Negatively Charged Muonium and Related Centers in Solids

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Muonium (Mu) centers formed upon implantation of $\mu^+$ in a solid have long been investigated as an experimentally accessible model of isolated hydrogen impurities. Recent discoveries of hydric centers formed at oxygen vacancies have stimulated a renewed interest in $H^+$ and corresponding Mu$^-$ centers in oxides. However, the two diamagnetic centers, Mu$^+$ and Mu$^-$, are difficult to separate spectroscopically. In this review article, we summarize established and developing methodologies for identifying Mu centers in solids, and review recent Mu studies on said centers supposedly formed in mayenite, oxygen-deficient SrTiO$_3$, and BaTiO$_3$, H$_2$ oxyhydride.

1. Introduction

Hydrogen is a ubiquitous impurity in most semiconductors and insulators, which can unintentionally enter crystalline lattices during crystal growth as well as subsequent processing. The incorporated hydrogen often has a significant impact on structural and electrical properties of these materials in spite of low hydrogen solubilities.\(^1\) It is beneficial to application of Si, where hydrogen passivates dangling bonds of undercoordinated Si at vacancies, impurities, surfaces, and interfaces. Meanwhile, hydrogen can also passivate deliberate dopants by forming H-dopant complexes. It has also been recognized that hydrogen isolated from other defects has an electrical activity, involving all allowed charge states: $H^+$, $H^0$, and $H^-$. The isolated hydrogen often shows amphoteric behavior, acting as both deep donor and acceptor in accordance with the Fermi level position in the band gap.\(^2\) It can also behave as shallow donor, which has been observed in several oxides, such as ZnO,\(^3\) or as shallow acceptor. Because of these complex electrical activities, a detailed understanding of hydrogen and related defects is vital for application of host materials. However, it is very difficult to experimentally characterize hydrogen in such trace quantities, particularly isolated hydrogen.

Muonium (Mu) centers formed upon implantation of $\mu^+$ in a solid have long been used as an experimentally accessible model of hydrogen.\(^1\) Indeed, the electronic states of H and Mu centers are nearly identical, as can be seen when comparing atomic Mu$^0 (= \mu^+ e^-)$ and H$^0$ in a vacuum: they have almost the same reduced mass. Microscopic insight into Mu centers can be obtained using the muon spin rotation, relaxation, and resonance ($\mu^+ SR$) spectroscopy, which is analogous to the $^1H$ nuclear magnetic resonance (NMR) spectroscopy. Technical details of the $\mu^+ SR$ method have been previously outlined in existing literature, such as Ref. [4]. Since only a small number of muons stay in a sample at a time, the $\mu^+ SR$ method can provide information on isolated Mu centers. In principle, the electronic structures of Mu centers can be investigated more precisely than those of corresponding H centers by measuring hyperfine frequencies or chemical shifts because the gyromagnetic ratio for $\mu^+$ is roughly three times larger than that for $^1H$. It should be also emphasized that the Mu centers observed may not be in global equilibrium\(^5\) because the formation of Mu centers and the observation of their states are completed in a relatively short time scale, which is comparable to the muon lifetime $\sim 2.2 \mu s$. Therefore, the $\mu^+ SR$ spectroscopy is potentially useful for investigating excited hydrogen configurations in heavily hydrogenated compounds as well, where Mu species are expected to behave as metastable excess hydrogen and interact with preexisting hydrogen in the host lattice.\(^6\)

Historically, the Mu approach has played an important role in microscopically establishing the amphoteric behavior of isolated interstitial hydrogen in many semiconductors, such as GaAs.

Fig. 1. (Color online) Defect-formation energy diagram for interstitial Mu in GaAs.

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as Si and GaAs. Figure 1 shows the Mu defect-formation energy diagram for GaAs obtained from comparisons with a theoretical model of H\(_2\)\(^0\) and the experimental results for Mu.\(^5\)

This indicates that the interstitial Mu counteracts prevailing conductivity as a donor \(\text{Mu}^+\) or an acceptor \(\text{Mu}^-\). In addition, the dominant equilibrium charge state changes from positive to negative at the charge-transition level \(E(+/-)\) as a function of the Fermi energy \(E_F\). According to Van de Walle and Neugebauer, \(E(+/-)\) for H should be universally pinned at a specific energy below the vacuum level.\(^23\) This was experimentally confirmed by Lichti \textit{et al.} for Mu analogs in Si, Ge, GaAs, GaP, ZnSe, and 6H-SiC.\(^3\)

The defect-formation energy diagram also suggests that the dominant equilibrium charge state is always \(\text{Mu}^+\) (\(\text{Mu}^-\)) when \(E(+/-)\) is in the conduction (valence) band. Indeed, such shallow donor (acceptor) behavior has been theoretically predicted for interstitial H in some oxides, nitrides, and sulfides,\(^7\)\(^-\)\(^12\) as well as indirectly confirmed by observing shallow donor (acceptor) Mu states.\(^13\)\(^-\)\(^21\)

Recent discoveries of hydric centers formed at oxygen vacancies \((V_O)^-\) have stimulated a renewed interest in H\(^-\) and corresponding Mu\(^-\) centers in oxides. Theoretically, the most stable form of hydrogen trapped at \(V_O\) is H\(^-\), where doubly charged \(V_O^2^+\) changes into singly charged \(H_O^+\).\(^10\),\(^11\),\(^22\),\(^23\) This indicates that the substitutional H\(^-\) serves as a single donor in sharp contrast to the acceptor behavior of the interstitial H\(^+\). A large amount of O\(^2^-\) in the host lattice can be replaced with H\(^-\) due to its structural stability (up to \(\sim 40\%\) in SmFeAsO\(_{1-x}\),\(^24\)\(^\mu\) and \(\sim 20\%\) in BaTiO\(_3\),\(^25\)). The substitutional H\(^-\) is becoming more and more important as an electron dopant in oxides\(^24\) and a novel charge carrier for solid-state ionic conductors.\(^25\) However, microscopic insight into substitutional H\(^-\) and related defect complexes is currently limited.

The \(\mu^+\)SR spectroscopy is potentially useful for the study of Mu\(^+\) analog in oxides, where attention should be focused on distinguishing between Mu\(^-\) and Mu\(^+\). Generally, it is difficult to separate these diamagnetic Mu species spectroscopically because they have quasi-identical responses to the applied magnetic field \(B\). In this review article, we summarize new and existing methodologies for identifying Mu\(^-\) centers. In addition, we review the recent \(\mu^+\)SR studies on said centers supposedly formed in mayenite, oxygen-deficient SrTiO\(_3\),\(^\alpha\), and BaTiO\(_3\)\(-\)H\(_2\) oxyhydride upon implantation of \(\mu^+\). Finally, we provide concluding remarks on the future prospects of Mu\(^+\) studies.

2. Methodologies for Identifying Mu\(^-\) and Related Centers

2.1 Local Structures

Computational studies on H impurities in semiconductors have revealed that correlations exist between their crystallographic sites and favorable charge states (Fig. 2).\(^26\) However, it is difficult to identify the structures of H-related defects due to their random distribution as well as low concentrations. Therefore, the information on the structures of Mu centers obtained from \(\mu^+\)SR spectroscopy is vital with respect to identifying Mu/H charge states. The structures of paramagnetic Mu\(^0\) centers can be easily estimated from hyperfine anisotropies.\(^27\),\(^28\) This is also the case for shallow and polaronic Mu centers, where a Mu\(^+\) or Mu\(^-\) core weakly binds an unpaired electron or hole.\(^13\)\(^-\)\(^21\),\(^29\) Contrastingly, diamagnetic Mu\(^\pm\) centers are much more difficult to characterize because they do not have unpaired electrons, and, accordingly, they lack hyperfine interactions. In such cases, magnetic-dipolar and electric-quadrupolar interactions between a muon and surrounding nuclei can be used to identify the structures of diamagnetic Mu centers. These interactions can be efficiently studied using the muon level-crossing resonance (\(\mu\)LCR) technique,\(^10\) as demonstrated in heavily doped GaAs.\(^30\),\(^31\)

Two paramagnetic and two diamagnetic Mu centers are primarily observed in GaAs.\(^13\) In heavily doped samples, only the diamagnetic Mu centers are detectable. Theoretical studies on H impurities\(^26\) suggest that they should be assigned to Mu\(^-\) at the tetrahedral site surrounded by Ga atoms (\(T_\text{Ga}\)) or Mu\(^+\) near the bond-center (BC) position (Fig. 2). The Mu\(_T\) and Mu\(_BC\) centers are theoretically stable in \(n\)-type and \(p\)-type carrier-rich environments, respectively.

Chow \textit{et al.} investigated the diamagnetic Mu center formed in \(n\)-type GaAs (Si concentrations between \(2.5 \times 10^{18}\) and \(5 \times 10^{18}\) \(\text{cm}^{-3}\)) using \(\mu\)LCR and conventional transverse-field (TF) \(\mu^+\)SR techniques to establish the Mu\(^-\) state from a structural point of view.\(^30\) Herein, the time-integrated muon spin polarization \(P\) was obtained in the longitudinal field (LF) configuration\(^4\) as a function of \(B\). The spin Hamiltonian relevant to this experiment comprises the Zeeman interactions for the muon and surrounding nuclei, the magnetic-dipolar interactions between the muon and the nuclei, and the electric-quadrupolar interactions for the nuclei that have an electric field gradient (EFG) primarily caused by the diamagnetic Mu. Resonant cross relaxation between the muon and the nuclei, observed as dips in \(P(B)\), occurs when the muon Zeeman splitting matches the separation of the combined quadrup-
lar and Zeeman energies levels for the nuclei. The resonance position depends on the electric quadrupolar parameter $Q_i$ for the on-resonance nucleus $i$ and the angle $\theta_i$ between $B$ and the muon-nucleus axis. For a given $Q_i$ and $\theta_i$, the intensity of the resonance line is a function of the muon-nuclear dipolar coupling $D$, which is dependent on the muon-nucleus distance $r_i$. Chow et al. observed a couple of doublets in the $P$ spectrum under $B \parallel (001)$, which were assigned to the two spin-3/2 isotopes of $^{60}$Ga and $^{71}$Ga. Another resonance was identified at the low-field end of the spectrum, assigned to $^{75}$As with spin 3/2. The small number of lines and the structure of the Ga doublets indicate that the principal axis of the EFG tensor, or the muon-Ga axis, is parallel to $T_{Ga}$ site, the $r_{Ga}$, of which is roughly 10% shorter than expected for an undistorted GaAs lattice.

The $\mu$LCR technique cannot be applied to systems that do not contain nuclei with a finite nuclear quadrupolar moment. Even in such cases, the local structures of diamagnetic Mu centers are occasionally determined via the magnetic-dipolar interactions between a muon and the surrounding nuclei. Characteristic oscillating features appear in zero field (ZF) $\mu$SR spectra when the muon is dipole coupled to a small number of nuclei, thus creating an entangled a-few spin system. Such a state often forms in materials containing fluorine or hydrogen, with relatively strong electronegativity, which causes muons to preferentially localize in their vicinity. In addition, the $^{19}$F and $^{1}$H nuclei with spin 1/2 have relatively large dipolar moments. Here we consider an entangled spin system consisting of a muon and a spin-1/2 nucleus. The powder-averaged muon spin relaxation function for the two-spin state (hereafter, referred to as 2S) in ZF can be expressed as

$$G_{2S}(t) = \frac{1}{6} + \frac{1}{6} \cos(2\pi f_dt)$$

$$+ \frac{1}{3} \cos(\pi f_dt) + \frac{1}{3} \cos(3\pi f_dt),$$

$$f_d = \frac{\mu_0 h \gamma_\mu \gamma_i}{8\pi^2 d^3},$$

where $d$ is the distance between the $\mu^+$ and the spin-1/2 nucleus and $\gamma_\mu$ and $\gamma_i$ are the gyromagnetic ratios for $\mu^+$ ($\gamma_\mu/2\pi = 135.53 \text{ MHz/T}$) and the nucleus ($\gamma_i/2\pi = 42.58 \text{ MHz/T}$ for $^1\text{H}$ or $40.08 \text{ MHz/T}$ for $^{19}\text{F}$), respectively (Fig. 3). The muon-nucleus distance, $d$, obtained by fitting eq. (1) is useful with respect to estimating the local structure of a diamagnetic Mu center. This method was applied to identify an $\text{H}^-\text{Mu}^+$ complex supposedly formed in the BaTiO$_3$-$\text{H}_x$ oxyhydride upon implantation of $\mu^+$ by Ito et al., as reviewed in Section 3.3.

### 2.2 Thermal Properties

As the temperature increases, the Mu site changes and/or charge-state transitions are thermally activated. Characteristic energies relevant to these processes are obtained from the temperature dependences of diamagnetic and paramagnetic Mu amplitudes and muon spin relaxation rates. The Mu species involved can be identified by mapping these energies to theoretically allowed transitions. The $H$/Mu defect-formation energy diagram, such as Fig. 1, obtained from first-principles calculations provides potential candidates for the transitions that are linked to Mu sites and charge states. In low-carrier systems, final Mu states can be different from promptly formed Mu states, which may be reached via a delayed process with a time constant comparable to the muon lifetime $\sim 2.2 \mu$s. The radio frequency (RF) $\mu$SR technique is suitable for investigating such final states, as demonstrated in the studies of Mu centers in Si, Ge, and GaAs.

Longitudinal $T_1$ relaxation is often linked to cyclic charge-state transitions between Mu$^0$ and Mu$^+$ or Mu$^0$ in thermal equilibrium. Chow et al. established that the Mu defect in heavily doped $n$-type GaAs:Si serves as a deep recombination center via the observation of a Mu$^{10}_T$ charge cycle. The longitudinal relaxation rate $1/T_1$ associated with the Mu$^{10}_T$ dynamics is expressed as a function of $\lambda_\mu$, $\lambda_0$, $A_\mu$, and $B$, where $\lambda_0$ and $\lambda_\mu$ are the rates of conversion for Mu$^0_T$ and Mu$^0_T$ respectively, and $A_\mu$ is the hyperfine coupling constant for Mu$^0_T$. The $\lambda_0$ (hole capture rate) exhibits Arrhenius-like behavior with an activation energy of 1.66(7) eV. This value is approximal to that of the band gap in GaAs, suggesting that a band-gap excitation governs this process. Contrastingly, the $\lambda_\mu$ (electron capture rate) is independent of temperature and much larger than the $\lambda_0$. This is expected since the electron-carrier concentration is nearly temperature-independent in heavily doped $n$-type GaAs.

The $T_1$ relaxation can also occur when a Mu$^{10}_T$ charge cy-
cle is activated. The values and behavior of charge-transition rates associated with this process in intrinsic Si are considerably different from those of $\lambda_0$ and $\delta_0$ in heavily doped $n$-type GaAs.\textsuperscript{43} This suggests that the charge state of diamagnetic Mu species involved in a Mu-charge cycle can be distinguished by carefully investigating the charge-transition rates.

2.3 *Photo-Detachment of the Second Electron from Mu*  

The optical excitation of electrons trapped at point defects to the conduction band (CB) is a useful method of investigating the corresponding defect levels formed in the band gap. Such a technique, combined with $\mu^+\text{SR}$, is also helpful with respect to distinguishing between Mu$^-$ and Mu$^+$ in semiconductors. The photoexcitation of the second electron from Mu$^-$ to the CB causes a paramagnetic Mu$^0$ center, which can be described as

$$\text{Mu}^- + h\nu \rightarrow \text{Mu}^0 + e^- (\text{CB}),$$

where $h\nu$ denotes a photon with energy corresponding to the optical excitation of the second electron to the CB minimum. The photogenerated Mu$^0$ center is detectable using conventional $\mu^+\text{SR}$ techniques due to the strong hyperfine interactions.

Shimomura et al. conducted optical $\mu^+\text{SR}$ experiments to identify the Mu$_{\text{C}}^-$ acceptor in $n$-type GaAs using a high-power pulse laser.\textsuperscript{46,47} The experiments were performed at the port 2 of the RIKEN-RAL muon facility, UK, using a broadband OPO laser system pumped by a 355-nm beam from a Nd:YAG laser. The laser system was operated in pulse mode at a 25-Hz repetition rate and synchronized to the arrival of muon pulses to a single-crystalline GaAs wafer doped with $3 \times 10^{16}$ cm$^{-3}$ Si. The decrease in $\mu^+\text{SR}$ asymmetry associated with the Mu$_{\text{C}}^- \rightarrow \text{Mu}^0$ conversion was recorded as a function of photon energy, which was scanned from 0.8 to 1.5 eV. Shimomura et al. found a broad feature centered at around 1 eV after normalizing the asymmetry decrease by laser power. This is consistent with the results obtained from the temperature dependence of RF-$\mu^+\text{SR}$ amplitude assigned for the Mu$_{\text{C}}^- \rightarrow \text{Mu}^0 + e^- (\text{CB})$ excitation.\textsuperscript{43} Moreover, a sharp feature was identified at around 1.5 eV, which was attributed to the spin or charge scattering between Mu$_{\text{C}}^-$ and photoexcited electrons. Subsequent experiments using circularly polarized laser light revealed that this effect depends on the polarization direction of conduction electrons with respect to the muon polarization direction; however, the exact mechanism is yet to be clarified.\textsuperscript{48,49}

2.4 *Chemical Shifts*  

Recent systematic $^1\text{H}$-NMR studies in Ca and Sr-mayenites (C12A7 and S12A7) have revealed that $^1\text{H}$ chemical shifts are useful with respect to distinguishing nominally H$^+$ and H$^-$ species.\textsuperscript{50} Mayenites comprise a class of cage-structured compounds that contain “extraframework” anions in their cages, such as $\text{O}^{2-}$, $\text{OH}^-$, $\text{H}^+$, and $e^-$.\textsuperscript{51} Hayashi et al. prepared mayenite samples incorporating $\text{OH}^-$ or $\text{H}^-$ extraframework anions with concentrations approximal to theoretical maxima and measured the isotropic chemical shifts $\delta_{iso}$ for said H species using the magic-angle-spinning technique. They obtained a $\delta_{iso}$ of $+5.1$ ppm ($+6.1$ ppm) for H$^-$ and $-0.8$ ppm ($-1.3$ ppm) for OH$^-$ (formally H$^+$) in C12A7 (S12A7) with respect to the tetramethylsilane (TMS) reference. Surprisingly, the observed values of $\delta_{iso}$ for H$^-$ are larger than those for H$^+$, falling within the typical range for the H$^+$ state from +20 to 0 ppm.\textsuperscript{52} This result suggests that the electron density around the $^1\text{H}$ nuclei, which is associated with the chemical-shielding effect, is larger for H$^+$ than H$^-$ species in mayenites. First-principles calculations using the periodic and embedded cluster approaches successfully reproduced such electronic states as well as the $\delta_{iso}(\text{H}^+) > \delta_{iso}(\text{H}^-)$ relation. The experimental and theoretical results for $\delta_{iso}$ are consistent with each other within 1 ppm, demonstrating that the combined approach based on $^1\text{H}$ chemical shift measurements and first-principles calculations is useful with respect to identifying the charge state of H species. Systematic surveying of the relation between the $^1\text{H}$ chemical shift and the local structure around H species has also been conducted for many oxides, ionic hydrides, and mixed-anion hydrides. The research suggests that the distance between the H species and the coordinating atoms strongly affects the chemical shift and that $\delta_{iso}$ for both H$^+$ and H$^-$ is distributed in a similar range. This indicates that the H$^+$ species can be separated by carefully analyzing the chemical shift; however, it does not serve as an easy fingerprint of the nominal charge states.

The chemical shift approach has also been applied to identify Mu$^+$ species supposedly formed in C12A7:O$^{2-}$ and C12A7:$e^-$ upon implantation of $\mu^+$ by Hiraishi et al.,\textsuperscript{53} as reviewed in Section 3.1.

3. Recent Mu$^+$ Studies in Oxides

3.1 Chemical Shifts of Diamagnetic Mu Centers in Mayenite \textsuperscript{[53]}  

The extraframework H species in C12A7 mayenite have attracted much attention in association with persistent photocconductivity in C12A7:H$^-$.\textsuperscript{54} and highly efficient ammonia synthesis using Ru-loaded C12A7:$e^-$.\textsuperscript{55,56} Hiraishi et al. adopted the $\mu^+\text{SR}$ technique to investigate the electronic structure and chemical activity of these centers using Mu analogs.\textsuperscript{53} Here, we focus on their attempts to distinguish extraframework OMu$^-$ (formally Mu$^+$) and Mu$^+$ species by measuring the Mu chemical shift $K_\mu$ according to the methodology outlined in Section 2.4. These species are supposedly formed in C12A7:O$^{2-}$ and C12A7:$e^-$, respectively, via

$$\{\text{O}^{2-}\} + \text{Mu}^0 \rightarrow \{\text{OMu}^0\} + \{e^-\},$$

$$\{e^-\} + \text{Mu}^0 \rightarrow \{\text{Mu}^-\},$$

where \{X\} indicates an extraframework anion X in a cage.

Mu chemical shift measurements were conducted on single-crystalline samples of C12A7:O$^{2-}$ (pristine insulator) and C12A7:$e^-$ (electride, $n \sim 10^{21}$ cm$^{-3}$) in the high-TF configuration\textsuperscript{57} at TRIUMF, Canada, using a spin-polarized sur-
face muon beam. A TF of 6 T was applied along the muon incident axis, which was nominally perpendicular to the (001) plane. For both samples, the value of $K_{\mu}$ was mostly independent of temperature below 300 K. The temperature-averaged $K_{\mu}$ was +0.3(4) ppm for C12A7:O$^-$ and +6.6(4) ppm for C12A7:e$^-$ using CaCO$_3$ as a zero-shift reference. These results are consistent with corresponding $^1H$ chemical shifts, specifically $\delta_{\text{iso}} = -0.8$ ppm for C12A7:OH$^-$ and $\delta_{\text{iso}} = +5.1$ ppm for C12A7:H$^+$, using TMS as a reference. On the basis of this similarity, Hiraishi et al. assigned the chemical state of diamagnetic muons in the C12A7:O$^-$ and C12A7:e$^-$ samples to {OMu}$^+$ and {Mu}$^+$, respectively. However, there seems to be some ambiguity associated with the difference in the gyromagnetic ratios for Mu$^+$ and $^1H$ ($\gamma_{\mu}/\gamma_H \sim 3.2$). Indeed, the value of $K_{\mu}$ for {Mu}$^+$ in C12A7:e$^-$ is considerably smaller than expected from the $^1H$ chemical shift for C12A7:H$^+$ ($5.1 \times 3.2 = 16$ ppm). This discrepancy was tentatively attributed to the metallic environment of Mu$^+$ in the C12A7:e$^-$ sample ($n \sim 10^{21}$ cm$^{-3}$).

3.2 Possible Charge-State Dynamics of Mu in Oxygen-Deficient SrTiO$_{3-x}$ [57]

Oxygen vacancies can act as electron donors in SrTiO$_3$, causing a wide range of interesting phenomena, such as superconductivity[59] and ferromagnetism[60]. The oxygen-deficient SrTiO$_{3-x}$ can be obtained by annealing the parent band insulator in highly reducing atmospheres. Hydrogen is often used as a reducing agent in this process. Systematic annealing studies have revealed that such a treatment does not only remove oxygen to obtain metallic SrTiO$_{3-x}$, but that it can also create other types of defects involving hydrogen.[61] The most common H-related defect in perovskite oxides is an interstitial H bound to an O$^-$ in the host lattice, which serves as a shallow donor in SrTiO$_3$.[62] This behavior has also been confirmed from Mu viewpoints.[29, 63] Contrastingly, subsequent hydrogen annealing of the metallic SrTiO$_{3-x}$ causes a decrease in conductivity.[61] This contradictory behavior against the interstitial H$^+$ implies that the site and charge state of hydrogen introduced by the subsequent annealing is considerably different from those of the interstitial H$^+$. First-principles studies suggest that the most stable form of hydrogen in SrTiO$_{3-x}$ is H$_2^-$ located at the anion site, where doubly charged V$^{2+}$ changes into singly charged H$_3O^+$.[11]

Motivated by these theoretical predictions, Shimomura et al. conducted $\mu^+$SR experiments in oxygen-deficient SrTiO$_{3-x}$ at the D1 area of J-PARC MUSE, Japan, with the expectation that implanted muons are preferentially trapped in V$_O$ where they form a substitutional Mu$^-$ center.[57] The SrTiO$_{3-x}$ sample was prepared by reducing single-crystalline wafers of SrTiO$_3$ with the (110) surface according to the procedure outlined in Ref. [61]. The $\mu^+$SR measurements were performed using a double-pulse surface muon beam and the DΩ1 spectrometer (maximum asymmetry ~ 0.20) in the LF geometry[4] under a weak TF of 2 mT applied perpendicular to the [110] direction.

$\mu^+$SR asymmetry spectra were fitted to a function composed of two exponentially-damped cosines with a shared diamagnetic frequency. Following [57], the fits were refined by taking into account double-pulse correction. Figure 4 shows the partial asymmetries $A_1$ and $A_2$ and the exponential relaxation rates $\lambda_1$ and $\lambda_2$ in SrTiO$_{3-x}$. These values were updated from those in Ref. [57] by taking account of double-pulse correction[58] in a series of fits. The dashed line indicates the maximum asymmetry for the DΩ$^+$ $\mu^+$SR spectrometer.
(see Section 2.2). However, there seem to be some difficulties in this interpretation. In particular, the \( \text{Mu}^{+} \) charge cycle model for \( n \)-type materials assumes that the \( \text{Mu}^{+} \) defect creates a deep level in the band gap and serves as a recombination center.\(^{44} \) However, according to computational studies, the defect level for the substitutional \( \text{H}^{+} \) falls in the valence band.\(^{11} \) Moreover, a characteristic energy of \( \sim 0.1 \text{ eV} \) estimated from the increase in \( A_{2}(T) \) is much smaller than the band-gap energy of \( 3.2 \text{ eV} \). Accordingly, a different model may be necessary to explain the unusual exponential relaxation possibly associated with \( \text{Mu} \)-state dynamics in \( \text{SrTiO}_{3-x} \).

### 3.3 Metastable Hydride-Related Center in \( \text{BaTiO}_{3-x} \text{H}_x \) \([6]\)

Oxyhydrides of perovskite titanates \( \text{ATiO}_{3-x} \text{H}_x \) (\( A = \text{Ba}, \) Sr, and Ca) comprise a new class of hydrogen ion conductors, which can be obtained from \( \text{ATiO}_3 \) parent insulators by \( \text{CaH}_2 \) reduction.\(^{25,64,65} \) Conventional diffraction techniques can be applied to identify the \( \text{H}^{+} \) site in \( \text{ATiO}_{3-x} \text{H}_x \) since a large amount of \( \text{H} \) up to \( x \sim 0.6 \) can be incorporated. A combined analysis of x-ray and neutron diffraction data revealed that \( \text{O}^{2-} \) ions in the perovskite lattice are randomly substituted by \( \text{H}^{-} \) ions without creating any detectable amount of \( \text{V}_0 \). The substitutional \( \text{H}^{+} \) in \( \text{ATiO}_{3-x} \text{H}_x \) is in sharp contrast with the interstitial protonic hydrogen (formally \( \text{H}^{+} \)) bound to an \( \text{O}^{2-} \) ion, which is a common impurity often found in \( \text{ATiO}_3 \). Macroscopic gas analysis revealed that the hydrogen in the solid phase is mobile and exchangeable in hydrogen gas environments above \( \sim 400 \text{°C} \). Moreover, the reduction treatment changes the parent band insulators into paramagnetic metals. These transport characteristics suggest that \( \text{ATiO}_{3-x} \text{H}_x \) compounds are suitable for application in mixed electron/hydrogen ion conductors and hydrogen membranes.

Several theoretical models have been proposed regarding the stability of \( \text{H} \) species in \( \text{ATiO}_{3-x} \text{H}_x \) and their kinetics.\(^{10,11,22,23} \) These studies commonly conclude that the substitutional \( \text{H}^{+} \) configuration is most stable in \( n \)-type carrier-rich environments. With respect to the dynamical aspect of \( \text{H} \) in the solid phase, two types of scenarios have been proposed. One is based on the concept of correlated migration of \( \text{H}^{+}, \) \( \text{O}^{2-} \), and \( \text{V}_0 \) in the network of the anion site [type-I \( \text{H} \) migration, Fig. 5(a)].\(^{22,25,66} \) The other model [type-II \( \text{H} \) migration, Fig. 5(b)] involves two metastable \( \text{H} \) configurations: the interstitial \( \text{H}^{+} \) bound to \( \text{O}^{2-} \), and two \( \text{H} \) atoms trapped at the same anion site in place of \( \text{O}^{2-} \). The former can support rapid proton diffusion via the Grothuss mechanism,\(^{29} \) and the latter can act as a hydrogen exchange center, which is expected to temporarily form due to the interaction between a substitutional \( \text{H}^{+} \) and an incoming interstitial \( \text{H}^{+} \). Two charge configurations, hydridic \( 2\text{H}^{-1} \) and molecular \( \text{H}_2 \),\(^{23} \) have been proposed for this center.

The \( \mu^{+} \)SR technique is useful for creating and investigating experimentally accessible models of such metastable \( \text{H} \)-related centers. This is based on the fact that the as-implanted mixture of \( \text{Mu} \) states is far from equilibrium, often involving metastable excited states.\(^{29} \) Ito et al. conducted \( \mu^{+} \)SR investigations of prototypical \( \text{BaTiO}_{3-x} \text{H}_x \) to obtain microscopic insight into the metastable \( \text{H} \) configurations associated with type-II \( \text{H} \) migration using Mu as a pseudoisotope of \( \text{H}^{+} \).\(^{6} \) The \( \mu^{+} \)SR measurements of powder samples of \( \text{BaTiO}_{3-x} \text{H}_x \) \((x = 0.1, 0.2, 0.3 \) and \( 0.5 \)) were carried out in the D1 area of J-PARC MUSE, Japan, and in the port 2 of RIKEN-RAL, U.K., using a spin-polarized surface muon beam. Muons implanted in the samples lose their kinetic energy via electromagnetic interactions with host atoms and are then trapped in local potential minima (not necessarily in the global minimum). In \( \text{BaTiO}_{3-x} \text{H}_x \), implanted muons are expected to serve as incoming excess hydrogen, creating \( \text{Mu} \) analogs of the metastable configurations involved in the type-II \( \text{H} \) migration model together with \( \text{H}^{-} \) in the host lattice. Information on their charge states was obtained via the local structure approach outlined in Section 2.1.

Figure 6(a) shows the time evolution of muon spin polarization \( P(t) \) at 15 K in ZF for the \( x = 0.3 \) and 0.5 samples. The \( P(t) \) curves have a damped cosine-like feature superposed on a Gaussian relaxation curve. The oscillating feature is a signature of the formation of the entangled \( 2\text{S} \) state composed of diamagnetic \( \text{Mu} \) and \( \text{H} \). The Gaussian relaxation part is usually ascribed to muons that interact with a large number of surrounding nuclei without creating such a special magnetic coupling.\(^{67} \) Therefore, the two components were tentatively assigned to the metastable configurations involved in the type-II model: the \( 2\text{S} \) component for a \( \text{Mu} \) analog of the hydrogen exchange center [Fig. 6(e)] and the Gaussian component for the interstitial \( \text{Mu}^{+} \) [Fig. 6(f)]. Accordingly, the ZF spectra at 15 K were fitted to the following function,

\[
P(t) = p_{2S}e^{-\lambda t}G_{2S}(t, f_{d}) + (1 - p_{2S})e^{-\lambda t^{2}},
\]

where \( \lambda, p_{2S}, \) and \( G_{2S}(t, f_{d}) \) denote the relaxation rate, the fraction, and the ZF relaxation function in eq. (1) for the

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**Fig. 5.** (Color online) (a) Type-I and (b) type-II \( \text{H} \) migration models for \( \text{ATiO}_{3-x} \text{H}_x \). The structure was drawn using VESTA.\(^{32} \)
separating Mu\(^-\) from Mu\(^+\) is yet to be established. A lot of beam time is still required to scan the vast parameter space of temperature, field, and carrier concentration to accumulate indirect evidence of Mu charge states and secure overall consistency with theoretical predictions. Pulsed muon beams are beneficial for these experiments due to the capability of the high-count-rate measurements. The major drawback of the pulsed \(\mu^+\)SR method (i.e., relatively low time resolution) can be mostly overcome by using the RF resonance technique. The RF technique is also indispensable with respect to the sensitivity to the Mu final state formed via a delayed process.\(^5\)\(^,\)\(^4\)\(^0\)\(^-\)\(^4\)\(^3\)

Unfortunately, the RF-\(\mu^+\)SR method has only occasionally been used for materials research, even though the majority of muon facilities support it. Obviously, further improvements of RF instruments (and their user interfaces) are vital for future Mu\(^-\) studies.

The Mu chemical shift approach reviewed in Section 2.4 and Section 3.1 is undoubtedly promising for separating Mu\(^-\) from Mu\(^+\); however, it also seems to require further improvements. This approach is based on comparisons with computational and/or experimental \(^1\)H chemical shifts. Unfortunately, the use of the different standard samples (TMS for \(^1\)H-NMR\(^\text{50}\)) and CaCO\(_3\) for \(\mu^+\)SR\(^\text{53}\)) may have resulted in some ambiguity in said comparison. These materials were employed to set a chemical shift of zero. It should be noted that the zero shift does not necessarily mean a null chemical-shielding effect on the \(^1\)H nuclei or muons. First-principles calculations revealed that the absolute screening constant for protons in TMS is about 30 ppm.\(^\text{58}\) This relatively high shielding results in the majority of \(^1\)H resonances occurring downfield within 20 ppm of TMS.\(^\text{52}\) Meanwhile, little is known about the chemical-shielding effect on the diamagnetic Mu species in CaCO\(_3\). The relation between the TMS and CaCO\(_3\) references must be clarified for establishing the Mu chemical shift strategy with respect to separating diamagnetic Mu species. The absolute screening constant for the diamagnetic Mu species in CaCO\(_3\) may be determined with high precision by using the apparatus for the MuSEUM (Muon Spectroscopy Experiment Using Microwave) project at J-PARC.\(^\text{69}\)

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Fig. 6. (Color online) (a) ZF-\(\mu^+\)SR spectra of BaTiO\(_3\)-\(\text{H}_2\) (\(x = 0.3\) and 0.5) at 1.5 K. The solid curves represent the best fits to eq. (6). The dashed curves show partial contribution from the 2S component. (b), (c), and (d): \(x\) dependences of \(f_d\) and \(d_{PSR}\), and \(\Delta\) at 1.5 K in ZF (e) and (f): the most probable atomic configurations associated with the 2S and Gaussian components. In the structure model (f) assigned to the Gaussian component, O\(^2-\) ions at the third nearest neighbor and further anion sites are randomly replaced by H\(^+\) with a probability of \(x/3\). The structure was drawn using VESTA.\(^\text{32}\)

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2S state, respectively. The distance \(d\) between a muon and a nearby H can be obtained from \(f_d\) through eq. (2). \(d\) is independent of \(x\) [Fig. 6(b)], which is expected since the Mu-H structure should be robust against changes in \(x\). The average value of \(d = 1.64(1)\) Å is consistent with the theoretical H\(^-\)-H\(^+\) distances of 1.64 and 1.67 Å for symmetric and asymmetric 2H\(^-\) centers in SrTiO\(_3\).\(^\text{11}\) however, this does not match \(d = 0.74\) Å for a molecular MuH configuration. On the basis of these results, Ito \emph{et al.} assigned the 2S component to a hydridic (Mu\(^-\), H\(^+\)) complex formed at V\(_O\). Meanwhile, the \(x\) dependence of the Gaussian relaxation rate \(\Delta\) associated with the interstitial Mu\(^+\) configuration can be reproduced by calculating the rms width of the nuclear dipolar field at the interstitial Mu\(^+\) site, as shown in Fig. 6(d) with a solid curve.

The temperature dependence of \(\Delta\) for the \(x = 0.5\) sample reveals that interstitial Mu\(^+\) diffusion (activation energy ~ 0.1 eV) and subsequent trapping in an unknown deep potential well occur above 100 K within the \(\mu^+\)SR time window. This re-trapping process may function as a rate-limiting step of macroscopic H transport in the BaTiO\(_3\)-\(\text{H}_2\) lattice. It is not taken into account in the type-II H migration model.

4. Future Prospects

The identification of Mu\(^-\) and related defects in solids remains a challenge due to the fact that an easy method of

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