

The muonium donor in rutile TiO_2 and comparison with hydrogen

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Muonium, a positive muon and an electron, is often used as an experimentally accessible substitute for hydrogen in materials research. In semiconductors and insulators, a large amount of information on the hydrogen behavior is deduced from this analogy; however, it is seldom demonstrated that this procedure is justified. We show here, via a comparison of the hyperfine interactions, that in TiO_2 muonium and hydrogen form the same configuration with the same basic electronic structure. A detailed description of the bonding characteristics of the muon to the Ti^{3+} polaron is presented. The special role of muon motion within the so-called oxygen channel in the rutile structure, which occurs at a lower temperature than for hydrogen, is emphasized.

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Muonium (Mu) is a pseudo-isotope of hydrogen in which the proton is replaced by a positive muon (μ^+), with a factor of nine lighter mass. Muon spin spectroscopy (μSR) uses muons implanted with 100% spin polarization and offers a very sensitive method to study the properties of this isolated pseudo-hydrogen in solids [1, 2]. It is usually assumed that information obtained from μSR can be transferred with appropriate modifications to H. However, overlapping experiments to support this assumption are scarce. A particularly relevant case is the doping character of H in semiconductors and oxides [3–6], where practically all calculations refer to the electronic structure of H whereas most experimental information comes from μSR [7–13]. Overlapping data exist only for ZnO where proton-ENDOR data [14] can be compared directly with μSR results [15–18]. A number of properties (e.g. ionization energy) are indeed similar for the two species. However, the measured hyperfine interaction (hfi), scaled with the magnetic moments, differs by almost a factor of ten. This raised the question of whether the same configuration is measured, or if the H center may involve an additional defect [19, 20].

Here we report a case where the same configuration can be established for H and Mu. We compare the hfi of the μSR experiment with the proton-ENDOR result, both for rutile TiO_2 . The H center in TiO_2 was extensively studied by Brant et al. [21] using EPR/ENDOR, who found that the electron is located at the Ti ion reducing it from Ti^{4+} to Ti^{3+} . H is bound to one of the six O atoms surrounding Ti and the magnetic interaction between the proton and the electron is mainly dipolar. This specific hfi permits a sensitive comparison of the two experiments. We have observed a dramatic change of the μSR spectra with increasing temperature and a complete disappearance of the hyperfine splitting at 10 K. We show that this is due to rapid jumps of the muon between

neighboring bonding positions to O atoms around Ti^{3+} . The very strong angle dependence of the dipolar interaction and the averaging over values in different positions lead to the reduction and final disappearance of the hfi splitting. We were able to identify the ground state and the excited state of the muon- Ti^{3+} complex: both correspond to a muon bound to one of the six O atoms around Ti^{3+} , but with different bonding configurations.

μSR measurements were performed with the MUSR instrument of the ISIS Facility (UK), in transverse geometry with a magnetic field of $B=20$ mT applied along the [110] axis, in a temperature range from 1.2 K to 10 K. A single crystal of TiO_2 acquired commercially (Alfa Aesar) was used. The sample orientation was confirmed by X-ray diffraction. The sample was mounted on top of a Fe_2O_3 background. Silver was used for calibrating the maximum asymmetry.

Figure 1 shows the Fourier transform of the μSR spectrum at 1.2 K. The central line corresponds to the Larmor precession of the diamagnetic muon. The two pairs of satellite lines are due to Mu with different hfi, corresponding to Mu in the two orientationally inequivalent sublattices of the rutile structure. Figure 2 shows the TiO_6 octahedron for one of the two sublattices. It consists of Ti^{3+} (Ti^{4+} plus one electron and some lattice distortion) in the center and six O atoms arranged in a slightly distorted octahedron. The second sublattice corresponds to Ti^{3+} located at a corner site and rotation of the octahedron by 90° around the c-axis. The H (or Mu) is bound to one of the six O atoms surrounding Ti^{3+} with the O-H bonds lying in the $a-b$ plane perpendicular to the Ti-O bond. At the lowest temperatures (1.2 K in μSR and 5 K in ENDOR) only the bond to O atoms in the same $a-b$ plane in which Ti^{3+} is situated occurs. The location of the extra electron (as Ti^{3+}) identifies the sublattice and dictates the relative energies of the now

TABLE I: Comparison of the frequencies obtained in our μ SR experiment with those calculated with the hyperfine parameters obtained from the hydrogen ENDOR experiment [21] scaled with the magnetic moment ratio of the muon and the proton (3.183). The fourth and seventh columns show the hyperfine splitting for an applied field of 20 mT along [110].

Frequencies	Outer lines (sublattice 1)			Inner lines (sublattice 2)		
	ν_1	ν_4	$\nu_4 - \nu_1$	ν_2	ν_3	$\nu_2 - \nu_3$
Experimental (MHz)	2.12(2)	3.43(2)	1.31(3)	2.30(2)	3.20(2)	-0.90(3)
Calculated from ENDOR (MHz)	2.05(3)	3.48(3)	1.43(3)	2.38(3)	3.15(3)	-0.77(3)

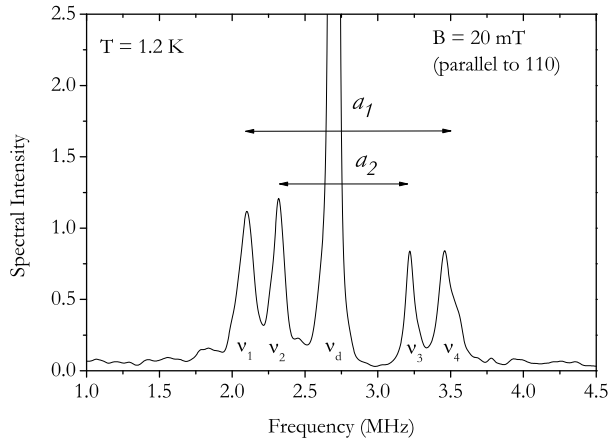


FIG. 1: μ SR Fourier spectrum of rutile TiO_2 at $T = 1.2$ K in an external magnetic field of $B = 20$ mT in the [110] direction. The diamagnetic component (central line at frequency ν_d) and two pairs of hfi-split lines (ν_1 to ν_4) are observed, the slightly different spectral intensities being an instrumental effect.

inequivalent H or Mu sites.

We begin by comparing (Table 1) the present results with the ENDOR hydrogen data [21] accounting for differences in the magnetic moments of the muon and proton (ratio 3.183). We calculated the line positions with the scaled hfi parameters of the ENDOR experiment, and compared these with the present data. In addition, we have also taken into account the strongly anisotropic electron g-factor [22], which introduces a slight frequency shift, by using Eq. 16 of Ref. [23]. The asymmetric placement of the lines in Fig. 1 can thus be reproduced using the scaled hfi parameters $A_1 = 1.96$ MHz and $A_2 = -1.28$ MHz, where we have interchanged indices 1 and 2 with respect to their use in Ref. [21] in order to clearly show the dipolar character of the interaction. In μ SR only two pairs of hyperfine lines are observed as expected from the corresponding H experiment at this magnetic field orientation. The line positions and splitting are consistent with the H data if the hfi parameters are scaled with the magnetic moment ratio. The line splitting, which is a measure of the hfi, deviates by about 10 to 15 % from the calculated value, slightly outside the quoted errors. Experimental uncertainties such as deviation from the nominal field orientation could account

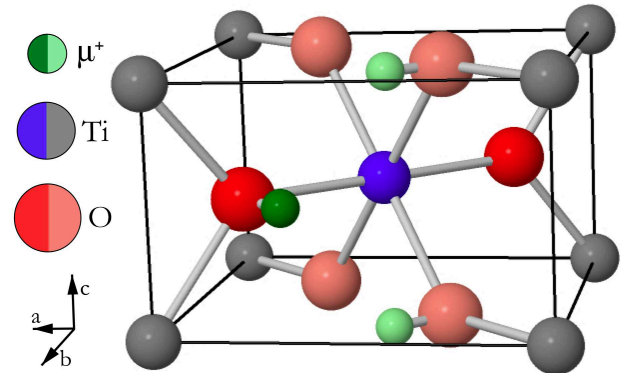


FIG. 2: TiO_6 octahedron in rutile TiO_2 with Ti^{3+} (blue sphere) in the center surrounded by six oxygen atoms. At low temperatures, the muon (hydrogen) is bound to one of the six oxygens of the slightly distorted octahedron. In the ground state only the bond to oxygen in the same $a-b$ plane as Ti^{3+} occurs. Only sites from sublattice 1 and a single channel are shown: sublattice 2 has Ti^{3+} at a corner site and is rotated by 90° around the c -axis. Darker and lighter colors are used for atoms forming the ground state and the excited state configurations, respectively.

for this discrepancy. However, a difference in the hfi (after scaling) cannot be excluded and may arise from the larger zero-point motion of the muon compared to that of H. The main result of this comparison is nevertheless that the probe atom is bound to an O of the TiO_6 octahedron around Ti^{3+} and that this geometry is the same for Mu and H. We note that we are comparing Mu results obtained at 1.2 K with H data measured at 5 K, which is justified since the static situation occurs in both cases.

The development of the spectral lines with increasing temperature is shown in Fig. 3. It can be seen that the hyperfine splitting decreases with increasing temperature and disappears completely at 10 K. Furthermore, the two pairs of lines merge into one visible pair above 3.8 K. We first address whether the disappearance of the hfi is due to dissolution of the muon-electron complex or to local dynamics. A separation of the muon from the electron would result in an increase of the diamagnetic and a decrease of the paramagnetic fraction in the μ SR experiment. This is, however, not the case up to 7.5 K. In this temperature range, the paramagnetic fraction de-

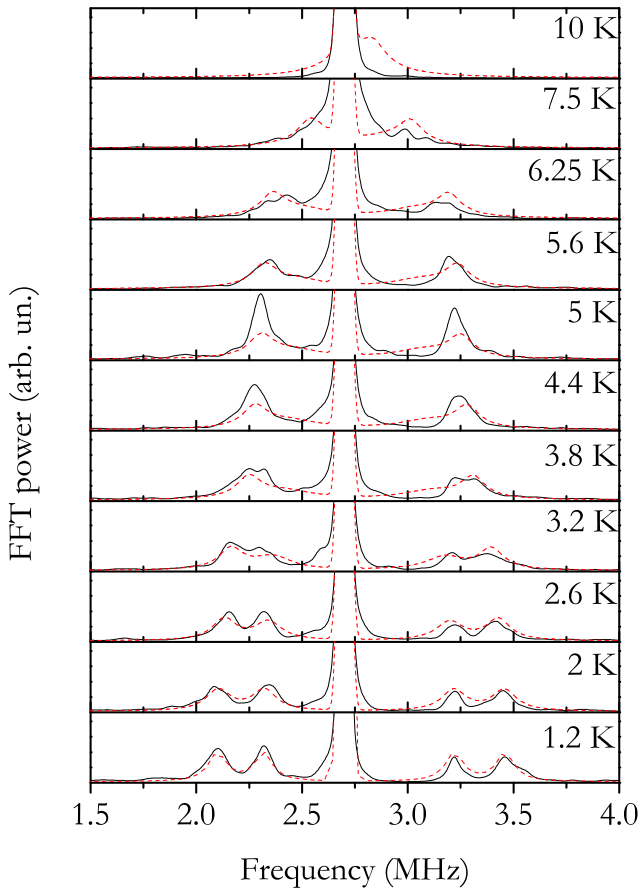


FIG. 3: Development of the line spectra as a function of temperature. The dashed lines are fits assuming motion of the muon between neighboring bonding positions as in Fig 4.

terminated by either adding the intensities of the hfi lines or, at the higher temperatures, by the intensity of the broader line, is constant and amounts to about 40% of all muons. We thus conclude that the collapse of the hyperfine splitting instead results from local dynamics.

The stability of the Ti^{3+} polaronic state is well known at low temperatures. The EPR signal of Ti^{3+} was observed at least up to 60 K in earlier studies [24, 25] and the temperature dependence of Ti^{3+} was investigated explicitly in a recent EPR experiment [26], where it was found that the Ti^{3+} center becomes unstable above 15 K on a time scale of 100 seconds, with an activation energy of 24 meV. We conclude that Ti^{3+} is definitely stable below 10 K on the μSR timescale of 10^{-6} s, i.e. at the conditions of the present experiment. The EPR experiment [26] also excludes fast spin flips below 10 K. These findings are for the intrinsic polaron but they apply as well to the trapped Ti^{3+} .

A local motion or site change of the muon must therefore be the cause for the observed temperature dependence of the μSR spectra. As mentioned above, the muon (and hydrogen) is bound to one of the six O atoms of the

TiO_6 octahedron (Fig. 2). However, these O-Mu bonds are not equivalent: the bond lying in the same $a-b$ plane as Ti^{3+} ('in-plane') is slightly different from the bond to O atoms below and above this plane ('out-of-plane'). The ground state is formed by a muon (hydrogen) bound to an in-plane O, which is the only configuration consistent with the experimental hfi at 1.2 K in μSR and at 5 K in ENDOR. The two pairs of hfi lines ν^0 seen in Fig. 1 both correspond to the ground state configuration, but arise from the two magnetically different sublattices. The excited state corresponds to the configuration where the muon (hydrogen) is bound to an out-of-plane O and becomes populated with increasing temperature. The same assignment was made in an IR study of vibrational modes of deuterium in rutile TiO_2 [27].

The hfi values of the out-of-plane configurations are not known experimentally, but were calculated from the ground state hfi tensor appropriately rotated to align with the excited state bonding directions. The predicted frequencies ν^* of the excited state in sublattice 2 are nearly identical to those for the ground state in sublattice 1, and the excited state frequencies for sublattice 1 lie in the wings of the diamagnetic line. For applied fields along [110], excited states are sensitive to the hyperfine parameter A_3 . With the magnetic field parallel to the c -axis we found an extremely small ground state A_3 value. This reduction of A_3 compared to the ENDOR value is likely due to the larger zero-point motion of the muon in the c -direction than will occur for H. We thus used $A_3 = 0$ when modeling the excited state frequencies.

Gradual population of the excited state, with fixed frequencies, cannot explain the reduction of the hfi splitting with temperature. We therefore assume that, at least for the muon, jumps between the two configurations occur.

A complete averaging over all bonding sites on the full TiO_6 octahedron seems unlikely due to geometric constraints. In the rutile structure there are empty channels parallel to the c -axis that are bounded by oxygens; the muon (hydrogen) sites are located inside these channels [28]. At these low temperatures, the muon can not escape from the channel due to a relatively large energy barrier. Motion among neighboring bonds within the same O channel is however possible. As indicated in Fig. 4, the muon may jump between position 1 and position 2 while remaining within the same channel. The Ti^{3+} remains stationary during these muon site changes.

We treat the muon site oscillations in the fast jump limit, which is justified since it leads to the observed reduction of the hfi splitting. For slow jumps the frequencies would basically stay fixed and only an intensity change would occur with temperature, which is not observed. In the fast jump limit the average frequency ν is given by $\nu_i = (1 - f) \times \nu_i^0 + f \times \nu_i^*$, where f is the occupation probability of the excited state. For ν_i^0 we take the four frequencies shown in Fig. 1 and for ν_i^* the estimated frequencies as discussed above. Averaging occurs

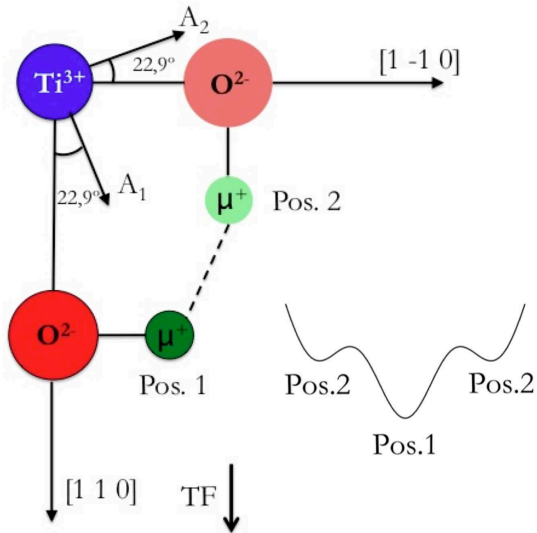


FIG. 4: Sketch of the two muon configurations in rutile TiO_2 projected onto the (001) plane. The particles with the darker colors and the solid borders lie in the same $a - b$ plane as Ti^{3+} ; the others are below and above this plane (adapted from Refs. [21, 22]). Site changes (dashed line) are possible between the two muon positions in the same oxygen channel. The insert is a sketch of the potential between the two sites. A_1 and A_2 represent the principal axes of the hyperfine tensor for Pos. 1 (indices are interchanged with respect to Ref. [21])

only for the ν_i pairs of the same O channel and the same sublattice. This corresponds to rapid jumps of the muon between position 1 and position 2 as indicated in Fig. 4. We fitted the spectra in Fig. 3 allowing the frequencies ν_i to vary according to the equation above; gaussian line widths were kept constant such that the only free parameter was the occupation f of the excited state.

The development of the spectra with temperature is well reproduced by this simple model (dashed lines in Fig. 3). The drastic change of the hfi with a relatively small change of the muon position results from the strong anisotropy of the dipolar interaction and its typical angular dependence with $(3 \cos^2 \theta - 1)$. In the present case, the frequencies to be averaged lie on opposite sides of the diamagnetic line and the averaging leads to a reduction of the hfi splitting, as observed experimentally.

Figure 5 shows the occupation probability f of the excited state, obtained from the fits described above. The line is a fit with a Boltzmann distribution $f = 2 \exp(-\Delta E/kT) / (1 + 2 \exp(-\Delta E/kT))$, where ΔE is the energy difference between the ground state and the excited state and the factor 2 takes into account that two bonds are available for the excited state whereas only one bond exists for the ground state. The fit to points below 6.3 K yields $\Delta E = 0.9(1)$ meV, in good agreement with IR values in rutile TiO_2 [29], where $\Delta E = 1.0$ meV for hydrogen and $\Delta E = 1.2$ meV for deuterium were reported.

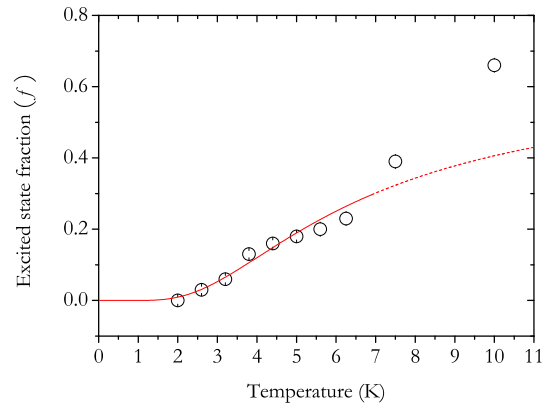


FIG. 5: Occupation probability f of the excited state as a function of temperature. The line is a Boltzmann distribution fit up to 6.3 K, with an activation energy $\Delta E = 0.9(1)$ meV.

In Ref. [29], as in the present analysis, only the ground state and the first excited state were considered. Stavola et al. included a third state in the analysis of their IR data [27], with an 11 meV excitation energy, which they assigned to H bound to the nearest O atom that is not part of the central TiO_6 octahedron; thus, directly across the channel from the ground state site. This third state likely plays a non-negligible role at our 7.5 K and 10 K points, thus justifying the poor fit at these temperatures and limiting our analysis to a maximum of 6.3 K.

In summary, via a comparison of the hyperfine interactions, we show that in rutile TiO_2 Mu and H form the same configuration with an identical electronic structure within experimental uncertainty. Small deviations of the hyperfine values beyond scaling with the magnetic moments are most likely due to the larger zero-point motion of Mu compared to H. We additionally present a detailed description of the low temperature bonding configurations: the central part consists of Ti^{3+} , at which the donor electron is localized on a Ti ion, surrounded by six O atoms. The muon (hydrogen) is bound to one of the six oxygens of this TiO_6 complex. However, these bonds are not equivalent. The ground state is formed by bonding to the in-plane oxygens only, which lie in the same $a - b$ plane as Ti^{3+} . Two different hyperfine splittings occur since the muon can be in either of the two orientationally inequivalent TiO_6 sublattices. In the excited state, jumps to out-of-plane oxygens of the same TiO_6 octahedron occur. The gradual population of the excited state with increasing temperature and rapid fluctuations between neighboring bonding sites lead to the collapse of the hyperfine interaction. These site changes occur within the same oxygen channel and on a single TiO_6 sublattice. The present data indicate an energy difference of about 0.9(1) meV between ground state and excited state. Such a low value should be anticipated since the bonds in the TiO_6 octahedron are almost equivalent.

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