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POSTERSESSION 1 Foyer G

P.471

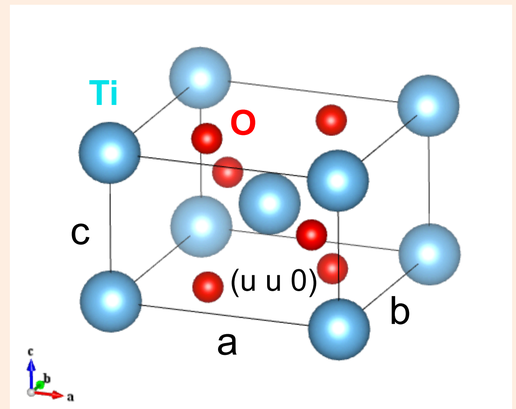
The structure of impurity hydrogen and Ti^{3+} ions in rutile TiO_2

[A]RIST, [B]TAIYO YUDEN CO., LTD., [C]Dept. Mater. Sci. Eng., Tokyo Tech, [D]Dept. of Phys., Univ. of Tokyo
Kanako Yoshizawa[A], Yoshiki Iwazaki[B], Yoshihiro Gohda[C], Shinji Tsuneyuki[D]

Introduction

- TiO_2 : photocatalysis, photosensitized solar cells, memristors, and so on
  → notable material
- Excess electrons in rutile TiO_2 → small polarons
  cause) reduction, oxygen vacancy (V_O), impurity hydrogen (H), and so on
  The electrons can localize at Ti 3d orbitals, forming Ti^{3+} ions
  electron localization → local lattice distortions → small polarons
  — The optical absorption doped with Nb and other impurities
  V. N. Bogomolov and D. N. Mirlin, Phys. Status Solidi **27**, 443 (1968).
  — Electron Paramagnetic Resonance (EPR)
  S. Yang, L. E. Halliburton, A. Manivannan, P. H. Bunton, D. B. Baker, M. Klemm, S. Horn, and A. Fujishima, Appl. Phys. Lett. **94**, 162114 (2009).
  — DFT calculations
  A. Janotti, C. Franchini, J. B. Varley, G. Kresse, and C. G. Van de Walle, Phys. Status Solidi RRL **7**, 199 (2013).
- How can small polarons be described by DFT calculations in rutile TiO_2 with H ?
  Where is the spin density located ?
- Muon spin rotation (μSR)
  K. Shimomura, R. Kadono, A. Koda, K. Nishiyama, and M. Mihara, Phys. Rev. B **92**, 075203 (2015).
  → hyperfine parameters
  We also calculate the parameters and evaluate the excess electron states by the comparison with μSR.

Rutile TiO_2 space group $P4_2/mnm$
Primitive cell Ti : 2, O : 4

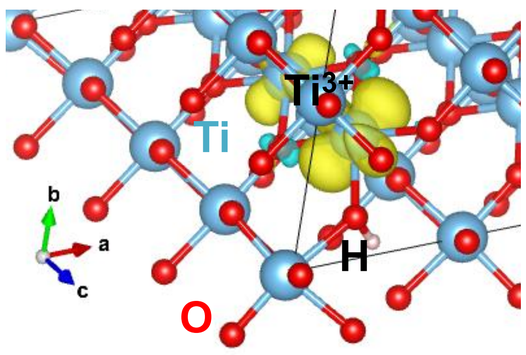


DFT calculations

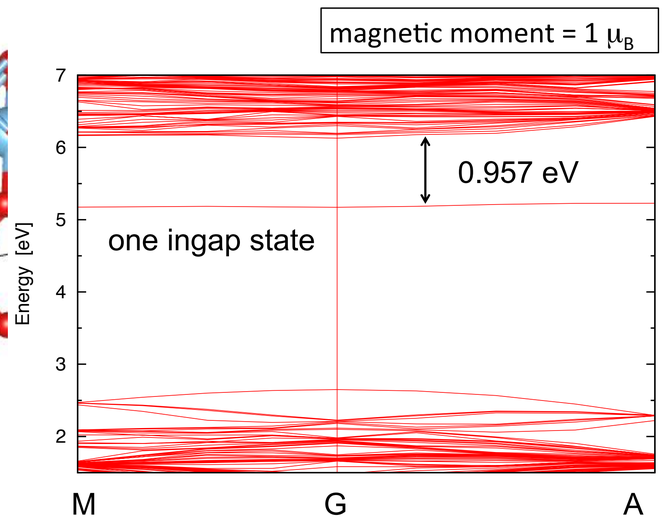
TiO_2 (perfect crystal) + H

TiO_2 : 216 atoms （3x3x4 supercell）
H : 1 atom
k-points : gamma only
exchange-correlation (xc) functional : HSE

The spin density for a localized electron in Ti site exists and it is verified that the excess electrons are described as localized small polarons by DFT calculation.



magnetic moment = 1 μ_B



H makes O-H bond (→ H^+)
→ one excess electron

hyperfine parameters

gyromagnetic ratio γ = 135.53 MHz T^{-1} （muon）

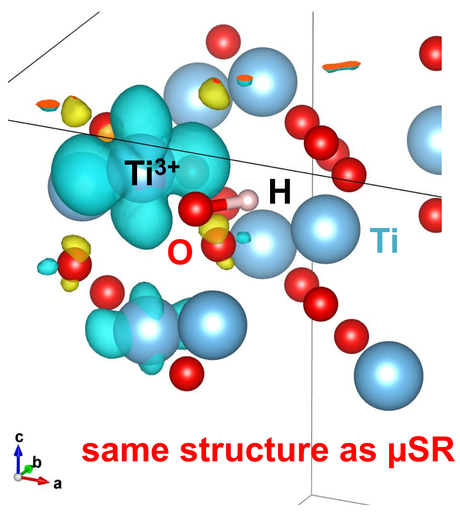
[MHz]	Axx	Ayy	Azz
H	−12.349	−9.136	22.243

→ hyperfine parameters has non-zero (anisotropy)

◎ Optimization for different initial structures

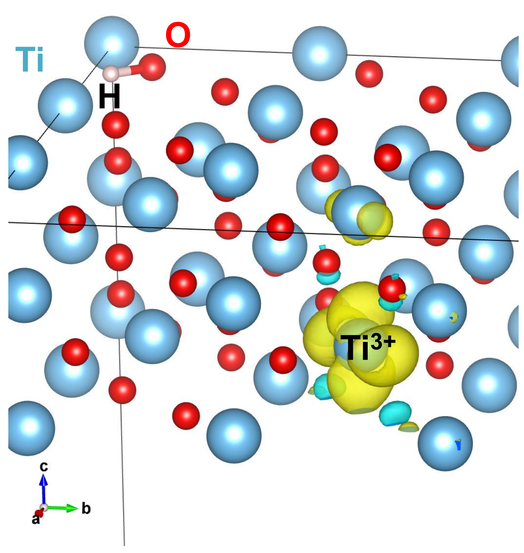
The position of the spin density depends on the initial structure.

(a)

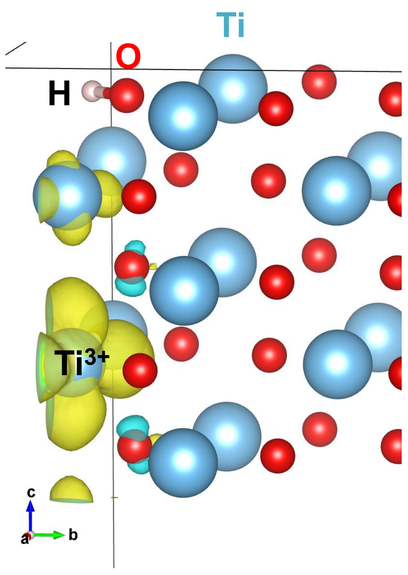


same structure as μSR

(b)



(c)



(a)～ (c) have almost the same energy.

hyperfine parameters

gyromagnetic ratio γ = 135.53 MHz T^{-1} （muon）

(a)

[MHz]	Axx	Ayy	Azz
H	−15.231	−13.761	26.074

(b)

[MHz]	Axx	Ayy	Azz
H	−0.201	−0.121	0.386

(c)

[MHz]	Axx	Ayy	Azz
H	-3.921	-1.810	6.612

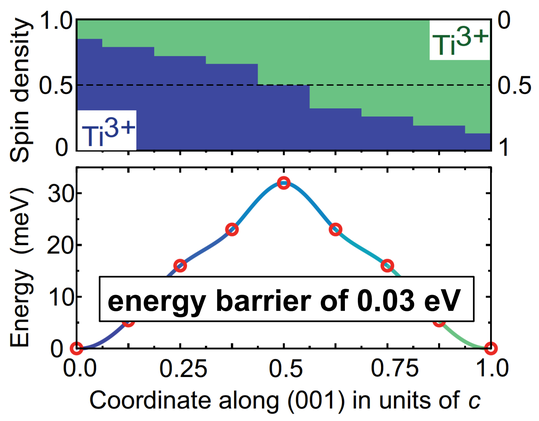
(a)～ (c) have the different parameters
→ different Ti^{3+} site

◎ Position of the spin density

previous study

TiO_2 (perfect crystal) + an electron

energy barrier



A. Janotti, C. Franchini, J. B. Varley, G. Kresse, and C. G. Van de Walle, Phys. Status Solidi RRL **7**, 199 (2013).

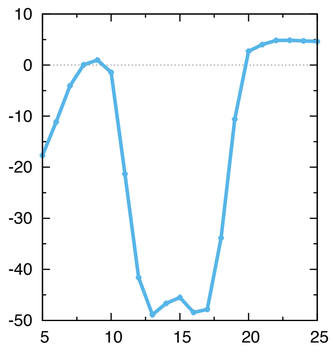
The position of the spin density depends on the initial structure.

TiO_2 (perfect crystal) + H

Electrostatic potential

O-H bonding

O site

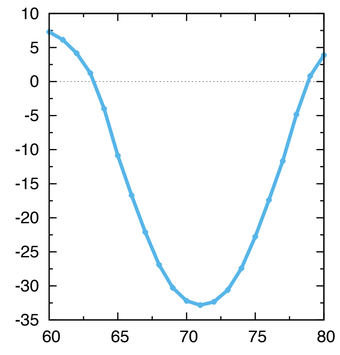


deeper

easy to make O-H (H^+)

Ti^{3+}

Ti site



shallow

electron localization

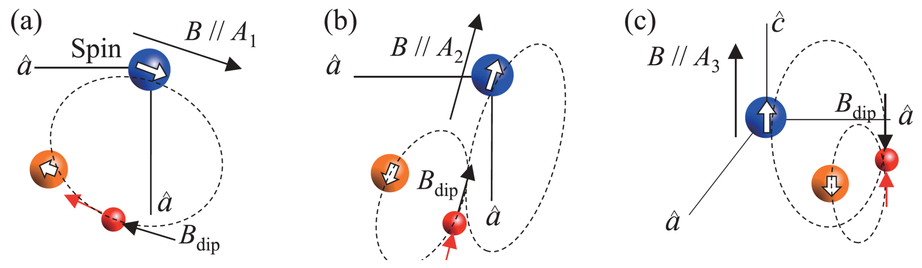
H^+ does not like the neighborhood of Ti^{3+} site with shallow potential.

Muon spin rotation (μSR)

hyperfine parameters

K. Shimomura, R. Kadono, A. Koda, K. Nishiyama, and M. Mihara, Phys. Rev. B **92**, 075203 (2015).

Mu	A_1 (MHz)	A_2 (MHz)	A_3 (MHz)	ϕ_0 (deg)
$A_\perp(\phi)$	−1.29(6)	+1.29(6)	–	25.5(1.4)
$A_\parallel(\theta)$	–	–	−0.17(2)	–
H	−1.276(3)*	+1.961(3)*	−1.076(3)*	22.1



Interstitial Mu forms a hydroxyl base (OH^-) with an unpaired electron loosely bound to the nearby Ti ion, comprising a Ti-O-Mu complex state in rutile TiO_2.

A comparison between DFT calculation and μSR

- The two are qualitatively the same.
  (The hyperfine parameters has anisotropy.)
- The Ti^{3+} site may be different
- DFT calculation suggest that the Ti^{3+} site differ depending on the measured TiO_2 crystal (material) .

Summary

DFT calculations for excess electrons in rutile TiO_2

- H is hard to be located in the neighborhood of Ti^{3+} site.
- If it's possible to get over the energy barrier, it follows the same structure as μSR.
- DFT calculation suggest that the Ti^{3+} site depends on the TiO_2 crystal .