Abstract. We report preliminary low-energy $\beta$-NMR measurements of $^8$Li$^+$ implanted in single crystal rutile TiO$_2$ at an applied field of 6.55 T and 300 K. We observe a broad 12 kHz wide quadrupole split resonance with unresolved features and a sharp component at the Larmor frequency. The line broadening may be caused by overlapping multi-quantum transitions or motion of $^8$Li$^+$ on the scale of its lifetime (1.21 s). We also find spin-lattice relaxation that is relatively fast compared to other wide band gap insulators. The origin of this fast relaxation is also likely quadrupolar and may be due to anisotropic $^8$Li$^+$ diffusion.

1. Introduction
Like the many TiO$_2$ polymorphs, rutile has applications as an anode material in lithium-ion batteries [1, 2]. Its tetragonal structure is comprised of edge-sharing TiO$_6$ octahedra that extend along the c-axis, forming natural channels which Li can occupy during electrochemical intercalation. For incorporation into functional devices, a detailed understanding of the diffusivity of Li$^+$ is necessary. Macroscopic methods (e.g., impedance spectroscopy) are often used to probe ionic diffusion, but are unable to distinguish between different conductive pathways. The applicability of NMR to probe dynamics in solids is well known [3], and can be especially useful in resolving multiple diffusive pathways activated in different thermal regions [4]. Li dynamics in TiO$_2$ polymorphs (and related compounds) have been studied by conventional NMR [5, 6, 7, 8, 9, 10], but no such investigation has been undertaken for rutile. We report here a preliminary look at Li$^+$ implanted (i.e., not doped) in rutile titania using beta-detected NMR ($\beta$-NMR) at room temperature and high magnetic field.
2. Experimental

A 10 mm × 10 mm single crystal rutile TiO$_2$ (100) substrate was purchased from Crystal GmbH. The rutile polymorph is tetragonal ($a = b = 0.4584$ nm, $c = 0.2953$ nm) with space group $P4_2/mmm$. The substrate appears transparent pale yellow in colour, qualitatively indicating a minor presence of defects [11]. The sample was cleaved for mounting on a cold finger cryostat (see Figure 1).

$\beta$-NMR experiments were performed at TRIUMF’s Isotope Separator and Accelerator (ISAC) facility using a low-energy ($\sim 20$ keV) radioactive beam of spin-polarized $^{8}$Li$^+$ with a typical flux of $\sim 10^6$ ions s$^{-1}$ and spot size of $\sim 2$ mm in diameter. The probe nucleus, $^{8}$Li, has spin $I = 2$, a quadrupole moment $Q = +31.4$ mb, a gyromagnetic ratio $\gamma = 6.3015$ MHz T$^{-1}$, and a mean lifetime $\tau = 1.21$ s. A large nuclear spin-polarization ($\sim 70\%$) is achieved by collinear optical pumping with resonant circularly polarized laser light [12] such that the direction of spin-polarization is aligned parallel or antiparallel to the static applied magnetic field, $B_0$. A high-voltage bias is used to decelerate the beam prior to implantation. Depth-profiles were estimated from Monte Carlo simulations of $10^6$ ions using SRIM [13] (see Figure 2). Details of the spectrometer can be found elsewhere [14, 15].

Resonance measurements were performed using a continuous $^{8}$Li$^+$ beam with a transverse rf-field $H_1$ operated in continuous wave (cw) mode. Application of an rf-field at the appropriate

![Figure 1](image)

**Figure 1.** Cleaved rutile TiO$_2$ (100) substrate from Crystal GmbH mounted in the $\beta$-NMR sample holder. The pale yellow colour is indicative of a minor presence of defects.

![Figure 2](image)

**Figure 2.** SRIM stopping profiles for $10^6$ $^{8}$Li$^+$ ions implanted in TiO$_2$, histogrammed into 1 nm wide bins. Here, $z$ is the distance from the substrate surface and $\rho_z$ is the stopping probability density. Mean and root mean square implantation depths are inset over the profiles.
3. Results & Discussion

Figure 3 (left) shows the spin-lattice relaxation (SLR) spectrum at 300 K of $^8$Li$^+$ implanted in rutile TiO$_2$ at 20 keV. The time-evolution of $^8$Li$^+$ asymmetry follows [16]:

$$A(t) = \frac{\int_t^\Delta \exp \left[ \frac{-(t-t')}{\tau} \right] f(t, t'; T_1) \, dt'}{\int_0^\Delta \exp \left[ \frac{-t'}{\tau} \right] \, dt'} \quad t \leq \Delta \tag{1}$$

$$A(t) = \frac{\int_0^\Delta \exp \left[ \frac{-\left(\Delta - t'\right)}{\tau} \right] f(t, t'; T_1) \, dt'}{\int_0^\Delta \exp \left[ \frac{-t'}{\tau} \right] \, dt'} \quad t > \Delta \tag{2}$$

where $\tau$ is the mean lifetime of $^8$Li, and $\Delta$ is the duration of the beam pulse, corresponding to the pronounced kink at $t = 4$ s. $f(t, t'; T_1)$ is the longitudinal relaxation function phenomenologically defined as a stretched exponential:

$$f(t, t'; T_1) = A_0 \exp \left[ -\left\{ \frac{(t - t')}{T_1} \right\}^\beta \right], \tag{3}$$

where $A_0$, $T_1$, and $\beta$ are the initial asymmetry, SLR relaxation time, and stretching exponent ($0 \leq \beta \leq 1$). A best fit of Eqs. 1–3 to the SLR spectra in Figure 3 (left) yields: $A_0 = 0.166 \pm 0.004$, $\beta = 0.386 \pm 0.020$, and $T_1^{-1} = 0.141 \pm 0.005$ s$^{-1}$. Such a relaxation rate is relatively high compared to other insulating metal oxides [17], where $^8$Li$^+$ can be nearly non-relaxing.\footnote{See e.g., W A MacFarlane et al. and Z Salman et al. in these proceedings.} As rutile is non-cubic and virtually without nuclear moments ($^{47}$Ti: $I = 3/2$, 7.28%; $^{49}$Ti: $I = 5/2$, 7.28%).
Figure 4. Crystal structure of rutile TiO$_2$ — oxygen and titanium atoms appear as red and light blue spheres, with bonded atoms connected by grey cylinders. Left: Unit cell. Right: View along the $c$-axis of a 3 × 3 rutile supercell. Octahedral Li sites are shown as dark blue spheres and the dashed blue line encloses the unit cell.

5.51%, $^{17}$O: $I = 5/2$, 0.038%), it is likely that the relaxation is predominantly quadrupolar in nature. It is worth noting that a previous $\beta$-NMR investigation of $^8$Li$^+$ in rutile TiO$_2$ reported a 30% preservation of nuclear spin-polarization at low magnetic fields in stark contrast to 100% retention for other implanted nuclear probes (e.g., $^{12}$B) [18]. This is consistent with our observation of appreciable $^8$Li$^+$ relaxation. Additionally, we find a depth dependence to the spin-lattice relaxation rate at 300 K, with $T_1^{-1}$ decreasing by a factor of $\sim 5$ when the implantation energy is decreased from 20 keV to 5 keV. The origin of this depth-dependence is not well-understood at this time.

A cw resonance spectrum of 20 keV $^8$Li$^+$ implanted in rutile TiO$_2$ at 300 K is shown in Figure 3 (right). The asymmetric time-integrated asymmetries from spin-polarization with different helicities ($A_{\pm}$) are characteristic of a quadrupole split resonance [17, 19]. From the combined asymmetry ($A$), we find a broad, 12.48 ± 0.12 kHz wide quadrupole split resonance with unresolved features. This is in stark contrast to the $^8$Li$^+$ resonance in Bi, where the four quadrupole satellite and three double-quantum transitions are well-resolved, or in the perovskite SrTiO$_3$, where the satellite splitting is greater by about an order of magnitude [17].

X-ray diffraction and reflectometry measurements do not reveal the presence of impurity phases, though static disorder (e.g., from oxygen vacancies, as indicated by the discoloration of the crystal, or transition metal impurities) is a possible cause for the broadening. A sharp, large amplitude, 0.76±0.05 kHz wide resonance is also observed at the Larmor frequency, $\nu_0 = 41.2715$ MHz. This may be a multi-quantum transition (e.g., the double-quantum $|\Delta m| = 2$ transition between $m = \pm 1$ states). Such transitions appear as large sharp (narrow) enhancements in the resonance spectrum and can be especially prevalent in cw $\beta$-NMR, where strong RF fields are often used [20], as is the case here. This can easily be tested by comparing spectra at different

\[ \text{See W A MacFarlane et al. in these proceedings.} \]
values of the RF magnetic field amplitude $H_1$. A multi-quantum resonance will be attenuated very strongly by a reduced $H_1$.

Another possibility is that the observed pattern is due to Li residing in multiple sites with overlapping resonances. Molecular dynamics (MD) and density functional theory (DFT) calculations of lithiated rutile (Li$_x$TiO$_2$: 0 < $x$ ≤ 1) [21, 22, 23, 24, 25] predict preferential sites for lithium at octahedral and tetrahedral oxygen-coordinated interstitial sites. Figure 4 shows the octahedral site for Li along the rutile $c$-axis, which is predicted to be energetically favourable over the tetrahedral site by $\sim 0.8$ eV [21, 22].

It is also possible that the sharp component of the resonance in Figure 3 (right) is from a motionally narrowed fraction of $^8$Li$^+$, as it experiences an average electric field gradient (EFG) from site hopping during its lifetime. MD and DFT calculations also predict fast, anisotropic 1D diffusion of Li$^+$ along the rutile $c$-axis with a low hopping-barrier of $\sim 0.05$ eV [21, 22, 24, 25]. These barriers are significantly lower than what is observed experimentally from macroscopic methods [26, 27], though such measurements are done far from the limit of infinitely dilute lithium, where the potential energy landscape is likely altered by lattice distortions and Li$^+$–Li$^+$ interactions [22, 28]. The broad component of the resonance may be due to fast-diffusion of $^8$Li$^+$ to Frenkel pairs, formed from irradiation, before they heal. Motion of $^8$Li$^+$ during its lifetime may also explain the relatively large SLR rate observed and measuring its temperature dependence would be a way of testing this. It will be interesting to see if the predicted low-barrier hopping can be probed with $\beta$-NMR, which is uniquely suited for diffusion measurements at such dilute lithium concentrations.

4. Summary
In a preliminary study of $^8$Li$^+$ in rutile TiO$_2$ at 300 K and $B_0 = 6.55$ T $\parallel$ the rutile (100) using $\beta$-NMR, we find a relatively fast relaxation compared to other wide band gap insulators and an unresolved quadrupole split resonance in contrast to well-resolved quadrupolar patterns in other materials. We propose that these may be due to motion of $^8$Li$^+$ during its lifetime. A full temperature scan of SLR rates and resonance lineshapes (at different RF powers) in future experiments will help determine the relaxation mechanism and elucidate the behaviour of Li$^+$ in rutile titania.

References
[1] Hu Y S, Kienle L, Guo Y G and Maier J 2006 Adv. Mater. 18 1421–1426
[2] Reddy M V, Subba Rao G V and Chowdari B V R 2013 Chem. Rev. 113 5364–5457
[3] Kuhn A, Kunze M, Steeraj P, Wiemhöfer H D, Thangadurai V, Wilkening M and Heitjans P 2012 Solid State Nucl. Magn. Reson. 42 2–8
[4] Kuhn A, Steeraj P, Pöttgen R, Wiemhöfer H D, Wilkening M and Heitjans P 2011 J. Am. Chem. Soc. 133 11018–11021
[5] Wagemaker M, van de Krol R, Ketjens A P M, van Well A A and Mulder F M 2001 J. Am. Chem. Soc. 123 11454–11461
[6] Wagemaker M, Ketjens A P M and Mulder F M 2002 Nature 418 397–399
[7] Wilkening M, Amade R, Iwaniak W and Heitjans P 2007 Phys. Chem. Chem. Phys. 9 1239–1246
[8] Wilkening M, Iwaniak W, Heine J, Epp V, Kleinert A, Behrens M, Nuspl G, Bensch W and Heitjans P 2007 Phys. Chem. Chem. Phys. 9 6199–6202
[9] Wilkening M, Lyness C, Armstrong A R and Bruce P G 2009 J. Phys. Chem. C 113 4741–4744
[10] Bottke P, Ren Y, Hanzu I, Bruce P G and Wilkening M 2014 Phys. Chem. Chem. Phys. 16 1894–1901
[11] Diebold U 2003 Surf. Sci. Rep. 48 53–229
[12] Levy C D P, Pearson M R, Kieff R F, Mané E, Morris G D and Voss A 2014 Hyperfine Interact. 225 165–172
[13] Ziegler J F, Ziegler M and Biersack J 2010 Nucl. Instrum. Methods Phys. Res. B 268 1818–1823
[14] Morris G D, MacFarlane W A, Chow K H, Salman Z, Arseneau D J, Daviel S, Hatakeyama A, Kreitzman

---

3 Barriers for diffusion in the $ab$-plane are predicted to be larger by an order of magnitude.
S R, Levy C D P, Poutissou R, Heffner R H, Elenewski J E, Greene L H and Kiefl R F 2004 Phys. Rev. Lett. 93 157601

[15] Morris G D 2014 Hyperfine Interact. 225 173–182

[16] Salman Z, Kiefl R F, Chow K H, Hessain M D, Keeler T A, Kreitzman S R, Levy C D P, Miller R I, Parolin T J, Pearson M R, Saadaoui H, Schultz J D, Smadella M, Wang D and MacFarlane W A 2006 Phys. Rev. Lett. 96 147601

[17] MacFarlane W A, Morris G D, Chow K H, Baartman R A, Daviel S, Dunsiger S, Hatakeyama A, Kreitzman S, Levy C, Miller R, Nichol K, Poutissou R, Dumont E, Greene L H and Kiefl R F 2003 Physica B 326 209–212

[18] Ogura M, Minamisono K, Sumikama T, Nagatomo T, Iwakoshi T, Miyake T, Hashimoto K, Kudo S, Arimura K, Ota M, Akutsu K, Sato K, Mihara M, Fukuda M, Matsuta K, Akai H and Minamisono T 2001 Hyperfine Interact. 136–137 195–199

[19] Parolin T J, Shi J, Salman Z, Chow K H, Dosanjh P, Saadaoui H, Song Q, Hessain M D, Kiefl R F, Levy C D P, Pearson M R and MacFarlane W A 2009 Phys. Rev. B 80 174109

[20] Dubbers D, Dörk K, Ackermann H, Fujara F, Grupp H, Grupp M, Heitjans P, Körblein A and Stöckmann H J 1977 Z. Phys. A 282 243–248

[21] Koudriachova M V, Harrison N M and de Leeuw S W 2001 Phys. Rev. Lett. 86 1275–1278

[22] Koudriachova M V, Harrison N M and de Leeuw S W 2002 Phys. Rev. B 65 235423

[23] Koudriachova M V, Harrison N M and de Leeuw S W 2003 Solid State Ionics 157 35–38

[24] Kerisit S, Rosso K M, Yang Z and Liu J 2009 J. Phys. Chem. C 113 20998–21007

[25] Yıldırım H, Greeley J P and Santhanaranayanan S K R S 2012 Phys. Chem. Chem. Phys. 14 4565–4576

[26] Johnson O W 1964 Phys. Rev. 136 A284–A290

[27] Bach S, Pereira-Ramos J and Willman P 2010 Electrochim. Acta 55 4952–4959

[28] Koudriachova M V, Harrison N M and de Leeuw S W 2002 Comput. Mater. Sci. 24 235–240