiO_2 single crystals (25 x 25 x 0.5 mm^3, Crystal Base, Japan) oriented to the (110) plane were used. The sample was calcined at 1073 K for 6 h in air followed by reduction at 1173 K for 2 h under an ultra-high vacuum environment (0.5 x 10^{-8} Pa). The color of sample became blue after the reduction procedure. Laser was irradiated from the opposite side of muon through a quartz glass by utilizing the sample cell developed by Prof. Torikai's group.

The ZF muon spin relaxation spectra with and without oxygen vacancies are obtained at various temperatures from 15 K to room temperature. The difference between two samples are observed at a temperature lower than 50 K. The spectra at 15 K are shown in Fig. 1. The relaxation of spectra without an oxygen vacancy is predictable to be derived from nuclear spins of Ti (^{47}Ti and ^{49}Ti) because of the absence of electronic spin. We expected a Gaussian field profile and fitted the plot with a Kubo-Toyabe relaxation function. The spectra without the oxygen vacancy was well fitted with $\Delta = 0.30$ MHz (Gaussian distribution: 0.71 mT), which is a typical value for nuclear spins. The Kubo-Toyabe relaxation function for a Lorentzian field distribution was added for fitting the relaxation of spectra with the oxygen vacancy. The Δ value and the Lorentzian distribution were 0.38 MHz and 1.9 mT, respectively.

We have also preformed pump and probe measurements to examine the existence of Mu^-. The "pump" laser irradiation is intended to remove one electron from the negative muonium ion, which makes the ion detectable by a transverse-field measurement. However, we could not detect obvious differences in the results obtained with and without laser irradiation. The remaining issue is to simulate the dynamics of Mu^- by laser irradiation and determine an approach to detect Mu^-.

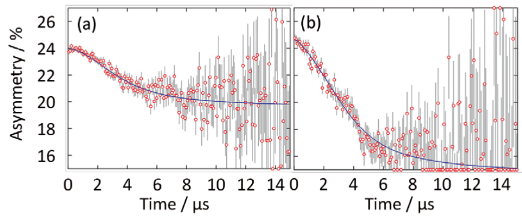

Fig. 1. Zero field μSR spectrum of rutile TiO_2 (a) with and (b) without oxygen vacancy at 15 K.

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