Microscopic dynamics of isolated lithium in crystalline solids revealed by nuclear magnetic relaxation and resonance of $^8$Li

by

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Abstract

This thesis reports measurements on the dynamics of isolated lithium in single crystal materials using ion-implanted $^8$Li $\beta$-detected nuclear magnetic resonance. From spin-lattice relaxation and resonance measurements, we identify the kinetic parameters describing the ion’s site-to-site hop rate — the elementary process in long-range solid-state diffusion — and compare the results with theoretical work in the literature, as well as experiments at higher concentration. In addition to these “ionic” details, the nuclear magnetic resonance probe provides information on the electronic properties of the host, whose most intriguing features are also discussed.

In the one-dimensional ion conductor rutile TiO$_2$, we find two sets of thermally activated dynamics: one below 100 K and another at higher temperatures. We suggest the low temperature process is unrelated to lithium motion, but rather a consequence of electron polarons in the vicinity of the implanted $^8$Li$^+$. Above 100 K, Li$^+$ undergoes diffusion as an isolated uncomplexed cation, characterized by an activation energy and prefactor that are in agreement with macroscopic diffusion measurements, but not with theory.

In Bi$_2$Te$_3$Se, a topological insulator with layered tetradymite structure, implanted $^8$Li$^+$ undergoes ionic diffusion above 150 K, likely in the van der Waals gap between adjacent Te planes. A comparison with structurally related materials reveals the mobility of isolated Li$^+$ is exceptional. At lower temperature, we find linear Korringa-like relaxation, but with a field dependent slope and intercept, accompanied by an anomalous field dependence to the resonance shift. We suggest that these may be related to a strong contribution from orbital currents or the magnetic freezeout of charge carriers in this heavily compensated semiconductor.

In the doped tetradymite topological insulators Bi$_2$Se$_3$:Ca and Bi$_2$Te$_3$:Mn, the onset of lithium dynamics is suppressed to above 200 K. At low temperatures, the nuclear magnetic resonance properties are those of a heavily doped semiconductor in the metallic limit, with Korringa relaxation and a small, negative, temperature-dependent Knight shift. From this, we make a detailed comparison with isostructural Bi$_2$Te$_3$Se.
Lay Summary

Ion transport in solids is crucial for the operation of many practical devices, such as lithium-ion batteries. At the microscopic level, this transport can be described in terms of the elementary translation motion between neighbouring empty sites in a crystal lattice. When many ions are moving at once, their local arrangement can greatly influence their trajectories, resulting in a complex situation that is challenging to understand. A much simpler situation, wherein only a single isolated ion moves, is much easier to consider theoretically; however, this situation is nearly impossible to study experimentally. Using a low-intensity radioactive Li$^+$ beam, we implanted lithium in crystalline solids, easily achieving the isolated limit, and measured the mobility of Li$^+$. Results from these novel experiments were compared against existing theoretical work, as well as other experiments at higher concentrations.
Preface

The work in this thesis is based on the synergistic collaboration between several research groups at the University of British Columbia and TRIUMF, as well as other contributors from across the globe. The unique experiments described herein required large accelerator facilities, where access to available instrument time is both highly competitive and limited. As a prerequisite, all such experiments required the successful evaluation of a research proposal and allotment of time at the facility. Scheduled experiments were run around-the-clock (i.e., 24 h a day) for blocks of time on the order of a week or two, typically several times annually. The labour of running the measurements was, consequently, split into shifts and shared among the experimenters. In all the work described herein, I participated in the data collection, with more specific contributions listed below.

Chapter 3 is based on the publications:


The original research proposal was written by W. A. MacFarlane, with all subsequent progress reports written by me and W. A. MacFarlane. The experiments were designed by me, in consultation with W. A. MacFarlane and R. F. Kiefl. I wrote the code and performed all of the analysis. The manuscript was written by me and W. A. MacFarlane. I wrote the first draft. All coauthors participated in the discussion of the results and the revision of the manuscript.

Chapter 4 is based on the work published in:


The original research proposal and progress reports were written by W. A. MacFarlane, who also designed the experiments. I wrote the code and performed all of the analysis. The manuscript
was written by me and W. A. MacFarlane. I wrote the first draft. All coauthors participated in the discussion of the results and the revision of the manuscript. The Bi$_2$Te$_2$Se crystal was synthesized by H. Ji at Princeton University under the supervision of R. J. Cava.

Chapter 5 is based on the draft manuscript:


The original research proposal and progress reports were written by W. A. MacFarlane. The experiments were designed by me and W. A. MacFarlane. I wrote the code and performed all of the analysis. The manuscript was written by me and W. A. MacFarlane. I wrote the first draft. All coauthors participated in the discussion of the results and the revision of the manuscript. The Bi$_2$Se$_3$:Ca and Bi$_2$Te$_3$:Mn crystals were synthesized by Y. S. Hor and H. Ji at Princeton University under the supervision of R. J. Cava.

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Glossary

C General purpose compiled programming language developed since the early 1970s. It is regarded as the classical systems programming language, but its speed and general capabilities make it well-suited for a diverse range of applications, including scientific computing. Its popularity and ubiquity have made it the lingua franca in computer science. xiv, xv, 45, 47, 167

C++ General purpose compiled programming language derived from C and developed since the late 1970s. It allows the simultaneous use of high-level abstractions, through object-oriented techniques, and low-level programming interfaces, without sacrificing performance. xiv, xv, 47, 48, 80, 108, 167

CERN Large physics laboratory near the France-Switzerland border operated by the European Organization for Nuclear Research. As home to the world’s largest and most powerful particle accelerator, the laboratory’s main area of research is particle physics; however, it also hosts research programmes in nuclear and materials science. xiv, xv, 47

Fortran General purpose compiled programming language developed since the 1950s. It finds heavy use for numeric computations, especially in the scientific community. xiv, xv, 47

Gaussian Spectral lineshape that follows a normal distribution: $G(x) \propto \exp\left[-0.5(x/\sigma)^2\right]$. xv, 161, 164

helicity The projection of a particle’s spin $\mathbf{S}$ onto its momentum $\mathbf{p}$. More precisely, the scalar projection $h = \mathbf{p} \cdot \mathbf{S}/|\mathbf{p}|$, which adopts maximum/minimum values of $\pm 1$ for parallel/antiparallel orientations. 27, 28

Lorentzian Spectral lineshape that follows a Cauchy distribution: $L(x) \propto 1/(x^2 + \gamma^2)$. xv, 11, 57, 59, 61, 109, 111, 114, 116, 126

Matplotlib Graphics library implemented in Python for creating publication quality plots with tight integration in the SciPy ecosystem. 167

MINUIT Numerical minimization routines in developed at CERN during the 1970s. Originally written in Fortran, modern implementations are available in C++ as part of the ROOT project. 47, 53, 80, 86, 108, 167
**Monte Carlo**  A computing method based on random sampling named after the casino in Monaco. This numeric procedure is typically used to solve problems with a probabilistic interpretation, especially where analytic approaches are not possible. xi, 32, 33, 52, 99, 100, 106, 123–125, 159

**NumPy**  Software library for efficient handling of arrays in Python and part of the SciPy ecosystem. 167

**OpenMP**  A collection of compiler preprocessor directives and software library for developing routines which run in parallel. The programming interface, available for Fortran, C, and C++, greatly simplifies the complexity of the task. 48

**Python**  An object-oriented scripting language with software libraries well-suited for scientific applications (e.g., reading, manipulating, and plotting data). xiv, xv, 161, 167

**ROOT**  An object orientated data analysis framework written in C++ and developed at CERN since the 1990s. It is the de facto standard software used by the nuclear and particle physics communities. xiv, 47, 53, 80, 86, 108, 167

**SciPy**  Python software library providing convenient access to fundamental algorithms for scientific computing. xiv, xv, 161, 167

**TRIUMF**  Canada's particle accelerator centre, located in Vancouver, BC. Historically known as the TRi-University Meson Facility, it is now owned and operated by a consortium of Canadian universities. As a facility for internal and external users, the laboratory hosts major research efforts in physical, accelerator, and life sciences. v, xi, xix, 19, 20, 25, 26, 28, 35–37, 44, 45, 52, 77, 106

**Voigt**  Spectral lineshape that is a convolution of Gaussian and Lorentzian profiles. Also known as the Faddeeva function, it is the real part of the scaled complex complementary error function. 31
## Acronyms

1D  one-dimensional. iii, xi, 3, 7, 12, 13, 17, 49, 59, 67, 69, 128, 160  
2D  two-dimensional. 12, 13, 44, 82, 89, 90, 95, 97, 105, 109, 110, 118, 129, 160, 161  
3D  three-dimensional. xiii, 11, 13, 24, 44, 59, 74, 78, 97, 98, 109, 110, 118, 119, 160, 161  

**ARPES**  angle-resolved photoemission spectroscopy. 75, 96, 105  


β-NQR  β-detected nuclear quadrupole resonance. xi, 34, 36, 37  

BCA  binary collision approximation. 32  

BPP  Bloembergen-Purcell-Pound. 11, 12, 81, 83, 84, 108, 113, 118, 127, 129  

BSC  Bi$_2$Se$_3$:Ca. iii, x, xii, xiii, 17, 105–108, 111, 113–118, 120, 121, 123–127, 129  

BTM  Bi$_2$Te$_3$:Mn. iii, x, xii, 17, 105, 106, 113–119, 122–124, 127, 129, 130  

BTS  Bi$_2$Te$_2$Se. iii, x, xii, 17, 74–85, 87, 88, 90–103, 105, 107, 108, 111–121, 123, 127, 129  

CCD  charge-coupled device. 33–35, 159, 161  

CGS  centimetre-gram-second system of units. 113  

CMMS  Centre for Molecular and Materials Science. xix, 35, 45  

CPU  central processing unit. 48  

CREATE  Collaborative Research and Training Experience Program. xix  

CW  continuous wave. 39, 40, 52, 78, 90, 159  

DC  direct current. 34  

DFT  density functional theory. 50, 64, 116  

EFG  electric field gradient. 13, 15, 38, 39, 43, 56, 57, 61, 64–66, 71, 72, 79, 84, 86, 88, 90, 98, 100–103, 110, 111, 116–118, 122
ENDOR  electron nuclear double resonance.  51, 65, 66
EOM  electro-optic modulation.  28
EPR  electron paramagnetic resonance.  50, 51, 65, 68, 119, 121, 122
FCC  face-centred cubic.  12
FWHM  full width at half maximum.  16, 112, 115, 160, 161
HB  hole-burning.  15, 128
HV  high-voltage.  35
HWHM  half width at half maximum.  31
IS  impedance spectroscopy.  8, 61, 62
ISAC  Isotope Separator and ACcelerator.  xi, 19, 26–28, 35, 77, 106
ISOL  isotope separation online.  25, 26
IsoSiM  Isotopes for Science and Medicine.  xix
KWW  Kohlrausch-Williams-Watts.  44
LE-μSR  low-energy muon spin rotation.  76
LLZO  Li$_7$La$_3$Zr$_2$O$_{12}$.  13, 14
LSAT  (La,Sr)(Al,Ta)O$_3$.  53
m/q  mass-to-charge ratio.  26
MD  molecular dynamics.  64
MIT  metal-insulator transition.  94
MNR  Meyer-Neldel rule.  xiii, 7, 67, 83, 89, 128, 165, 166
MPMS  magnetic property measurement system.  106
MUD  MUon Data.  45
μSR  muon spin rotation/relaxation/resonance.  2, 18, 19, 23, 25, 35, 39, 41, 44, 45, 48, 71, 105, 118, 122, 158
NBM  neutral beam monitor.  30
NQR  nuclear quadrupole resonance.  36
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Chapter 1

Introduction

This thesis is about the study of the elementary, microscopic motions of Li\(^+\) in crystalline materials. The sum of these individual atomistic displacements can give rise to long-range ion transport, such as diffusion or conductivity (when driven by a gradient of the electrostatic potential), a quality that is crucial for the operation and modelling of many functional devices (e.g., rechargeable batteries [1] or iontronics [2]). In real devices, this macroscopic transport is often limited by imperfections of the solid host (e.g., defects, interfaces, grain boundaries, etc.), but in order to clarify the origin of the bottleneck, a microscopic understanding of ionic mobility is required.

While most practical devices relying on ion transport contain a large number of mobile ions (i.e., at the atomic % level), at high concentrations the interactions between, as well as the local configurations of, the mobile ions become influential on their transport. For example, the repulsive Coulomb interaction between cations traversing through a solid will bias their trajectory, leading to correlated motion, making it challenging to simulate from first principles (see e.g., [3, 4]). On the other hand, as the concentration of the diffusing species is decreased to the dilute limit, ion-ion correlation vanishes, greatly simplifying the transport dynamics; however, infinitely dilute conditions are nearly impossible to realize and study in most experiments. Such a situation is precisely what the experiments in this thesis aim to probe. Here, we study the dynamics of isolated Li\(^+\) in the dilute limit. This situation is amenable to simulation with theory — the foothold for understanding the basic bulk behaviour before considering other influences.
Specifically, this thesis applies β-detected nuclear magnetic resonance (β-NMR) of the ion-implanted β-emitter $^8$Li [5] to study the mobility of the simple (closed shell) light ion Li$^+$ in highly ordered crystalline hosts. This unique spectroscopic approach is akin to conventional nuclear magnetic resonance (NMR) using stable nuclei [6, 7], which is well-suited for the study of atomic motions in solids (see e.g., [8–11]); however, the use of high-energy radioactive decay products in the β-NMR detection scheme (see e.g., [5, 12]) affords it with the necessary sensitivity to probe the ultra-dilute limit. In this respect, it is quite similar to muon spin rotation/relaxation/resonance (μSR), which uses the positive muon $\mu^+$ as a probe [13–15]. A key distinction between $^8$Li β-NMR and μSR is that, in the former, the implanted $^8$Li acts as both the dopant and the NMR probe, providing a direct measure of Li$^+$ dynamics.\(^1\) The short nuclear lifetime $\tau_\beta = 1.21$ s [18] of $^8$Li ensures its maximum concentration never exceeds $\sim 10^{14}$ cm$^{-3}$ (see Chapter 2 and Appendix A), providing experimental access to a regime where all the diffusers are effectively isolated.

In the rest of this chapter, we begin with a short introduction to the mobility of ions in solids in Section 1.1. In Section 1.2, an overview of NMR methods for probing ionic motion is given. Finally, an outline of the organization of the remainder of the thesis is presented in Section 1.3.

### 1.1 Dynamics of ions in solids

It may at first seem surprising that crystals — the most stable and rigid physical phase of matter — can support diffusive motion. To be clear, most of the atoms in a solid are not undergoing appreciable translational motion, otherwise the crystal would melt! That said, no crystal is perfectly rigid and it is well-known that all atoms in a crystal vibrate about their equilibrium positions, giving rise to quantized normal modes or phonons. A key distinction between vibrational and translational forms of motion is the relatively low energy cost for displacement and the zero average net displacement for the former. While the two are both driven by random thermal excitations of the host “bath”, diffusive motion involves a non-zero displacement of an atom.

\(^1\)Of course, μSR has been used to study ion dynamics in solids (see e.g., [16]); however, its sensitivity is primarily proximal and complicated by the muon’s own propensity to mobilize at relatively low temperatures (see e.g., [17]).
While diffusion in all media requires vacant space in the immediate vicinity of the migrating atom (i.e., for it to move into), solids constrain these available sites based on the framework of static atoms. The availability of these sites necessitates the presence of point defects — atomistic imperfections in the crystal, which are always present (at some level) to entropically lower the material’s overall free energy. The most common defects in solids are vacancies, consisting of an empty site nominally occupied by an atom, and interstitials, where an atom resides in the unoccupied space between lattice sites. At the microscopic scale, diffusion in a crystalline material is composed of elementary hops wherein an atom passes through either site. The migration scheme for both defects is direct; an empty site and sufficient energy is all that is required for transport.\(^2\) These discrete displacements are a random, stochastic process, which we consider further in the next section.

### 1.1.1 Diffusion in a lattice: discrete random walks

A simple mathematical treatment of the motion of atoms in crystal is the discrete random walk \([19]\), wherein the mobile ions occupy sites on a discrete lattice in space and undergo stochastic hopping. An illustration of the one-dimensional (1D) discrete random walk is given in Figure 1.1. Here, the walker has an average residence time \(\tau\) in each site, corresponding to a hop rate \(\tau^{-1}\) for traversing the lattice. By analogy with a real solids, the jump length \(\ell\) is approximately fixed, defined by the distance separating nearest-neighbour sites. Superimposed on these translational motions are the vibrational displacements of the diffusing atom within its potential well before making its jump to the next site. As we shall see later, these lattice vibrations play an important role on the overall site-to-site hop rate \(\tau^{-1}\).

With the basic ideas of a discrete random walk sketched above, we consider the diffusivity of the migrating species, which depends on the quantities that describe the elementary jump process for the walker. Explicitly, the connection is given by the Einstein-Smoluchowski expression \([20, 21]\):

\[
D^* = \frac{\rho^2}{2d} \tau^{-1}, \tag{1.1}
\]

\(^2\)Note that other, more complicated diffusion mechanisms are possible (e.g., interstitialcy, where two (or more) atoms move together simultaneously); however, they are unimportant for this work and will not be considered further.
Figure 1.1: Sketch of a discrete random walk in one dimension. At each site, the walker resides for an average time \( \tau \) before making a stochastic jump to a vacant neighbouring site separated by a distance \( \ell \). The small displacements much shorter than \( \ell \) represent the harmonic vibrational motion of the walker in the potential well at each lattice site. While the residence time at each position is drawn here to be identical, in reality it will vary according to a probability distribution.

where \( D^* \) is the diffusivity or diffusion coefficient, \( \ell^2 \) is the mean-squared jump length, \( \tau^{-1} \) is the hop rate (i.e., the reciprocal of the mean residence time), and \( d = 1, 2, 3 \) is the dimensionality of the lattice. These ideas were first considered by Einstein [20] and Smoluchowski [21] for the case of Brownian motion in fluids, but remain applicable to the solid state. In the limit of many small steps, the theory of discrete random walks crosses over to continuum diffusion, familiar for fluid phases (see Appendix B).

For interstitial diffusers at dilute concentrations, Equation (1.1) holds; however, for other diffusion mechanisms (or higher mobile ion concentrations), the motion of the walkers becomes biased and the true diffusivity \( D \) is related to \( D^* \) by:

\[
D = f_D D^*,
\]

where \( f_D \) is the so-called correlation factor, whose value depends on the geometric details of ion transport [22] and interactions among the diffusing species. In the work presented here, it is
taken that \( f_D \approx 1 \) and the terms \( D/D^* \) are synonymous.

### 1.1.2 Temperature dependent kinetics

As mentioned earlier, diffusive motion is driven by random thermal excitations which supply the mobile ion with enough energy to surmount a potential barrier to reach an adjacent vacant site. In many ways, atomistic diffusive motion is quite similar to a chemical reaction, where the reaction rate constant often increases exponentially with increasing temperature, following a simple Arrhenius relation \([23]\) that is the result of a Boltzmann distribution of energies in thermal equilibrium at a temperature \( T \). The hop rate in solid state diffusion also generally follows such a relation:

\[
\tau^{-1} = \tau_0^{-1} \exp \left( -\frac{E_A}{k_B T} \right),
\]

(1.3)

where \( E_A \) and \( \tau_0^{-1} \) are the Arrhenius activation energy and prefactor, respectively. Consequently, by analogy with Equation (1.1), the diffusivity follows a similar temperature dependence:

\[
D = D_0 \exp \left( -\frac{E_A}{k_B T} \right),
\]

(1.4)

where the prefactor \( D_0 \) can be written as:

\[
D_0 = \frac{\ell^2}{2d} \tau_0^{-1}.
\]

(1.5)

The Arrhenius temperature dependence of \( \tau^{-1} \) (or \( D \)), can be understood in terms of ideas developed from transition state theory (TST), which describe how reaction rate constants depend on temperature (see e.g., [24]). Within thermodynamic rate theory, the atomic hop rate \( \tau^{-1} \) is given by [25, 26]:

\[
\tau^{-1} = \tau_0^{-1} \exp \left( -\frac{\Delta H_m}{k_B T} \right),
\]

(1.6)

where \( \Delta H_m \) is the enthalpy of migration and the prefactor \( \tau_0^{-1} \) is given by:

\[
\tau_0^{-1} = \bar{\tau}_0^{-1} \exp \left( \frac{\Delta S_m}{k_B} \right).
\]

(1.7)
Here, $\Delta S_m$ is the migration entropy and

$$\tau_0^{-1} = \prod_i^{3N} \nu_i \prod_i^{3N-1} \nu_i,$$

(1.8)

where $\nu_i$ are the vibrational modes in the equilibrium (numerator) and saddle-point (denominator) configurations, respectively. The interpretation of $\tau_0^{-1}$ (and by extension $\tau_0^{-1}$) is that this prefactor or “attempt” frequency is related to the vibrational mode of the mobile atom along the migration pathway [26]. Based on a simple sinusoidal lattice potential between adjacent equilibrium sites [25], this “fundamental” migration frequency can be estimated, within the harmonic approximation, as:

$$\tau_0^{-1} \approx \sqrt{\frac{V_0}{2m\ell^2}},$$

(1.9)

where $V_0$ is the potential barrier, $m$ is the mass of the diffusing atom, and $\ell$ is the distance between equilibrium sites. This simple picture is compatible with the findings from many experiments; a simple Arrhenius analysis of $\tau^{-1}$ vs. $1/T$ yields prefactors typically in the range of $10^{12}$ s$^{-1}$ to $10^{14}$ s$^{-1}$, in good agreement with values predicted by Equation (1.9) (see Figure 1.2) [25].

The goal then of any measurement of solid state ionic mobility is thus to quantify $E_A$ and $\tau_0^{-1}$ (or $D_0$), from which all other quantities (with some elementary knowledge of the lattice) can be derived. Unsurprisingly, analyzing experimental data using a model of the form of Equation (1.3) is most useful in practice, and valid so long as no curvature in a plot of $\tau^{-1}$ vs. $1/T$ is apparent (e.g., from multiple diffusion mechanisms or transport mediated by quantum tunneling$^3$).

While the determination of $E_A$ is usually quite robust, as pointed out by Hänggi et al. [30]:

In rate measurements, just as with theory, the detailed prefactor behavior of the rate is naturally more difficult to extract from measured data sets.

Key to this difficulty is estimating the entropic contribution to $\tau_0^{-1}$ ($\exp(\Delta S_m)$ in Equation (1.7)). Using the model in Equation (1.9), such an estimate is possible from the ratio of the experimental and predicted prefactors [31]. Note that, for reasonable values of barriers and jump lengths,

$^3$For all but the lightest isotopes, quantum mechanical effects, such as tunnelling, are unimportant and the migration process can be treated as a purely classical traversal of a potential barrier. For example, quantum effects are important for the muon at low-temperature [28, 29]; however, these are completely suppressed for the (relatively) much heavier lithium isotopes.
Figure 1.2: Sketch of a mobile ion in a periodic 1D potential. (A) The migration path of an ion in a solid, approximated by a 1D sinusoidal potential with a barrier height $V_0$ and a jump distance $\ell$. The solid and dashed segments of the line denote the potential between neighbouring sites and the periodicity of the potential, respectively. (B) The attempt frequency $\tau_0^{-1}$ (i.e., the Arrhenius prefactor) for a mobile ion traversing a 1D potential barrier within the (classical) harmonic approximation [25], given by Equation (1.9). The magnitude of the prefactor is represented by the cividis colourmap [27]. For typical values of $\ell$ ($\sim$1 Å) and $V_0$ ($\sim$0.5 eV) in solids, $\tau_0^{-1}$ remains on the order of $\sim$10$^{13}$ s$^{-1}$. The mass $m = 8.0225$ u used here corresponds to that of the radionuclide $^8$Li.

Equation (1.9) invariably yields $\tau_0^{-1} \sim 10^{13}$ s$^{-1}$ (see Figure 1.2). It is not uncommon, however, to find experimental prefactors which are different (i.e., larger or smaller) by several orders of magnitude. Such prefactor “anomalies” [32] imply either large or small migration entropies, depending on the scale of the anomaly. Alternatively, one complication that can arise is the strong correlation between the measured activation barriers and prefactors, due to the relatively few degrees of freedom available to parametrize the kinetic process (cf. Equation (1.3)). This correlation can manifest as an empirical compensation “law” known colloquially as the Meyer-Neldel rule (MNR) [33], wherein for related measurements of a single kinetic process, $\tau_0^{-1}$ (or $D_0$) increases exponentially with increasing $E_A$. A more detailed account is given in Appendix C and we shall consider the influence of such effects later in Chapters 3 and 4.
1.2 Measurement techniques

Quite commonly, ion diffusion is studied using techniques sensitive to ionic motions over macroscopic length scales, such as electrical conductivity (e.g., impedance spectroscopy (IS)) or various means of measuring concentration profiles within a solid (e.g., optical absorption (OA)). Such macroscopic methods, however, yield only the overall diffusivity of all migration pathways, making no microscopic distinction among them. Their results could thus be dominated by small, highly mobile regions of a sample that are not representative of its intrinsic behaviour. Similarly, conductivity measurements become increasingly difficult if the material is a mixed ionic/electronic conductor, where it can be challenging to isolate the respective contributions.

Key to the study of microscopic diffusion is the ability to distinguish between such regions (and contributions). NMR techniques are one approach well-suited to just such a task [8–11, 34–38]. Comprehensive treatments of the subject can be found in several authoritative monographs (e.g., [6, 7]) and only the essentials will be given here.

1.2.1 NMR

NMR is based on the Boltzmann polarization of nuclear moments of stable nuclei, which produces a macroscopic magnetization $\mathbf{M}$ in a static applied magnetic field $\mathbf{B}_0$. At normal temperatures, $\mathbf{M}$ is very small, but measurable. For a collection of nuclei with nuclear spin $I$ and number density $N$, the (thermal) equilibrium magnetization $\mathbf{M}^\text{eq}$ is given by:

$$\mathbf{M}^\text{eq} \approx N \frac{\gamma^2 \hbar^2 I(I + 1)}{3k_B T} \mathbf{B}_0,$$

which is just the familiar $1/T$ (nuclear) Curie law and a macroscopic measure of the degree of nuclear spin-polarization. The remaining factors are the reduced Planck constant $\hbar$, the nuclear spin quantum number $I$, and the gyromagnetic ratio $\gamma$, which defines the proportionality between $B_0$ and the NMR (or Larmor) frequency $\omega_0$ for a given nucleus:

$$\omega_0 = 2\pi\nu_0 = \gamma B_0.$$


In the case of purely magnetic interactions, $\omega_0$ is a measure of the energy splitting between the $2I + 1$ Zeeman magnetic sublevels levels $m_i$ (with $i = -I, -I + 1, \ldots, I - 1, I$), typically in the radio frequency (RF) range. Inside a material, local electromagnetic fields modify the precise energy splitting of these levels. These small perturbations $\Delta \omega$ provide a sensitive measure of the NMR probe’s immediate environment, including any dynamic modifications to it.

In a typical NMR measurement, a large homogeneous $B_0 \gtrsim 1$ T is applied along the $\hat{z}$ direction, producing a magnetization $\mathbf{M} = \mathbf{M}^{\text{eq}}$ parallel to $B_0$ (i.e., an $M_2^{\text{eq}} \neq 0$). Subsequently, this longitudinal component of $\mathbf{M}$ is manipulated and its time-evolution monitored, usually in two steps:

1. resonantly tilting $\mathbf{M}$ out of equilibrium using a (pulsed) transverse RF field $\mathbf{B}_1(t)$;
2. and detecting $\mathbf{M}(t)$ (after a time-delay $t$) as it “relaxes” back to equilibrium.

The time evolution of the reorientation of $\mathbf{M}$ can be described classically by the phenomenological Bloch equations [39], written here in vector form:

$$\frac{d\mathbf{M}}{dt} = \gamma (\mathbf{M} \times \mathbf{B}) - \mathbf{\hat{R}} \cdot (\mathbf{M} - \mathbf{M}^{\text{eq}}),$$

(1.12)

where $\mathbf{B} = B_0 + B_1(t)$ and $\mathbf{\hat{R}}$ is the relaxation matrix:

$$\mathbf{\hat{R}} = \begin{pmatrix}
1/T_2 & 0 & 0 \\
0 & 1/T_2 & 0 \\
0 & 0 & 1/T_1
\end{pmatrix}.$$

Here, $T_1$ and $T_2$ are the (longitudinal) spin-lattice relaxation (SLR) and (transverse) spin-spin relaxation (SSR) times, respectively, which are the key timescales in the recovery of $\mathbf{M}(t) \rightarrow \mathbf{M}^{\text{eq}}$. Most important in the study of ionic motion is the quantification of $T_1$ at different $T$ and $\omega_0 (B_0)$, which we now consider further.

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Note that Equation (1.12) is a macroscopic model of the collective behaviour of nuclei. To obtain a purely microscopic picture, one requires more general treatment, such as the density matrix of the spin system [6, 7]. In such treatments, it is possible to generalize Equation (1.12) to higher orders of spin interactions (see e.g., [40, 41]); however, most importantly, the physical picture provided by Equation (1.12) remains unchanged.
Spin-lattice relaxation

SLR involves the exchange of energy between a nuclear spin and its surrounding environment (i.e., the “lattice”). $1/T_1$ denotes the rate at which this exchange takes place, resulting from transitions between magnetic sublevels, as the spin system returns to (thermal) equilibrium. More specifically, $T_1$ is the characteristic $1/e$ time in the return of a non-equilibrium state to thermal equilibrium. In a SLR measurement, the goal is to quantify the recovery time $T_1$, which is dependent on the dynamical properties of the material that cause the local field at the NMR probe site to fluctuate. When these fluctuations have spectral weight at $\omega_0$, the NMR frequency at the specific applied field, transitions among the magnetic sublevels ensue, effectively re-orientating the spin ensemble back to equilibrium. Many types of dynamic phenomena are effective at causing relaxation, each with their own signature temperature and/or frequency dependence. For example, in a metal, spin-flip scattering with (polarized) conduction electrons leads to “Korringa relaxation” with a characteristic $T$-linear dependence to $T_1(T)$ [7, 42]. Quite distinct from these origins is relaxation induced by the motion of ions, which we consider in more detail below.\(^5\)

When, for example, an NMR probe atom undergoes site-to-site hopping, the motion from the random walk causes stochastic changes (i.e., fluctuations) to its local (electro)magnetic field.\(^6\) While the chief determinant of the local field is $B_0$, the sites traversed by the probe dictate the subtle perturbations $\Delta \omega$ to its Zeeman levels. Independent of the precise interaction mechanism (e.g., magnetic dipolar or electric quadrupolar), these fluctuations can be described by a correlation function $G(t)$, which describes how the local field (or $\Delta \omega$) varies with time from a specified initial condition (see e.g., [44]). As nearly all NMR interactions depend on the relative positions of interacting spins, any motion — including ionic diffusion — will randomly alter the local field. This correlation function can be written quite generally as:

$$G(t) = \langle \Delta \omega(0) \cdot \Delta \omega(t) \rangle = G(0) \cdot g(t),$$  \hspace{1cm} (1.13)

\(^5\)Beyond the account given here, more comprehensive treatments can be found elsewhere (see e.g., [6–11, 34–38]).

\(^6\)In contrast to translational motion, changes to the local field by lattice vibrations are ineffective at causing SLR, as their frequency range is too high. In order to be effective, a Raman-like process for phonon relaxation is required (see e.g., [43]).
where \( \langle \cdots \rangle \) denotes the ensemble average, which, for simplicity, we separate into time-dependent and time-independent components \( g(t) \) and \( G(0) \), respectively. Noting that longitudinal fluctuations won’t cause SLR, we restrict ourselves to the transverse component of the local field. Implicitly, \( G(t) \) encapsulates the temporal and spatial information of the dynamic process causing SLR by way of how the motion modulates the spin interactions described in the NMR Hamiltonian. If the dynamics are caused by a “stationary” random process, \( G(t) \) is a monotonic function that decreases from \( G(0) \rightarrow 0 \), where \( G(0) \) is the strength of the fluctuating interaction. To connect these fluctuations to SLR, it is necessary to consider their spectral density \( J(\omega) \), which is directly obtained from the Fourier transform of \( g(t) \):

\[
J(\omega) = \int_{-\infty}^{\infty} g(t) \exp(-i\omega t) \, dt.
\]

When \( J(\omega) \) has weight at \( \omega_0 \), the fluctuations become effective at inducing transitions between Zeeman levels, resulting in SLR. Alternatively stated, the SLR rate \( 1/T_1 \) is driven by the component of the fluctuation spectrum whose Fourier component matches the NMR frequency, or

\[
1/T_1 \propto J(\omega_0).
\]

In the simplest case, the decay of \( g(t) \) (and \( G(t) \)) is exponential with a time constant \( \tau_c \), the correlation time. Assuming this simplest form, together with three-dimensional (3D) isotropic fluctuations, leads to the Bloembergen-Purcell-Pound (BPP) result [34], with:

\[
J_n^{3D}(\omega_0) \approx \frac{\tau_c}{1 + (n\omega_0\tau_c)^{\alpha}},
\]

where the exponent \( \alpha = 2 \). Clearly, \( J_n^{3D} \) is maximized when \( n\omega_0\tau_c = 1 \). In the case of SLR from ionic diffusion, \( \tau_c^{-1} \) is, to an excellent approximation, a measure of the site-to-site hope rate \( \tau_c^{-1} \). If \( \tau_c^{-1} \) follows an Arrhenius temperature dependence (cf. Equation (1.3)), the ideal BPP response yields, in an Arrhenius plot of the SLR rate, a symmetric Lorentzian shape (i.e., a “rooftop” curve), whose asymptotic slopes are proportional to the activation energy \( E_A \) characteristic of \( \tau_c^{-1} \). The low- and high-\( T \) flanks of the \( 1/T_1 \) maximum are referred to as the slow- and fast-fluctuation limits, corresponding to whether \( \tau_c^{-1} \ll \omega_0 \) or \( \tau_c^{-1} \gg \omega_0 \). By changing the \( \omega_0 \) (i.e., \( B_0 \) used in
the experiment), one can shift the temperature of the $1/T_1$ peak position, though this principally only modifies the values of $1/T_1$ when $\tau_c^{-1} \ll \omega_0$. An example of this is shown in Figure 1.3.

Quite commonly, deviations from the idealized BPP result are encountered and these departures reveal additional information about the dynamics causing SLR. For example, structural disorder in the host material or Coulomb interactions between (mobile) ions can lead to correlations between successive site-to-site hops, resulting in a reduction in the quadratic dependence of $\omega_0$ in the low-$T$ regime predicted by Equation (1.14) [45, 46]. Such correlations reduce the apparent slope of the SLR peak’s low-$T$ flank, resulting in a BPP peak that is asymmetric with $1 \leq \alpha < 2$. In the highly crystalline, dilute-limit studies to be shown here, we do not expect deviations from $\alpha = 2$, but this provides a means of confirming such local character. Alternatively, when the nature of the fluctuations causing SLR are dimensionally constrained (e.g., from motion confined to a plane or tunnel) [47], $J_n$ can have a form considerably different from Equation (1.14). In the case of two-dimensional (2D) diffusion, a phenomenological expression introduced by Richards [35, 50], which is correct in the asymptotic limits [51], has the form:

$$J_n^{2D}(\omega_0) \approx \tau_c \ln \left[ 1 + (n\omega_0 \tau_c)^{-\alpha} \right],$$

(1.15)

where $1 \leq \alpha \leq 2$ [52], similar to the (generalized) BPP case in Equation (1.14). While no analytic form of $J_n$ for the case of 1D fluctuations has been derived, its asymptotic limits are known [51], and a summary of the limiting behaviour for diffusive $1/T_1$ in different dimensions is given in Table 1.1. Most importantly, the effect of dimensionally confined fluctuations on SLR show up only on the high-$T$ flank of the $1/T_1$ peak, distinct from the influence of disorder/correlation effects.

While the details of ionic motion dictate the exact form of $J_n$ (e.g., dimensional character, correlations, etc.), the most salient features of all reasonable models remain largely independent of such factors; $1/T_1(T, \omega_0)$ is peaked at a temperature $T_{\text{max}}(\omega_0)$ when $\tau^{-1} \approx \omega_0$. It is permissible then to simply identify $T_{\text{max}}$ from a series of $1/T_1(T)$ measurements, where $\tau^{-1}$ may be equated

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7 The deviation in $J_n$ from the ideal BPP result in Equation (1.14) can be traced to the fact that, for spatially restricted fluctuations, $G(t)$ in Equation (1.13) deviates from a simple exponential. This can be derived from detailed modelling of the spin interactions occurring during a random walk on a given lattice (cf. diffusion on a plane [48] vs. diffusion on a face-centred cubic (FCC) lattice [49]). For example, in the case of diffusion on a plane, the autocorrelation functions are thought to be power laws decaying as $1/t^4$ instead of exponentials [48].
Table 1.1: Expected asymptotic limits of the SLR rate $1/T_1$, depending on the dimensionality of the fluctuations causing relaxation [35, 51]. While the limiting behaviour in the slow-fluctuating regime, expected at low temperatures, is dimension independent, different behaviour is expected when the fluctuations are faster at high temperatures. After [37].

<table>
<thead>
<tr>
<th>Dimensionality</th>
<th>$\omega_0 \tau_c \gg 1$ (low temperature)</th>
<th>$\omega_0 \tau_c \ll 1$ (high temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D</td>
<td>$1/T_1 \propto \tau_c^{-1} \omega_0^{\alpha}$</td>
<td>$1/T_1 \propto \tau_c$</td>
</tr>
<tr>
<td>2D</td>
<td>$1/T_1 \propto \tau_c^{-1} \omega_0^{\alpha}$</td>
<td>$1/T_1 \propto \tau_c \ln(1/\omega_0 \tau_c)$</td>
</tr>
<tr>
<td>1D</td>
<td>$1/T_1 \propto \tau_c^{-1} \omega_0^{\alpha}$</td>
<td>$1/T_1 \propto \tau_c/\sqrt{\omega_0 \tau_c}$</td>
</tr>
</tbody>
</table>

with $\omega_0$. This approach has the advantage of being (minimally) model-dependent and applicable when the analytic form of $J_n$ is not known a priori (e.g., for SLR from 1D diffusion [51]). For a complete description of $\tau^{-1}$, it is thus always preferable to measure $1/T_1(T, \omega)$ over as wide a temperature and frequency range as possible. This allows for $\tau^{-1}$ to be determined over the widest possible dynamic range. A nice example of this is shown for the garnet-type fast Li$^+$ conductor Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) in Figure 1.3, where the mobility of Li$^+$ situated in (distorted) octahedral intersticies dominate its conductivity. As an Arrhenius plot, the connection between the $1/T_1$ maxima and the absolute hop rate is illustrated in Figure 1.3.

While NMR SLR is well-suited to probe relatively fast atomic motion, complementary information on slower motion can be gained from features of the NMR spectrum, which we now consider briefly.

**Motional narrowing**

Complementary information can be obtained from motion induced changes to the NMR lineshape. In the low temperature limit, where all translational motion is effectively suppressed, one obtains the ideal static resonance lineshape. Its detailed form is characteristic of the lattice site, with features such as: magnetic dipolar broadening [58, 59] from, for example, the nuclei of neighbouring atoms; and quadrupolar splitting [60] from a finite electric field gradient (EFG) in a non-cubic environment. As the temperature increases and the hop rate exceeds the characteristic frequency $\Delta \nu$ of these spectral features, usually on the order of kHz for Li isotopes, dynamic

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8The NMR signal-to-noise ratio ($S/N$) is proportional to the square of the NMR frequency (i.e., $B_0$), so it is generally only pragmatic to do experiments at high field. So-called $1/T_{1\rho}$ measurements, using another (transverse) locking probe field are used to interrogate slower motions with faster SLR (see e.g., [7, 10, 53–55]).
Figure 1.3: Example of diffusion-induced SLR. (A) Arrhenius plot of the $^7$Li NMR relaxation rates $R_i \equiv 1/T_i$ in LLZO determined by Kuhn et al. [56]. Values for the SLR rate $R_1$, the SLR rate in the rotating reference frame $R_{1p}$, and the SSR rate $R_2$ obtained at different NMR frequencies $\omega_0$ (indicated in the inset) are shown. Here, the solid lines denote a fit to a model describing $R_i(T, \omega)$, described elsewhere [10, 56]. The position of the $1/T_i$ maximum shifts to higher temperature as the (effective) NMR frequency is raised. (B) Arrhenius plot comparing the Li$^+$ hop rate $\tau^{-1}$ extracted from NMR [56] and ionic conductivity [56, 57] measurements in LLZO. The vertical dashed lines show the connection of the $1/T_i$ maximum position and the extracted $\tau^{-1}$. The agreement between the techniques demonstrates that NMR is sensitive to the elementary motions responsible for long-range Li$^+$ diffusion. Adapted from [10]. Copyright © 2012, Elsevier B. V.
averaging yields substantially narrowed spectra with sharper structure (see e.g., [61–63]). In slightly more precise terms, this phenomenon, collectively known as “motional narrowing”, occurs when

\[ \tau^{-1} \gtrsim 2\pi \Delta \nu. \]  

(1.16)

A typical example of motional narrowing in a solid, shown as the \(^6\text{Li}\) NMR in the glassy Li\(^+\) conductor, LiAlSi\(_2\)O\(_6\) [62], is given in Figure 1.4. To extract quantitative information on the kinetics of the process causing the narrowing, several approaches are available [6, 34, 64, 65]; however, the results are often model-dependent — much more so than for SLR. A simple approach successful in practice is to identify the temperature of the inflection point along the narrowing “curve” and estimate \(\tau^{-1}\) as \(2\pi \Delta \nu\) [6]. Together with SLR, motional narrowing provides access to the rate kinetics spanning nearly six decades (see e.g., Figure 1.3B).\(^9\)

1.2.2 \(\beta\)-NMR

Like conventional NMR, \(\beta\)-NMR allows you to infer the motion of ions through the dynamical effects on the local electromagnetic fields experienced by probe nuclei [37, 67]. While the framework for studying atomic motion is largely the same, NMR is inapplicable to situations where the number of probes are dilute (i.e., below \(\sim 10^{17}\) in a typical sample). Conversely, a salient feature of \(\beta\)-NMR is its enhanced sensitivity (per nucleus) [5, 12], allowing it to uniquely access this concentration regime in solids.\(^10\)

Historically, \(\beta\)-NMR has been used successfully to study Li\(^+\) in materials already containing Li atoms using activation by absorption of polarized neutrons [67].\(^11\) For example, experiments in metal alloys [70–72], lithiated graphites [73–80], glassy Li\(_2\)O \(\cdot\) 3 B\(_2\)O\(_3\) [81, 82], and the superionic conductor Li\(_3\)N [83, 84], were shown to be in excellent agreement with results from conventional NMR [85–88]. This approach cannot be used to study extrinsic Li\(^+\) conductors (i.e., those which

\(^9\)Note that there are other NMR methods available which can extend this dynamic range to even slower motions (i.e., sub-kHz rates). For example, spin-alignment echos (SAEs) can be used measure atomic jump rates between sites with inequivalent EFGs (see e.g., [38]) and resonant hole-burning (HB) can be used to follow spectral diffusion of the probe nuclei (see e.g., [66]). However, neither technique is used in this thesis and the methods will not be considered further.

\(^10\)While it is true that this situation can be probed directly on surfaces (e.g., with scanning tunnelling microscopy (STM)), this is environmentally distinct from inside a solid [68, 69].

\(^11\)Of course other \(\beta\)-NMR probes have been used successfully to study atomic motion in solids; however, for brevity, we shall not list them here.
Figure 1.4: Example of motional narrowing of a NMR line from translational motion. (A) Temperature dependence of the $^6$Li NMR lineshape in glassy LiAlSi$_2$O$_6$. As the temperature increases, the line sharpens and its width decreases. (B) Temperature dependence of the $^6$Li NMR full width at half maximum (FWHM) in glassy LiAlSi$_2$O$_6$. A low temperature rigid lattice linewidth of $\sim 3$ kHz narrows substantially between 300 K to 400 K (highlighted in grey). The inflection point at $T \approx 375$ K along the narrowing curve can be identified where $\tau^{-1} \approx 2 \times 10^4$ s$^{-1}$ [see Equation (1.16)]. Adapted from [62]. Copyright © 2008, American Physical Society.

nominally contain no lithium) or materials in the form of thin films. In this thesis, this limitation is overcome by use of an ion beam of $^8$Li [5], wherein, the implanted $^8$Li$^+$ behaves both as the dopant and the probe. The first hint that the dilute limit may be different from “bulk” conditions came in the polymer electrolyte polyethylene oxide (PEO) [89], where the addition of a lithium-salt was shown to appreciably inhibit the dilute limit Li$^+$ dynamics. Further experiments in PEO suggested this was related to the ionicity of the lithium-salt [90], but this situation could be quite different in a host whose immobile sublattice is both more rigid and ordered.

Besides this sensitivity to “ionic” material properties, the light interstitial probe $^8$Li is also sensitive to the host’s electronic properties with a characteristically small hyperfine coupling [5], similar to $\mu^+$ [91, 92]. Indeed, a principal use of $^8$Li $\beta$-NMR to date has been to study the electronic
and magnetic properties of solids [5], which give rise to additional contributions to the SLR and modifications to the resonance line. Generally, these features are distinct from those originating from ionic diffusion and the two contributions may be separated. In the materials studied in this thesis, characterizing the low-temperature electronic properties is an important step in the quantification of the ion dynamics taking place at elevated temperatures. As will be seen later on, these electronic properties are also of interest and, accordingly, Chapters 3 to 5 each contain a discussion of the most intriguing features.

1.3 Thesis organization

The remainder of this thesis is organized as follows: first, a detailed account of the ion-implanted β-NMR technique is given in Chapter 2; results in the 1D ion conductor rutile TiO$_2$ are given in Chapter 3; in Chapter 4, results on the ionic electronic properties of the layered material Bi$_2$Te$_2$Se (BTS) are given; and, in Chapter 5, the influence of doping in Bi$_2$Se$_3$:Ca (BSC) and Bi$_2$Te$_3$:Mn (BTM), both structurally related to BTS, are presented. Finally, a summary of the main findings and an outlook for future work is given in Chapter 6.
Chapter 2

Principles of ion-implanted $\beta$-NMR

$\beta$-detected nuclear magnetic resonance ($\beta$-NMR) is a sensitive and versatile nuclear technique, used here as a microscopic probe of condensed matter at the nanoscale \cite{5, 12}. It is akin to conventional nuclear magnetic resonance (NMR) of stable nuclei \cite{6, 7}, wherein the nuclear spins of a probe isotope are used to interrogate electromagnetic fields inside a host material. In both NMR and $\beta$-NMR, the goal of any experiment is to characterize the spectral and temporal (or even spatial) dependence of these “internal” fields, which are connected to the fundamental properties of the system under study.

By-and-large, the machinery of NMR and $\beta$-NMR is quite similar; however, a key difference is how these internal fields are detected. Instead of using the weak (macroscopic) magnetism from the dipole moments of the probe nuclei, $\beta$-NMR uses the high-energy $\beta$-emissions from an unstable (i.e., radioactive) isotope. This is made possible by the anisotropic property of $\beta$-decay, wherein the $\beta$-ray emission direction is correlated with the orientation of the nuclear spin at the moment of decay. In this respect, $\beta$-NMR is quite similar to muon spin rotation/relaxation/resonance (μSR) \cite{13, 14}, which uses (almost exclusively) the positive muon $\mu^+$ as its “sensor”. The main advantage of this detection scheme is the tremendous boost in sensitivity it affords. For example, in a typical conventional NMR experiment, about $\sim 10^{17}$ nuclear spins are needed to achieve a reasonable signal-to-noise ratio ($S/N$), whereas in $\beta$-NMR (or μSR) $\sim 10^7$ (cumulative) decay events are often sufficient to produce a spectrum. This $\sim 10^{10}$ enhancement in sensitivity (per nucleus) uniquely allows $\beta$-NMR to interrogate material situations where NMR is effectively
impossible. Moreover, as the radioactive probes are extrinsic to the material under study, the technique can be used to investigate any material (i.e., not only those containing elements with “good” NMR isotopes).

Despite these advantages, the use of β-NMR has not flourished compared to similar nuclear methods, due to the significant infrastructure required for a working implementation. Specifically, the necessity of large reactor or accelerator facilities to produce the probe radionuclides, in both high quantity and isotopic purity, is perhaps the limiting factor. While this requirement is shared by μSR, by contrast, it has benefited from decades of use and refinement, thanks to the global proliferation of so-called meson “factories” over the last half-century [93, 94]. Interest in β-NMR is, however, growing thanks to modern radioactive ion beam (RIB) user facilities — principally the Isotope Separator and ACcelerator (ISAC) at TRIUMF [95, 96].

In principle, any radionuclide with a non-zero nuclear spin that undergoes β-decay can be used in a β-NMR experiment. In fact, the primary historic use of β-NMR was to measure the electromagnetic moments of short-lived nuclei [97, 98], whose values could be used to test theories on nuclear structure and search for physics beyond the standard model [99, 100]. For condensed matter applications, the requirements are more stringent; the probe must be compatible with performing high-throughput measurements and produce a large S/N. In general, it is desirable that the probe [101, 102]:

1. have a high production efficiency;
2. be easy to spin-polarize;
3. have a large β-decay asymmetry;
4. have a small mass and charge;
5. have a small (non-zero) nuclear spin;
6. and have a nuclear lifetime comparable to the lifetime of spin-polarization decaying to equilibrium, which is usually on the order of (or less than) ~1 s.

While the first three criteria can be considered essential, the remaining items are merely ideal. Naturally, many radionuclides are a reasonable fit and a several possibilities are listed in Table 2.1; however, considering all of the above qualities, $^8$Li is really the best and most widely used probe, making it the tool of choice in this thesis.
### Table 2.1: Properties of radionuclides used in β-NMR experiments. Here, $I$ is the nuclear spin quantum number, $\gamma$ is the gyromagnetic ratio, $Q$ is the electric quadrupole moment, $\tau_\beta$ is the nuclear lifetime, and $R_p$ is the approximate production yield at TRIUMF. For comparison, the properties of the positive muon $\mu^+$ are also included. Probes used in condensed matter experiments are indicated with a $\star$. 

<table>
<thead>
<tr>
<th>Probe</th>
<th>$I$</th>
<th>$\gamma/2\pi$ (MHz T$^{-1}$)</th>
<th>Q (mb)</th>
<th>$\tau_\beta$ (s)</th>
<th>$R_p$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^+$</td>
<td>1/2</td>
<td>135.54</td>
<td>0</td>
<td>0.000 002 2</td>
<td>10$^7$ $\star$</td>
</tr>
<tr>
<td>$^8$Li</td>
<td>2</td>
<td>6.3016</td>
<td>32.6</td>
<td>1.21</td>
<td>10$^8$ $\star$</td>
</tr>
<tr>
<td>$^9$Li</td>
<td>3/2</td>
<td>17.46</td>
<td>-31.5</td>
<td>0.257</td>
<td>10$^7$ $\star$</td>
</tr>
<tr>
<td>$^{11}$Be</td>
<td>1/2</td>
<td>-25.636</td>
<td>0</td>
<td>19.9</td>
<td>10$^6$ $\star$</td>
</tr>
<tr>
<td>$^{12}$B</td>
<td>1</td>
<td>7.645</td>
<td>13.2</td>
<td>0.0202</td>
<td>- $\star$</td>
</tr>
<tr>
<td>$^{15}$O</td>
<td>1/2</td>
<td>10.8</td>
<td>0</td>
<td>176</td>
<td>10$^6$ $\star$</td>
</tr>
<tr>
<td>$^{19}$O</td>
<td>5/2</td>
<td>4.67</td>
<td>3.7</td>
<td>38.2</td>
<td>10$^4$ $\star$</td>
</tr>
<tr>
<td>$^{20}$F</td>
<td>2</td>
<td>7.98</td>
<td>56</td>
<td>16.1</td>
<td>10$^4$ $\star$</td>
</tr>
<tr>
<td>$^{17}$Ne</td>
<td>1/2</td>
<td>12.0</td>
<td>0</td>
<td>0.158</td>
<td>10$^4$ $\star$</td>
</tr>
<tr>
<td>$^{19}$Ne</td>
<td>1/2</td>
<td>-28.7</td>
<td>0</td>
<td>24.9</td>
<td>10$^7$ $\star$</td>
</tr>
<tr>
<td>$^{31}$Mg</td>
<td>1/2</td>
<td>-13.47</td>
<td>0</td>
<td>0.334</td>
<td>10$^3$ $\star$</td>
</tr>
</tbody>
</table>

In this chapter, the principles of β-NMR will be detailed. The relevant fundamentals will first be discussed in Section 2.1, followed by the specific implementation used in this thesis in Section 2.2. An explanation of the types of experiments is given in Section 2.3, and the chapter concludes with a discussion of the elements crucial to the data analysis in Section 2.4.

### 2.1 Fundamental properties of β-decay

Essential to β-NMR are certain details of radioactive β-decay. A nucleus undergoes β-decay when the charge state of one of its nucleons (i.e., a proton $p^+$ or neutron $n^0$) is transmuted in order to achieve a more stable nuclear configuration. Formally, a progenitor nucleus $X$ is transformed into a progeny nucleus $Y$ such that

$$^{AX}\rightarrow^{A+1}_{Z+1}Y,$$

where $Z$ is the atomic number and $A$ is the atomic mass number of the parent $X$. Several quantities are conserved in the decay process, such as the mass number, electrical charge, and lepton number. To conserve charge, an electron $e^-$ (or positron $e^+$) — for historic reasons called
Figure 2.1: Radioactive decay scheme for $^8\text{Li}$. For each nuclear level, the spin and parity $I^\pi$ (left), as well as energy in keV (right), are indicated. With a half-life $\tau_{1/2} \approx 838 \text{ ms}$ [18], $^8\text{Li}$ in its ground state undergoes $\beta^-$ decay ($Q_{\beta^-} \approx 16 \text{ MeV}$) to the $\sim 3 \text{ MeV}$ excited state of $^8\text{Be}$, yielding an end-point energy of $\sim 13 \text{ MeV}$ for the reaction. The decay has a nearly $\sim 100\%$ branching ratio, with a comparative half-life $\log_{10}f_{\tau_{1/2}}$ of $\sim 5.6$. Following the $\beta$-decay, the $^8\text{Be}$ progeny decays almost instantaneously into two $\alpha$-particles (with $\tau_{1/2} \approx 8.19 \times 10^{-17} \text{ s}$). Adapted from [103]. Copyright © 1999, Wiley-VCH.

A $\beta^\pm$ particle — is spontaneously created and emitted from the nucleus.\footnote{Note that so-called electron capture $\beta$-decay — the inverse of this process — wherein an electron is “taken” from atomic orbital, is also possible, but not considered here.} Simultaneously, an “invisible” neutrino $\nu_e$ (or antineutrino $\bar{\nu}_e$) is emitted to conserve lepton number. For example, the (proton deficient or neutron rich) $^8\text{Li}$ nucleus undergoes $\beta^-$-decay:

\[
^8_3\text{Li} \rightarrow ^8_4\text{Be} + e^- + \bar{\nu}_e,
\]

yielding $^8\text{Be}$ (in an excited nuclear state), an electron, and an electron antineutrino.

$\beta$-decay always produces a three-body final state; the energy released by the decay process, $Q_{\beta^\pm}$, is distributed among the decay products. This produces a continuous energy spectrum for the emitted $\beta$-particles up to an end-point energy, defined by the difference in $Q_{\beta^\pm}$, the rest-mass of the emitted (anti)neutrino, and (if applicable) the state of the progeny. Note that, due to conservation of momentum, there is a finite energy associated with the recoil of the decay progeny. It is, however, very small and can be ignored in most cases. The $Q_{\beta^-}$ for the decay of $^8\text{Li}$ in Equation (2.1) is $\sim 16 \text{ MeV}$ (see Figure 2.1), which contributes to its short radioactive lifetime $\tau_\beta \approx 1.21 \text{ s}$ [18]. Note, however, that the end-point energy for the reaction is $\sim 13 \text{ MeV}$, due to the decay to the excited $^8\text{Be}$ state.

$\beta$-decay, unlike all other radioactive decay processes, is governed by the weak interaction,
Figure 2.2: Parity violation in the $\beta$-decay of the positive muon $\mu^+$ [14]. First, mirror images of particle collisions in a container are shown on top. As both situations are observable in reality, their translation motion is deemed a parity conserved process (i.e., the total energy is the same). Similar mirror images of the positron $e^+$ emissions from a muon whose spin $s_\mu$ is oriented. Since spin is chiral, its handedness is not preserved upon reflection. If parity was conserved, the direction of the $\beta$-emissions would be identical in both images; however, this is not what is observed experimentally [104, 105]. Consequently, parity is violated in $\beta$-decay. Adapted from [14]. Copyright © 1999, Taylor & Francis.

which is unusual in the context of the fundamental physical forces. Unlike in gravitational, electromagnetic, and strong (nuclear) interactions, parity — which was thought to be a universal conservation law — is not conserved! Simply put, any process that is not invariant under a mirror or inversion coordinate transformation does not conserve parity. For example, the interactions describing “classical” collisions of dilute gaseous particles inside a sealed container are preserved upon a change in coordinate system. By contrast, for a collection of oriented nuclei undergoing $\beta$-decay, the emission directions of the $\beta$-particles are not preserved under a mirror-plane (or inversion) symmetry operation. This is illustrated pictorially in Figure 2.2 for the decay of $\mu^+$.

The theoretical prediction that $\beta$-decay may violate parity was revolutionary [106]. More
surprising still, was the confirmation of such predictions only a year later in the decay of $^{60}$Co polarized at very low temperature [104] and in the decay of the positive muon $\mu^+$ [105], which is produced spin-polarized naturally from positive pion $\pi^+$ decay. The pragmatic consequence of parity violation is simple; the direction of $\beta$-emissions from an ensemble of spin-polarized nuclei (or particles) are probabilistically correlated with the spin-orientation at the instant of decay. The great implications of this discovery were quickly realized, even beyond the realm of the particle physics community. Within the following years, the basic principles of the technique were laid [107] and the first experiments were performed [108]. In parallel, the entire field of $\mu$SR was born, with statements like [105]:

...polarized positive and negative muons will become a powerful tool for exploring magnetic fields in nuclei..., atoms, and interatomic regions.

clearly coming true in time [13–15]. Of course, $\mu$SR is just a special case of $\beta$-NMR and it too, in spite of technical barriers, prevailed as a fruitful tool for materials science [5, 12] — albeit at a much slower pace.

The complete, general theory describing the details of (allowed) $\beta$-decay transitions can be found elsewhere [99, 100, 109, 110], but, for our purpose, the main property is the directional distribution of the $\beta$-rays for an ensemble of “oriented” nuclei. The emission probability $W$ is given by the simple expression:

$$W(\theta) = 1 + \frac{v}{c}AP \cos \theta,$$

(2.2)

where $\theta$ is the angle between the spin direction and the $\beta$-electron emission direction, $v/c$ is the $\beta$-electron velocity (as a fraction of the speed of light $c$), $P$ is the nuclear spin-polarization, and $A_\beta$ is the $\beta$-decay anisotropy coefficient, denoting how asymmetric the $\beta$-emissions are. Note that since the electron rest mass $m_0c^2$ is only 511 keV, it is often a reasonable approximation that $v/c \sim 1$ for all but the lowest energy $\beta$s (i.e., those with a kinetic energy less than the rest mass).

When $Q_\beta \gg m_0c^2$, such low energy $\beta$s only account for a tiny fraction of the full $\beta$-spectrum (e.g., in $^8$Li). Moreover, a real experiment is usually desensitized to the low-energy range as these electrons are more easily shielded and deposit less energy in the detectors.

An example showing the angular distribution described in Equation (2.2) for oriented $^{60}$Co...
nuclei [111] is shown in Figure 2.3. Excellent agreement, at the % level, is attained between theory and experiment, confirmed by subsequent more detailed measurements [112]. It is this simple expression on which all the capabilities of β-NMR are based.

While the connection to the fundamental properties of β-decay are clear, notice that, for a measurement at fixed \( \theta \), Equation (2.2) also offers a path to monitor the polarization of the β-emitters. In a nuclear physics experiment, this is just a detail, but, for condensed matter applications, this is the connection to the surrounding environment! In a real experiment, all one measures are the “counts” (i.e., decay events registered) in a detector \( N_\theta \) at fixed \( \theta \), subtending some finite solid angle \( \Omega \) of the full three-dimensional (3D) emission distribution. Based on Equation (2.2), if we consider a measurement using two identical detectors at angles 0° and 180°, we ought to obtain maximally different count rates for the opposed detectors. A little more
explicitly:

\[
\frac{W(0)}{W(\pi)} \propto \frac{N_0}{N_\pi} = \frac{1 + \frac{v}{c}AP}{1 - \frac{v}{c}AP},
\]

which is easily rearranged to give:

\[
\frac{v}{c}AP = \frac{N_0 - N_\pi}{N_0 + N_\pi}.
\]

This normalized difference in counts between two anti-parallel detectors is referred to as the (experimental) asymmetry and is the hallmark measurable quantity in any β-NMR (or μSR) experiment. The clear benefit of this construct is the proportionality to the spin polarization of the β-decaying probe. Most importantly, the relation provides a direct experimental way to monitor \( P \) — a microscopic quantity — through the relatively easy-to-measure high-energy decay products of a collection of unstable nuclei.

While this framework was established almost immediately after parity violation was discovered [107], it is technically challenging to put into practice. The main bottleneck of any implementation is the production and preparation of the probe radionuclides. One approach, made possible by high-intensity RIB facilities, is using the isotope separation online (ISOL) method, wherein the radionuclides are simultaneously generated and extracted from a “generator” and delivered to the experiment as an ion beam. All preparation of the probe spin-states takes place during the beam delivery. This is the approach taken at TRIUMF and used in this thesis. It is outlined in the following section.

### 2.2 The TRIUMF implementation

The key components of TRIUMF’s implementation of the β-NMR technique can be broken down into: the production and collection of the probe radioisotopes; the polarization of the probe nuclear spin; implantation of the probe ions in a sample under study; and the detection and measurement of the β-NMR signal. Each of these will be discussed in separate sections below.
2.2.1 Isotope production & transport

At TRIUMF, a ~500 MeV H^- cyclotron is used to produce up to a ~100 µA p^+ beam. One of several p^+ beams are delivered to the ISAC facility where it interacts with one of two dedicated isotope production target stations. For ^8Li production, the most commonly used production target material is Ta. Specifically, a typical target consists of a stack of D-shaped Ta metal foils housed within a Ta tube 19 mm in diameter and 20 cm long. The (radio)isotopes are produced by nuclear reactions (e.g., fragmentation and spallation) caused by the incident high-energy protons, creating a radioactive “soup” inside the target foils (i.e., many species are produced, not just the one desired). Invariably, at least one of the produced species needs to be extracted and this is achieved through the ISOL method.

The easiest way of extracting a radioisotope is by out-diffusion from the target foils. To ensure fast diffusion, the target container is heated to very high temperature (i.e., above 2000 K) limited by the mechanical stability of Ta. The heat is supplied resistively, but a substantial portion results from the energy deposition of the p^+ beam (up to 10 kW). Only a fraction of all produced isotopes are extracted and delivered to experiments. Once a radionuclide has escaped the foil, it effuses along a 3 mm transfer tube, where it undergoes adsorption-desorption cycles, each time with a finite probability of undergoing surface ionization. A Re foil is typically used along the transfer tube, due to its high work function ~4.8 eV. For elements with low first ionization potentials (e.g., alkali metals), the surface ionization method is simple and nearly 100% efficient at yielding monovalent cationic species.

Once the radioisotopes are ionized, they are transported to the experiment. The ions are accelerated out of the transfer tube with a large electrostatic bias typically on the order of ~20 kV (and a maximum of 60 keV). The extracted RIB is nearly mono-energetic, with only a small energy spread (~1 eV). The beam is then “filtered” through a high-resolution magnetic dipole mass separator [113], where it is purified based on mass-to-charge ratio (m/q). For heavier isobars (i.e., different elements with the same mass number), further measures may be necessary to achieve an isotopically pure beam; however, for light elements (e.g., Li), contamination is not an issue. The beam is then transported through a high vacuum beamline (~10^-6 Torr)

---

2 If the target tube and foils melt it no longer works!
3 This is particularly true for ^6Li, since there are no stable species with A = 8.
using electrostatic optical elements [114] to the experiment station. The nuclei at this stage are, however, unpolarized and require additional preparation to be useful in the experiment. This crucial step will be discussed in the following section.

2.2.2 Polarization

During the beam transport, a crucial step is the polarization of the RIB [115], wherein the nuclear spins of the ions become oriented. This is achieved through optical pumping [116], where laser light is used to induce a high degree of electronic polarization, which, as a consequence of the coupling of (total) electronic and nuclear angular momentum, is also transferred to the nuclei. In practice, this is done using circularly polarized resonant laser light that’s co-linear with the RIB and a dedicated setup for this exists at ISAC [117]. The detailed mathematics of the pumping process are described elsewhere [116] and the following discussion will be limited to the case of Li, which has the simplest alkali scheme [115].

The process consists of several steps. The $^8\text{Li}^+$ beam is first passed through an alkali vapour charge-exchange cell, where it is neutralized to atomic lithium (i.e., $^8\text{Li}^0$). Following neutralization, any remaining $^8\text{Li}^+$ is electrostatically removed (i.e., steered into a beam dump), while the neutralized fraction of the beam continues to drift down the beamline though a 1.9 m long optical pumping region. This section of the beamline is shown in Figure 2.4.

We now consider the pumping of $^8\text{Li}^0$. The neutral atoms interact with the counter-propagating light tuned to 671 nm, corresponding to the $2S_{1/2} \rightarrow 2P_{1/2}$ D1 electronic transition, illustrated in Figure 2.5. The coupling of $^8\text{Li}^0$’s total electronic angular momentum ($J = 1/2$) to its nuclear spin ($I = 2$) results in the splitting of both the $2S_{1/2}$ and $2P_{1/2}$ levels into $F = 3/2$ and $F = 5/2$ hyperfine states. A small longitudinal holding field (typically ~1 mT) parallel to the beam lifts the degeneracy of the $2F + 1$ magnetic hyperfine sublevels $m_F$ and the helicity $\sigma^\pm$ of the circularly polarized laser light ensures absorptive transitions of $\Delta m_F = \pm 1$. Any resonant transition is subsequently followed by spontaneous emission (exited state lifetimes of ~50 ns) with the usual selection rules (i.e., $\Delta m_F = 0, \pm 1$) over the $\mu$s transport times through the pumping region.

---

4 Variations on the approach described here can, however, be used for elements in other groups on the periodic table (e.g., $^{11}\text{Be}^+$ [118, 119] or $^{31}\text{Mg}^+$ [120]).

5 Historically, Na was used for this task; however, a switch to Rb was made in ~2015, after it was found to have an equivalent neutralization efficiency, but with the benefit of vaporizing at far lower temperatures.
This results in the $m_F$ sublevel populations being biased to either the highest or lowest rung of the $m_F$ states (see Figure 2.5). At typical transport energies, the interacting neutral atoms undergo 10 to 20 absorption/emission cycles, which is sufficient to produce a high degree of electronic and nuclear polarization, the latter being on the order $\sim 70\%$ [125–127]. Note that this is orders of magnitude higher than the thermal equilibrium value achievable with all but the most extreme temperatures and fields (see Figure 2.6). Equally important is the axis of the produced polarization, which is defined by the laser’s helicity direction and is accurately parallel to the beam and the holding field in this region.

In a real experiment, the polarizing laser is operated at a fixed bandwidth ($\sim 1$ MHz) and electro-optic modulation (EOM) is used to broaden the laser’s spectral width to cover the range of all hyperfine transitions (cf. Figure 2.5). While the nominal transition frequencies are predictable, as a consequence of the Doppler effect, they depend intimately on the precise energy of the RIB. In practice, one sweeps through a small range of biases (i.e., on the order of $\sim 100$ V) just upstream of the neutralizer cell to find the setpoint that induces optimal resonant overlap between $^8\text{Li}^0$ and the laser light. This is determined unambiguously by the emergence of non-zero $\beta$-decay asymmetry, and a typical scan is shown in Figure 2.7. Once determined, the optimal bias is set and held constant for the remainder of the experiment.

**Figure 2.4:** Schematic of the low-energy beamline at TRIUMF’s ISAC facility (ca. 2003) [102]. Shown is the polarizer section [117] upstream of the dedicated high [121–123] and low [122–124] field $\beta$-NMR spectrometers. Note that, since $\sim 2015$, Na has been supplanted with Rb in the neutralizer cell. Adapted from [102]. Copyright © 2003, Elsevier B. V.
Figure 2.5: Top: Electronic structure of the neutral of $^8$Li atom. Shown qualitatively (from left to right) are the energy levels for the $n = 2$ atomic orbitals, their splitting into distinct electronic states for different total angular momentum $J = L + S$, and the hyperfine splitting $F = J + I$ of the electronic levels by the $^8$Li nuclear spin. The rightmost plot shows the magnetic splitting of hyperfine levels in the $^2S_{1/2}$ atomic ground state. Adapted from [128]. Copyright © 1995, American Institute of Physics. Bottom: Optical pumping scheme for the $^8$Li$^0$ D1 transition using $\sigma^+$ laser light. Here, an exciting $\Delta m_F = +1$ transition (thick arrow) is followed by spontaneous emission (thin arrow) with a $\Delta m_F$ of −1, 0, or +1. After several absorption/emission cycles, the population of atoms accumulate in the $m_F = +5/2$ state, eventually approaching 100% (in the absence of any relaxation mechanism). Note that energy differences in the $m_F$ sublevels have been omitted for clarity. Adapted from [115]. Copyright © 2008, American Institute of Physics.
Figure 2.6: Comparison of the $^8$Li nuclear spin-polarization obtained from optical pumping with thermal equilibrium. The polarization from optical pumping ($\sim 70\% \ [127]$) is orders of magnitude larger than the equilibrium value, and independent of both temperature and field. Only in very large applied fields at extremely low temperatures does the equilibrium polarization $P_{eq}^z$ become comparable to the optically pumped state. In the temperature and field range accessible in these $\beta$-NMR experiments (3 K to 317 K and up to 6.55 T), to an excellent approximation, $P_{eq}^z \approx 0$ (see Section 2.3.2).

Following optical pumping, the neutral beam is re-ionized by passing through a helium gas cell. For the charge “liberation” reaction

$$Li^0 + He_{(g)} \rightarrow Li^+ + e^- + He_{(g)}$$

the process has an efficiency of $\sim 50\% \ [131]$ and, most importantly, does not disturb the nuclear spin-polarization.\footnote{It does, however, increase the beam emittance slightly.} The charged beam is then electrostatically steered through a 45° bend followed by another 45° switchyard (see Figure 2.4), where it may be “kicked” to one of two dedicated spectrometers [5, 121, 122, 124]. The fraction of the beam that fails to be re-ionized continues to drift into the aptly named neutral beam monitor (NBM), comprised of a Pd foil target, used as an independent diagnostic for the experimental stations (e.g., it was used to produce the
**Figure 2.7:** Typical alkali vapour cell bias scan used to spin-polarize a $^8$Li$^+$ beam. Here, an incident 20 keV $^8$Li$^+$ beam is Doppler-shifted by the bias voltage (ordinate) onto resonance with collinear $\sigma^\pm$ circularly polarized laser light. This is achieved by a small deceleration bias upstream of the alkali vapour cell (see Figure 2.4) where the beam gets neutralized. Spin-polarization is evidenced by the non-zero $\beta$-decay asymmetry. The solid coloured lines show fits to a sum of six Voigt lines [129, 130], corresponding to the expected number of $^8$Li$^0$ D1 hyperfine transitions (see Figure 2.5). The baseline asymmetry, corresponding to zero polarization, is indicated by dashed black lines. The optimum bias is indicated by the vertical grey band, whose width represents the peak half width at half maximum (HWHM). Small, systematic differences between the two helicities are shown in the bottom panel, which are minimized at the optimum bias.

spectra in Figure 2.7). The foil has a central aperture 5 mm in diameter for transmission of the laser beam [117].

With the polarized RIB now delivered up to the experiment, it is ready for implantation in a “sample” to be studied.
2.2.3 Ion-implantation

Ion-implantation is the means in which the probe nuclei are introduced into the material under investigation. This is specific to this type of β-NMR; other approaches may use in situ neutron activation, placing the probes randomly over the full volume of typical targets [12], or the high-energy recoils from a target foil which implant with a range of much higher energies [132]. In contrast to these methods, the essentially mono-energetic beams used here allow for maximal control over the stopping range of the probes. In general, this provides a potentially important degree of freedom to a series of measurements that is unachievable by other techniques. The penetration depth of the incident ions is dependent on the incident kinetic energy of the RIB, which is defined by the extraction bias of the isotope production target. Further control over the stopping depth is achieved with a high-voltage deceleration bias, made possible by the electrically isolated spectrometer platforms [121, 122, 124].

The stopping of ions in solids is a stochastic process; each ion follows a discrete path as it scatters off atoms in the host material. These atomic collisions can be statistically simulated using Monte Carlo codes, which allow one to predict the profile of the stopped ions. For example, the Stopping and Range of Ions in Matter (SRIM) software package [133], which treats all scattering events within the binary collision approximation (BCA), is known to give reliable estimates of the implantation profile for light atoms and is used here. In these simulations, the beam and target properties can be flexibly specified (e.g., isotope, energy, target thickness and density, etc.) From the simulation, one obtains the stopping profile of the probe in the target material, which is, like the energy distribution of the products from β-decay (see e.g., Equation (2.1)), a continuous distribution. The distribution details, in the nomenclature of the ion-implantation literature, such as the range and straggle (i.e., the mean and standard deviation), are highly sensitive to the properties of the beam and target materials. Generally though, a positively skewed asymmetric distribution is obtained for light ions at keV energies in most solids. Typical implantation profiles simulated using SRIM are shown in Figure 2.8.

It has been shown that results from BCA Monte Carlo codes are in good agreement with experiment, especially those using implanted hyperfine probes. For example, this has been demonstrated for μ⁺ (treated as a light H⁺ ion) in noble metal [135] and Al [136] films on
Figure 2.8: Typical stopping profiles for an implanted ion simulated using the SRIM Monte Carlo code [133]. Shown are profiles at two energies for $10^6 \, ^{8}\text{Li}^+$ ions implanted in TiO$_2$, histogrammed with 1 nm wide bins. The ion range and straggle (i.e., the mean and standard deviation) at each energy are indicated. Adapted from [134]. Copyright © 2014, the Author(s).

SiO$_2$, based on the contrast between $\mu^+$ and Mu precession signals. In YBa$_2$Cu$_3$O$_{6+x}$ (YBCO), a comparison was made by a direct imaging approach using an inhomogenous magnetic field [137]. For $^8\text{Li}$, a comparison of stopping fractions has been done for Al and Au films [138] using the normalized resonance amplitude. This approach, however, unlike the case of $\mu^+$, depends on details of the resonance technique which complicates the comparison (see Section 2.3.1). Despite this difficulty, reasonable agreement was obtained. Another confirmation of the SRIM profiles for $^8\text{Li}$ comes from the measurement of the magnetic penetration depth in the Meissner state of NbSe$_2$ [139], which compares well with other methods. Ways to directly measure the implantation profile have also been considered when the incoming ions are not mono-energetic [132].

Just as important as how deep the probe ions penetrate is the macroscopic position of the beam on the target. In almost all experiments, a well-focused beam spot centred on the sample is desirable, preferably without any diffuse “halo”. An approximate image of the beam can be obtained using materials that scintillate under ionizing radiation. For a $^8\text{Li}^+$ beam, the $\alpha$-emissions from $^8\text{Be}$ progeny are particularly useful to this end. A “snapshot” of the beam profile is obtained from the scintillating region using a fixed charge-coupled device (CCD) camera. In
Figure 2.9: Typical $^8\text{Li}^+$ beamspot at the low field spectrometer. Shown is a CCD image of a 12.5 mm $\times$ 12.5 mm $\times$ 0.5 mm $\alpha$-$\text{Al}_2\text{O}_3$ (0001) single crystal irradiated with a DC $^8\text{Li}^+$ beam over a 10 s exposure time. The bright outline inside the dashed box corresponds to a 8 mm $\times$ 8 mm area of the crystal backside visible while mounted in the spectrometer's cold-finger cryostat. The beamspot corresponds to a 20 keV $^8\text{Li}^+$ transport energy (for a 0 kV platform bias) in a 20 mT magnetic field perpendicular to the beam.

In fact, defective $\alpha$-$\text{Al}_2\text{O}_3$ turns out to be a good scintillator [140, 141] — a fortuitous convenience, as it's often used as a substrate for mounting small crystals. A typical beamspot on the $\beta$-detected nuclear quadrupole resonance ($\beta$-NQR) spectrometer obtained with a CCD camera under a direct current (DC) $^8\text{Li}^+$ beam is shown in Figure 2.9.

For experiments aiming to measure a depth-dependent quantity, one would additionally like a beamspot that is equally focused and at the same position for all implantation energies. In practice, both the macroscopic position and profile of the beamspot can change when beam energy is modified, creating a further systematic that is convoluted with any depth dependence. The extent of this depends on the quality of the ion beam “tune”. The main results in this thesis are, however, not concerned with depth dependent quantities and the impact of the use of different beam energies is unimportant.

With the beam energy and position set, the $\beta$-NMR experiment can proceed. Before considering the experimental details, it is instructive to review the technical capabilities of the facility spectrometers, which are described in the following section.
2.2.4 β-NMR & β-NQR spectrometers

TRIUMF is home to two dedicated β-NMR spectrometers [121–124], each residing in the low-energy branch of its ISAC facility [95, 96]. The instruments are maintained by TRIUMF’s Centre for Molecular and Materials Science (CMMS) [123], which also oversees the lab’s μSR program. More complete descriptions can be found elsewhere [5, 121–124], but the essential details are described here.

Each instrument is equipped with: a pair of scintillation detectors for counting β-rays; a helium-flow cold-finger cryostat, providing stable temperature operation between 3 K to 317 K; a magnet for applying a homogeneous longitudinal field; and a small (approximately Helmholtz) coil for producing transverse radio frequency (RF) magnetic fields. The sample environment operates at ultra-high vacuum (UHV) (i.e., \( \sim 10^{-10} \) Torr), which is necessary to prevent build-up of residual gas adsorbents at cryogenic temperatures. As a corollary, all studied materials must be compatible with UHV. The UHV chambers are accessed through load-locks using separate vacuum systems and the time-duration of a sample removal/reinsertion cycle is typically about \( \sim 1 \) h (i.e., the UHV is not vented during a sample change). Upstream of the spectrometers, additional vacuum pumps and small apertures are used to transition the beamline pressure down to the required UHV. Both spectrometer platforms are electrically isolated, allowing them to be biased to high-voltage (HV), enabling controlled deceleration of the incoming RIB. The full deceleration is achieved within the last few cm of the ion beam flight path. Note that there are difficulties associated with sustaining a HV bias while operating a high magnetic field >1 T (e.g., the production of a corona discharge) and the β-NMR spectrometer requires extensive HV “conditioning” in advance of use. The high quality RIBs at ISAC are nearly monoenergetic with minimal transverse momentum, providing focused beamspots at the sample. Beamspots from scintillation can be imaged using a CCD camera mounted on a beamline viewport. Typical beamspots are \( \sim 2 \) mm in diameter and samples as small as 5 mm × 5 mm are routinely measured (without the use of any beam collimation). Key to controlled deceleration during experiments is the stability of the HV bias, which can be achieved up to \( \sim 30 \) kV, providing RIB energies on the order of \( \sim 30 \) keV down to \( \sim 100 \) eV. This translates roughly to mean stopping ranges on the order of \( \sim 100 \) nm down to a only a few nm below the sample surface.
With these basic elements common to both spectrometers, where the instruments differ is in their geometry and range of applied fields. A high field spectrometer, “β-NMR”, is equipped with a 9 T superconducting solenoid on axis with the incoming RIB. The field is thus applied normal to a sample’s surface. Its detectors are positioned (inside the vacuum of the beamline) asymmetrically about the sample position (one ~10 cm downstream and the other ~75 cm upstream). Experiments rely on the high field to focus the βs in the upstream detector, which gives the two detectors similar effective solid angles, even though they differ substantially in zero field. Consequently, measurements at fields <1 T suffer from low counts, but only in the “backward” detector. The β-NMR spectrometer’s cryostat admits samples with lateral dimensions up to 8 mm × 12 mm with a typical thickness of 0.5 mm. A schematic of the instrument is shown in Figure 2.10.

The other spectrometer covers a complementary range of lower fields (0 mT to 24 mT) using a normal conducting Helmholtz magnet. Additionally, it is equipped with auxiliary trim coils in orthogonal directions, which can be used to accurately zero the (vector) magnetic field at the sample position (see e.g., [142]), allowing for pure nuclear quadrupole resonance (NQR) experiments to be performed. Consequently, the instrument is called “β-NQR”. While the longitudinal geometry is strictly required at high fields to limit the deflection of the beam, this is not the case in (sub-)mT fields. Consequently, the polarization (and primary field) are transverse to the incoming beam (i.e., parallel to the sample surface). In contrast to the high field instrument, the detectors are located outside the beamline, but positioned symmetrically.
about the sample. While the high field instrument uses a single sample manipulator rod, the
β-NQR spectrometer uses a ladder which can house up to four samples at a time. One may,
by simply changing the ladder position, perform measurements on different samples without
breaking the UHV. The procedure is quick, typically taking <1 min. Samples with maximum
lateral dimensions 12.5 mm × 12.5 mm are compatible with the β-NQR cryostat. Figure 2.11
shows a schematic of the instrument.

2.3 Experiments

By direct analogy with conventional NMR [6, 7], there are two primary types of β-NMR
experiments: resonance and relaxation. Each mode provides access to different details about the
local electromagnetic fields inside a sample, which can be connected to its fundamental material
properties. Distinct to ion-implanted β-NMR is the way the measurements are performed, which
is described in the subsequent sections.

2.3.1 Resonance

In many ways, β-NMR is very similar to stable isotope NMR [6, 7]. The nuclear spin senses
the local magnetic fields via the Zeeman interaction and their time-averages contribute to the
resonance shift and lineshape. In addition, since $^8$Li possesses a non-zero nuclear quadrupole moment, the nuclear spin is coupled to the local electric field gradient (EFG) [6, 7, 60],

$$eq = \frac{\delta^2 V}{\partial x_i \partial x_j},$$

a tensor that is zero under cubic (or higher) symmetry. When the EFG tensor is non-vanishing, the quadrupolar interaction splits the resonance into a set of $2I$ satellites. The integer spin $I = 2$ (nonexistent in conventional NMR) of $^8$Li has the important consequence that the quadrupolar spectrum has no “main line” at the Larmor frequency, determined by the gyromagnetic ratio $\gamma$ of the NMR nucleus and the (dominant) static applied magnetic field $B_0$, given by Equation (1.11).

In contrast, for the more familiar case of half-integer $I$, the $m = \pm 1/2$ transition yields, to first order, a line at $\nu_0$ unperturbed by quadrupole effects [60]. While the quadrupole interaction is often the most important perturbation to the nuclear spin energy levels in nonmagnetic materials, for $^8$Li it is still relatively small (in the kHz range), because its nuclear electric quadrupole moment $Q$ is small, compared, for example, to $^{209}$Bi (see Table 4.1).

In a $\beta$-NMR (or NMR) spectrum, the scale of the quadrupolar splitting is given by the quadrupole frequency [60, 143]:

$$\nu_q = \frac{e^2 qQ}{8h}. \tag{2.4}$$

As the splitting is typically small relative to the NMR frequency (i.e., $\nu_q \ll \nu_0$), it can be treated accurately as a perturbation. Explicitly, the satellite positions can be written as [60, 143]:

$$\nu_{m-1\rightarrow m} = \nu_0 + \sum_n \nu^{(n)}_{m-1\rightarrow m}, \tag{2.5}$$

where $\nu_0$ is the NMR frequency, given in Equation (1.11), and $\nu^{(n)}_{m-1\rightarrow m}$ are the $n$th-order contributions to the $m - 1 \rightarrow m$ sublevel transition. These corrections, up to second-order, can be written as [143]:

$$\nu^{(1)}_{m-1\rightarrow m} = \nu_q \sqrt{\frac{6}{3}} (1 - 2m) f_0 \tag{2.6}$$

$^7$This is also true in the NMR of $I = 1$ nuclei, such as $^3$H, $^4$Li, or $^{14}$N.

$^8$Note that this definition of $\nu_q$ is not unique and differs with those by other authors by a factor of two (see e.g., [6, 60]); however, in Equation (2.4), $\nu_q$ corresponds to the absolute (inner) satellite spacing about the resonance centre-of-mass (to first-order).
for the first-order contribution and

$$\nu_{m-1\rightarrow m}^{(2)} = \frac{-2\nu_0^2}{9\nu_0} \left\{ [24m(m-1)-4I(I+1)+9]|f_1|^2 + [12m(m-1)-4I(I+1)+6]|f_2|^2 \right\}$$

(2.7)

for the second-order treatment.\(^9\) The factors \(f_n\) in Equations (2.6) and (2.7) scale the magnitude of the splitting according to the symmetry and orientation of the EFG tensor relative to the external field. More precisely, these factors can be expressed in terms of the polar and azimuthal angles (\(\theta\) and \(\phi\)) between \(B_0\) and the EFG principal axis, along with the EFG asymmetry parameter \(\eta \in [0, 1]\). In the common case where the EFG has axial symmetry, \(\eta = 0\) and the angular factors in Equations (2.6) and (2.7) can then be written as \[143\]:

$$f_0 = \frac{\sqrt{3}}{2} (3 \cos^2 \theta - 1),$$

(2.8)

$$|f_1|^2 = -\frac{3}{4} (-3 \cos^4 \theta + 3 \cos^2 \theta),$$

(2.9)

and

$$|f_2|^2 = \frac{3}{2} \left( \frac{3}{8} \cos^4 \theta - \frac{3}{4} \cos^2 \theta + \frac{3}{8} \right).$$

(2.10)

The definitions in the above expressions are tied to the convention \(|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|\) that labels the EFG principle axes.

Distinct from conventional NMR, the probe is extrinsic to the host, and its lattice site is not known a priori. Like the implanted positive muon in \(\mu\)SR, the \(^8\)Li\(^+\) ion generally stops in a high-symmetry site in a crystalline host. Some site information is available in the resonance spectrum, since the local field and EFG depend on the site, but generally one has to combine this information with knowledge of the structure and calculations to make a precise site assignment (see e.g., the case of the muon \[145\]).

Resonances are typically acquired in a continuous \(^8\)Li\(^+\) beam with a continuous wave (CW) transverse RF magnetic field stepped slowly through the \(^8\)Li Larmor frequency. In this measurement mode, the spin of any on-resonance \(^8\)Li is rapidly precessed by the RF field (i.e., the participating magnetic sublevel populations become equalized in the limit of saturation), result-

\(^9\)Note that third-order expressions have also been derived \[144\], but are unnecessary here.
ing in a loss in the average time-integrated asymmetry. If the resonance is traversed too quickly (relative to $\tau_\beta$), an asymmetric lineshape results due to the slow recovery of the polarization (i.e., a history dependence). Dealing with this polarization “drag” complicates the analysis and this situation is generally avoided. In the rare circumstance that the fast sweeping is desired, it is possible to encapsulate the form of the skewed line, provided the RF sweep rate is known [146].

Unique to this mode of measurement, the resonance amplitudes are determined by several factors, some quite distinct from conventional pulsed RF NMR. First, the maximum amplitude is determined by the baseline asymmetry [147], which represents a time integral of the spin-lattice relaxation (SLR). It also depends on the magnitude of the RF magnetic field $B_1$ relative to the linewidth, since the RF will only precess $^8$Li within a frequency window of width $\sim \gamma B_1$. The resonance amplitude may be enhanced by slow spectral dynamics occurring up to the second timescale, since the RF is applied at a particular frequency for an integration time of typically 1 s, and any $^8$Li that are resonant during this time will be precessed by it. Quadrupole satellite amplitudes are reduced by the simple fact that saturating a single quantum transition (i.e., $\Delta m = \pm 1$) can, at most, reduce the asymmetry by 25% for $I = 2$ [127]. Unsplit resonances can, in contrast, be much larger, since all the $\Delta m = \pm 1$ transitions are resonant at the same frequency and, if saturated, the RF will precess the full polarization giving the full amplitude equal to the off-resonance asymmetry.

In spite of these complexities, the main strength of the CW method is that it provides the most expedient way to measure a resonance; it provides a measure of the line with the greatest counting statistics within the shortest possible measurement time. The importance of this pragmatism is paramount given the finite allotment of beamtime. A typical measurement takes $\sim 30$ min to acquire, though quadrupole split spectra can take much longer.

It is preferable to acquire resonances in the dedicated high-field spectrometer [121, 122], where, at $B_0 > 1$ T, the resonance frequency can be precisely calibrated, typically using an independent measurement in single crystal MgO (100) at room temperature [148]. This choice of reference is arbitrary, but sensible; MgO is a wide band gap insulator with cubic rocksalt structure, whose (bulk) magnetic susceptibility is weakly diamagnetic [150] and the internal

\footnotesize
\begin{itemize}
  \item[10] In this range, first-order treatment of quadrupolar effects is sufficient for $^4$Li.
  \item[11] Note that the aqueous salt solutions typically used as references in conventional NMR (see e.g., [149]) are incompatible with the required beamline UHV.
\end{itemize}
field experienced by an implanted probe is expected to be essentially zero. This calibration thus provides access to the average local field at the site of the nucleus — the NMR (relative) shift:

$$\delta = 10^6 \left( \frac{\nu_0 - \nu_{\text{MgO}}}{\nu_{\text{MgO}}} \right),$$  

(2.11)

where $\nu_0$ and $\nu_{\text{MgO}}$ are the resonance frequencies in the sample and MgO, respectively. Typically, $\delta$ is reported in parts per million (ppm). This field is the sum of several contributions, one being demagnetization for the host material, which generates a relative shift in the resonance position, but can be easily corrected for given the knowledge of the sample’s geometry and (bulk) susceptibility [151].

### 2.3.2 Relaxation

As with conventional NMR, the SLR is determined by fluctuations at the Larmor frequency — typically in the RF range. Specific to the $\beta$-NMR (or $\mu$SR) mode of detection, the range of measurable $T_1$ relaxation times are determined by the radioactive lifetime $\tau_\beta$. As a rule of thumb, measurable $T_1$ values lie in the range $0.01 \tau_\beta$ to $100 \tau_\beta$ [12]. Near the upper end of this range, the spin relaxation is very slow and exhibits little or no curvature on the timescale of the measurement. One can still measure the relaxation rate from the slope, but it is significantly correlated to the initial amplitude of the relaxing polarization signal. At the other end of the timescale, most of the polarization vanishes before radioactive decay of the probe, resulting in a step or “missing fraction” of the signal.

In conventional NMR, the $S/N$ is proportional to the square of the Larmor frequency, favouring high applied fields. Consequently, for practical reasons, NMR is often done at a single fixed field in the range of $\sim 10$ T. In contrast, the signal in $\beta$-NMR is independent of frequency, and the field can easily be varied. This can be useful, for example, in identifying relaxation mechanisms with distinct field dependencies. In addition, this enables $\beta$-NMR in the realm of low applied fields (up to 10s of mT). As the applied field approaches zero, fluctuations of the stable magnetic nuclei of the host often become the dominant source of relaxation. At such low fields, distinction of different nuclei by their Larmor frequency is suppressed, and the isolated $^8$Li begins to resonantly lose its spin polarization to the bath of surrounding nuclear spins (see
e.g., [139, 152]). Effectively, this simply appears as another relaxation mechanism active only at low fields. The extent of the low field regime depends on the moment, density, and NMR properties of the host lattice nuclei.

SLR measurements are performed by monitoring the transient decay of spin-polarization both during and following a short (e.g., 4 s) pulse of beam [153, 154]. During the pulse, the polarization approaches a steady-state value, while after the pulse, it relaxes to $\sim 0$. This is an approximation, but reasonable for spins in thermal equilibrium over the conditions accessible in $\beta$-NMR experiments (see Figure 2.6), where $P^{\text{eq}}$ is essentially zero on the scale of the highly polarized initial state from optical pumping. Note that the sharp “kink” at the edge of the beam pulse (see e.g., Figures 2.12 and 2.13) is characteristic of $\beta$-NMR SLR data acquired in this manner. Unlike conventional NMR, no RF field is required for the SLR measurements, as the probe spins are implanted in a spin state already far from equilibrium. As a result, it is generally both faster and easier to measure SLR than the resonance; however, as a corollary, this type of relaxation measurement has no spectral resolution and represents the spin relaxation of all the $^8\text{Li}$ — even ones whose resonance cannot be resolved. A typical SLR measurement takes $\sim 20$ min.

Accounting for the polarization during and after the beam pulse is, at face value, a complication; however, using this portion of the data makes maximal use of a spectrum’s counting statistics, which are highly inhomogenous with time (see Figure 2.12). Similarly, it is straightforward to deal with the distribution of probe arrival times. Considering all $^8\text{Li}$ arriving at time $t’ < t$, the spin-polarization $P(t)$ at time $t$ can be written as [153, 154]:

$$
P(t) = P_0 \times \begin{cases} 
\frac{\int_0^t \exp \left[ -\frac{(t - t’)}{\tau_\beta} \right] R(t, t’) \ dt’}{\int_0^t \exp \left[ -\frac{t’}{\tau_\beta} \right] \ dt’}, & t \leq \Delta \\
\frac{\int_0^\Delta \exp \left[ -\frac{(\Delta - t’)}{\tau_\beta} \right] R(t, t’) \ dt’}{\int_0^\Delta \exp \left[ -\frac{t’}{\tau_\beta} \right] \ dt’} + \frac{\int_0^\Delta \exp \left[ -\frac{(t - \Delta)}{\tau_\beta} \right] R(t, t’) \ dt’}{\int_0^\Delta \exp \left[ -\frac{t’}{\tau_\beta} \right] \ dt’}, & t > \Delta \end{cases} 
$$

(2.12)

where $P_0$ is the degree of polarization at $t = 0$ determined by the optical pumping of $^8\text{Li}$ prior to
implantation, $\Delta$ is the duration of the $^8$Li$^+$ beam pulse, and $R(t, t')$ is the relaxation function.

Quite generally, $R(t, t')$ can be written as a sum of decaying exponentials, where a single exponential is the simplest case with a single SLR rate $1/T_1$. The latter is, however, the exception, rather than the rule; the non-zero quadrupole moment of $^8$Li makes it sensitive to fluctuations in the local EFG, which, a priori, can produce biexponential relaxation for spin $I = 2$ [71, 155, 156], even for a single implantation site. More common is the case that the SLR is well-described by a

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\[ \text{Figure 2.12: Illustration of the temporally inhomogeneous (statistical) error bars in a pulsed } \beta\text{-NMR SLR measurement. The statistical weight of each point } 1/\delta^2 \text{ — see Equation (2.15) — is represented by the cividis colourmap [27], showing a maximum near the end of the beam pulse at 4 s, and minima at the edges of the spectrum's time-window. This temporal dependence is quite unlike similar nuclear techniques, where the statistical uncertainty usually grows monotonically with time. For clarity, the spectrum has been binned by a factor of 20.} \]

---
(phenomenological) stretched exponential or Kohlrausch-Williams-Watts (KWW) function [157–161]:

\[ R(t, t') = \exp\left\{-\left[\frac{1}{T_1}\right]^{\beta}(t - t')\right\}, \]  

(2.13)

where \(\lambda = 1/T_1\) is the relaxation rate and \(0 < \beta \leq 1\) is the stretching exponent. This form of \(R(t, t')\) is quite general and can arise from a continuous distribution of exponential relaxation times [160], with special cases of \(\beta = 1/2\) [162, 163] or \(\beta = 1/3\) [84] coming from SLR that is inhomogenously averaged in 3D or two-dimensional (2D) limits. The approach is often used in conventional solid-state NMR [164], though chiefly as an expedient simplification of the multi-exponential magnetization transients, particularly when quadrupolar interactions are present [165]. In disordered or glassy materials like polymers a distribution of relaxation times is expected and a stretched exponential works works well [89, 90, 166–169]. While it may not be a priori obvious why a relaxation transient appears stretched, the function has the following advantages as a phenomenological model: 1) it accurately captures the characteristic \(1/e\) relaxation time; and 2) it contains relatively few degrees of freedom (i.e., less than a biexponential model).

Given these complexities, some care is required when choosing a particular \(R(t, t')\). Generally though, the salient features in the raw data prevail, independent of what model is chosen for the analysis (see e.g., Figure 2.13). Consequently, a model’s self-consistency may be checked against what is plainly apparent in the data.

### 2.4 Data & Analysis

Quite distinct from more common techniques, there is no de facto standard software widely available for the processing and analysis of ion-implanted \(\beta\)-NMR data — commercial or otherwise. For comparison, the similar, but more widely used \(\mu\)SR has a rich set of tools available for taming (or wrangling with) their data (e.g., WIMDA [170], Musrfit [171],\(^{14}\) or Mantid [172]). While this situation is improving [173], the lack of “standard” options usually requires development of custom software to tackle even relatively routine analyses. Here this process is briefly delineated, starting first with the storage format.

\(^{14}\)Note that Musrfit [171] is capable of handling a subset of the \(\beta\)-NMR data taken at TRIUMF; however, its functionality does not cover all work presented in this thesis.
Figure 2.13: Comparison of $^8$Li SLR data in common oxide insulators near room temperature at high field. Notice the dramatic difference in the haste of the SLR in each material, which is clearly distinguished prior to considering any detailed analysis. The solid black lines denote fits to a biexponential model [see Equation (3.1)] convolved with a 4 s square beam pulse [153, 154]. For clarity, the spectra have been binned by a factor of 20.

The archival record of all β-NMR experiments performed at TRIUMF are stored in the laboratory’s MUon Data (MUD) format, which are binary encoded — a relic of from the days when disk space was expensive — and require a C library for reading/writing. In brief, the files consist of a table of histograms containing the count rate in each detector as a function of an independent variable (e.g., time, frequency, etc.), as well as some header information describing the measurement. Only a summary of the raw decay events is stored (i.e., as a pre-binned histogram), rather than a discrete array of every detected decay event. This has the advantage of greatly reducing the size of the data files (each measurement, colloquially abstracted as a single “run”, occupies only 50 kB to 500 kB of storage space), but limits the upper resolution of the data (i.e., the bin size). All μSR and β-NMR data taken at TRIUMF are publicly available through an online repository maintained by the CMMS group.

The objective of any detailed analysis is to accurately model the data and encapsulate how it
evolves (e.g., with temperature, field, etc.). This requires finding the best fit parameters $p_{opt}$ and their associated uncertainty estimates $\delta p_{opt}$ for one (or several) model functions. Accounting for the uncertainty of each point in a spectrum (reliably determined by counting statistics) is critical to this task. Like in all radioactive techniques, the statistics per point are inhomogeneous across a spectrum (see e.g., Figure 2.12), and, as such, they must be weighted appropriately in the analysis. For a general non-linear least-squares fit, the quantity $\chi^2$, which is the weighted sum of the squared fit residuals, is minimized. Explicitly, for a set of $N$ pairs of experimental data points $(x_i, y_i)$, where $i$ denotes the index,

$$\chi^2 = \sum_{i} \left( \frac{y_i - f(x_i; p)}{\delta_i} \right)^2. \quad (2.14)$$

Here, $f(x_i; p)$ is the fit function, which is dependent on a vector of variable parameters $p$. The squared residuals are weighted by the effective variance $\delta_i^2$, defined as (see e.g.: [174]):

$$\delta_i^2 = \delta y_i^2 + \left( \frac{\partial f(x_i; p)}{\partial x} \right)^2 \delta x_i^2, \quad (2.15)$$

where $\delta x_i$ and $\delta y_i$ as the uncertainties in $x_i$ and $y_i$, respectively. In essence, this approach serves to transform the uncertainty in the $x$ coordinate to the $y$ coordinate, at the expense of some additional complexity in the fitting procedure. For instance, this transforms a linear problem to one that is non-linear. Additionally, an analytic form for $\partial f(x_i; p)/\partial x$ may not be available, requiring the partial derivative to be estimated numerically. Notice, however, that when $|\delta x_i|$ or $|\partial f(x_i; p)/\partial x|$ become small, $\delta_i^2 \approx \delta y_i^2$, which is the usual weighting in a least-squares analysis.

When performing any analysis, it is beneficial to constrain the vector of variable parameters $p$ to an acceptable minimum number. This not only increases the available degrees of freedom in the fit, but often reduces the uncertainty in the extracted parameter values. Similarly, it also avoids overparameterization. While the values of most parameters depend on the particular conditions of a measurement (e.g., temperature, magnetic field, etc.), some are independent of such quantities and common to subset of experiments. It is desirable that these parameters be shared between $\chi^2$ calculations for different measurements, such that an overall optimum value is determined. This so-called “global” fitting procedure ensures that an optimum in precision
is achieved from a fit, within the confines of using a particular model. The global $\chi^2$, $\chi^2_{global}$, following Equation (2.14), is simply:

$$
\chi^2_{global} = \sum_i^n \chi^2_i = \sum_i^n \sum_j^N \left( \frac{y_{ij} - f(x_{ij}; p'_i)}{\delta_{ij}} \right)^2,
$$

(2.16)

where $n$ is the number of data sets with indices $i$, $N$ is the number of data points with index $j$ of the $i^{th}$ data set, and $p'_i$ is vector of fit parameters for the set $i$. $p'_i$ is determined by a mapping function $\Lambda$ that translates a

$$
p'_i = \Lambda(i; p_{global}),
$$

(2.17)

where $p_{global}$ denotes the global list of fit parameters. The complexity in this seemingly straightforward task reduces to bookkeeping; the total number of global shared and locally free parameters must be defined and organized such that $\Lambda$ correctly maps them between the individual $\chi^2$ calculations.

The global fitting procedure usually requires a considerable number of numeric computations and model iterations before converging to an optimum answer. It is therefore favourable to implement such a routine in a compiled programming language, such as Fortran, C, or C++. The work in this thesis uses custom C++ code that interfaces with the fitting classes implemented within ROOT [175] — an object-orientated data analysis framework developed at CERN high-energy physics experiments. The minimization of $\chi^2$ is carried out by ROOT’s implementation of the MINUIT algorithms [176, 177], which were originally written in Fortran. Parameter uncertainties are computed using the MINOS algorithm [178], wherein the parameter space is naively scanned about $\chi^2_{min}$ for positions where $\chi^2(p'_i) - \chi^2_{min}(p_i) = 1$. The approach has the advantage of making no assumptions about the shape of the minimum near $\chi^2(p_{opt})$ and accounts for the fact that, in general, parameter uncertainties are asymmetric. In the work presented here, this is mainly a precaution; the parabolic errors are generally in good agreement with their asymmetric counterparts and are used throughout the remainder of this thesis.

When the fit function has an analytic form, the calculation time of $\chi^2_{global}$ can be relatively expedient. Where the process slows is if there are an extraordinary number of data points to
evaluate. Using a compiled language (e.g., C++), allows for computer architecture optimized machine code to be generated, speeding up fitting appreciably. On modern machines with multi-core central processing units (CPUs), the fitting procedures can be further optimized by recognizing that the calculation of $\chi^2$ in Equation (2.16) is an “embarrassingly parallel” problem, whose work can in principle be easily split between all available CPU cores. That is, since all of the individual $\chi^2_i$ calculations are independent, they can each be computed concurrently. Modern software tools, like OpenMP [179], make this task straightforward for the amateur programmer. For the work in this thesis, calculations following Equation (2.16) were parallelized over the outer double sum. Independent of the precise implementation details, with compiled and parallelized code, it is possible to perform sophisticated data treatment in a reasonable time. For example, a global fit to a set of ~30 SLR measurements on a CPU with 4 cores can be achieved within a few min, provided a good initial guess to the solution was provided at the outset.

In some cases, however, the fit function does not have a closed analytic solution and numerical methods (e.g., numerical integration of Equation (2.12)) must be used in its evaluation. This balloons computation times from minutes to days, making the process of testing fit models slow and arduous. With careful selection of the numerical algorithm (e.g., evaluating stretched exponential SLR during the beam pulse using double-exponential integration techniques [180, 181]), one can alleviate this tedium tremendously and reduce computation times by nearly a factor of 10.

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15 In the notation of Equation (2.16), the total number of points to evaluate is $\sum_i^N N_i$, where both $n$ and $N$ may be large.

16 Note that this approach differs somewhat from the implementation used in Musrfit [171], which parallelizes the calculations of the inner double sum. The difference in approaches reasonable; $\mu$SR experiments often have orders of magnitude more points-per-run, making the inner sum the bottleneck in the fitting procedure.
Chapter 3

Microscopic dynamics of Li$^+$ and electron polarons in rutile TiO$_2$

3.1 Introduction

The mobility of lithium ions inserted into rutile TiO$_2$ is exceptionally high and unmatched by any other interstitial cation [182, 183]. Even at 300 K, the Li$^+$ diffusion coefficient is as large as $10^{-6}$ cm$^2$ s$^{-1}$ [184], exceeding many state-of-the-art solid-state lithium electrolytes [185, 186]. Moreover, this mobility is extremely anisotropic [184], and rutile is a nearly ideal one-dimensional (1D) lithium-ion conductor. This is a consequence of rutile’s tetragonal structure [187], which has open channels along the $c$-axis that provide a pathway for fast interstitial diffusion (see Figure 3.1). This has, in part, led to a keen interest in using rutile as an electrode in lithium-ion batteries [188], especially since the advantages of nanosized crystallites were realized [189]. Simultaneously, much effort has focused on understanding the lithium-ion dynamics [190–202]; however, many underlying details in these studies are inconsistent with available experimental data. For example, a small activation energy of around 50 meV is consistently predicted [192–194, 196, 198–202], but measured barriers are greater by an order of magnitude [184, 203, 204]. This disagreement is troubling considering the simplicity of both the rutile lattice and the associated Li$^+$ motion. One explanation for the discrepancy is that most experimental methods sense the macroscopic ion transport, while theory focuses on elementary microscopic motion. The two
Rutile TiO$_2$

$P4_2/mnm$ (136)

$a = b = 4.593$ Å

$c = 2.959$ Å

**Figure 3.1:** The rutile TiO$_2$ crystal structure [187]. (A) Titanium-centred conventional unit cell showing titanium (blue) and oxygen (red) ions. Bonds (grey) are drawn to emphasize coordination. (B) View along the 4-fold c-axis, revealing the channels for fast interstitial Li$^+$ diffusion. Lithium (green) are shown in the channel centre (4c sites) surrounded by the blue Ti-centred octahedra. (C) Off-axis view revealing the 1D channels. The structures were drawn using CrystalMaker [205]. Adapted from [206]. Copyright © 2017, American Chemical Society.

would only be related if the macroscopic transport were not strongly influenced by crystal defects, as might be expected due to the highly one-dimensional mobility. Thus, for a direct comparison with theory it is important to have microscopic measurements of the Li$^+$ dynamics.

The electronic properties of rutile are also of substantial interest [207, 208]. While it is natively a wide band-gap (3 eV) insulator, it can be made an n-type semiconductor by introducing electrons into vacant titanium 3$d$ $t_{2g}$ orbitals, reducing its valence from 4+ to 3+. This is easily achieved through optical excitation, extrinsic doping, or by oxygen substoichiometry. Rather than occupying delocalized band states, these electrons form small polarons, where the Ti$^{3+}$ ion is coupled to a substantial distortion of the surrounding oxygen octahedron. Polaron formation in rutile is not predicted by naive density functional theory (DFT), and to obtain it one must introduce electron interactions [209]. Recently, the polaron has been studied optically [210] and using electron paramagnetic resonance (EPR) [211]. Compared to delocalized band electrons,
polaron mobility is quite limited and often exhibits thermally activated hopping. Calculations predict that the polaron mobility, like interstitial Li\textsuperscript{+}, is also highly anisotropic, with fast transport along the c-axis stacks of edge sharing TiO\textsubscript{6} octahedra [196, 209, 212, 213]. Importantly for our results, the positive charge of an interstitial cation like Li\textsuperscript{+} can bind the polaron into a Li\textsuperscript{+}-polaron complex, effectively coupling the electronic and ionic transport [214]. Even before this complex was observed by EPR and by electron nuclear double resonance (ENDOR) [215], its effect on the mobility of Li\textsuperscript{+} was considered theoretically [196, 216].

To study lithium-ion dynamics in rutile, a technique sensitive to the local environment of Li\textsuperscript{+} is desirable. Nuclear magnetic resonance (NMR) is a sensitive microscopic probe of matter with a well-developed toolkit for studying ionic mobility in solids [8–11, 34–38]. In particular, spin-lattice relaxation (SLR) measurements provide a means of studying fast dynamics. As described in Section 1.2.1, they are sensitive to the temporal fluctuation in the local fields sensed by NMR nuclei, which induce transitions between magnetic sublevels and relax the ensemble of spins towards thermal equilibrium. When these stochastic fluctuations induced by, for example, ionic diffusion, have a Fourier component at the Larmor frequency $\omega_0$ (typically on the order of MHz), the SLR rate $\lambda \equiv 1/T_1$ is maximized. Complementary information can be obtained from motion induced changes to the resonance lineshape. In the low temperature limit, the static NMR lineshape is characteristic of the lattice site, with features such as the quadrupolar splitting and magnetic dipolar broadening from the nuclei of neighboring atoms. As temperature increases and the hop rate exceeds the characteristic frequency of these spectral features, dynamic averaging yields substantially narrowed spectra with sharper structure. This phenomenon is collectively known as “motional narrowing” and is sensitive to slow motion with rates typically on the order of kHz. Together, SLR and resonance methods can provide direct access to atomic hop rates over a dynamic range up to nearly 6 decades.

Here, we use $\beta$-detected nuclear magnetic resonance ($\beta$-NMR) [5, 12] to measure the Li\textsuperscript{+} dynamics in rutile. Short-lived $^7$Li\textsuperscript{+} ions are implanted at low-energies ($\sim 20$ keV) into single crystals of rutile, and their NMR signals are obtained by monitoring the $^7$Li nuclear spin-polarization through the anisotropic $\beta$-decay. $1/T_1$ measurements reveal two sets of thermally activated dynamics: one low-temperature process below 100 K and another at higher temperatures. The dynamics at high temperature are due to long-range Li\textsuperscript{+} diffusion, in agreement with macroscopic...
diffusion measurements, and corroborated by motional narrowing of the resonance lineshape. We find a dilute-limit activation barrier of $0.32(2)$ eV, which is consistent with macroscopic diffusivity, but inconsistent with theory. We suggest that the dynamics below 100 K and its much smaller activation barrier are related to the low-temperature kinetics of dilute electron polarons.

The rest of this chapter is organized as follows: experimental details are given in Section 3.2; the results and analysis are described in Section 3.3; a detailed discussion that includes comparison to the extensive literature is presented in Section 3.4; and, finally, a concluding summary is given in Section 3.5. Some further detail on the SLR model and the candidate site for interstitial Li$^+$ is also given in Sections 3.6.1 and 3.6.2, respectively.

### 3.2 Experiment

β-NMR experiments were performed at TRIUMF in Vancouver, Canada. A low-energy $\sim 20$ keV hyperpolarized beam of $^8$Li$^+$ was implanted into rutile single crystals mounted in one of two dedicated spectrometers [5, 121, 122, 124]. The incident ion beam had a typical flux of $\sim 10^6$ ions/s over a beam spot $\sim 3$ mm in diameter. At these implantation energies, the $^8$Li$^+$ stop at average depths of at least 100 nm [134], as calculated by the Stopping and Range of Ions in Matter (SRIM) Monte Carlo code [133] (see Figure 2.8). Spin-polarization was achieved in-flight by collinear optical pumping with circularly polarized light, yielding a polarization of $\sim 70\%$ [127]. The TiO$_2$ samples were one-side epitaxially polished (roughness < 0.5 nm), commercial substrates with typical dimensions $8 \times 10 \times 0.5$ mm$^3$ (Crystal GmbH, Berlin). All the samples were transparent to visible light, but straw-coloured, qualitatively indicating a minor oxygen deficiency [217]. Details of the SLR and continuous wave (CW) resonance measurements are given in Section 2.3. A typical SLR measurement took about 20 min, while a resonance measurement required about 1 h.
3.3 Results and analysis

3.3.1 Spin-lattice relaxation

Typical SLR data at high and low field are shown in Figure 3.2 for several temperatures. The spectra have been normalized by their apparent \( t = 0 \) asymmetry (i.e., \( A_0 \)), as determined from a global fitting procedure described below. In high magnetic fields, the relaxation is remarkably fast compared to other oxide insulators, consistent with an earlier report in an intermediate field of 0.5 T [218]. It is also immediately evident that the SLR rates are strongly dependent on both temperature and field; the rate of relaxation increases monotonically as the magnetic field is decreased towards zero (see Figure 3.2). At fixed field, however, the temperature dependence of the relaxation is nonmonotonic, and there is at least one temperature where the relaxation rate is locally maximized. Moreover, the temperature of the relaxation rate peak is field-dependent, increasing monotonically with increasing field.

To make these observations quantitative, we now consider a detailed analysis. The relaxation is not single exponential at any field or temperature, but a phenomenological biexponential relaxation function, composed of fast and slow relaxing components yields a good fit. For an \(^8\text{Li}^+\) ion implanted at time \( t' \), the spin polarization at time \( t > t' \) follows [153, 154]:

\[
R(t, t') = f_{\text{slow}} \exp\{-\lambda_{\text{slow}} (t - t')\} + (1 - f_{\text{slow}}) \exp\{-\lambda_{\text{fast}} (t - t')\},
\]

(3.1)

where the rates are \( \lambda_{\text{fast/slow}} \equiv 1/T_1^{\text{fast/slow}} \), and \( f_{\text{slow}} \in [0, 1] \) is the slow relaxing fraction. We discuss possible origins for biexponential \( R(t, t') \) in Section 3.6.1.

With this model, all the data at each field are fit simultaneously with a shared common initial asymmetry (\( A_0 \)) using the MINUIT [176] minimization routines within ROOT [175] to find the optimum global nonlinear least-squares fit. Notice that the statistical error bars are highly inhomogenous with time, characteristic of the radioactive \(^8\text{Li}\) decay. During the beam

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1See, for example, SrTiO\(_3\) [146], MgO [148], LaAlO\(_3\) [219], yttria-stabilized zirconia (YSZ) [220], or (La, Sr)(Al, Ta)O\(_3\) (LSAT) [220]. This is also illustrated in Figure 2.13.

2We emphasize that, in contrast to the results presented in Chapters 4 and 5, the stretched exponential discussed in Section 2.3.2 does not adequately encapsulate the \(^8\text{Li} \) SLR in TiO\(_2\). Generally, when the SLR is described by a biexponential with components that are sufficiently different in rate and amplitude (like they are in rutile), a fit using Equation (2.13) adopts a \( \beta \lesssim 0.2 \), causing the model to: 1) be highly divergent at early times and miss the data; and 2) yield an optimum rate and amplitude that both are unphysically large.
Figure 3.2: $^8$Li SLR data in rutile TiO$_2$ with $B_0 = 6.55$ T $\parallel$ (100) [left] and 10 mT $\perp$ (100) [right]. The relaxation becomes faster with decreasing magnetic field and is a non-monotonic function of temperature. The solid lines are a fit to biexponential relaxation function [Equation (3.1)] convolved with a 4 s square beam pulse [153, 154]. These fit curves were obtained from a global fitting procedure where a temperature independent overall amplitude $A_0$ is shared for all spectra at each field, as described in the text. The obtained $A_0$s are used to normalize the displayed spectra, which have been binned by a factor of 20 for clarity. Adapted from [206]. Copyright © 2017, American Chemical Society.

pulse, the uncertainty decreases with time as the statistics increase, reaching a minimum at the trailing edge of the 4 s beam pulse. Following the pulse, the error bars grow exponentially as $\exp(t/\tau_0)$ (see e.g., Figure 3.2). Accounting for this purely statistical feature of the data is crucial in the analysis. A subset of the results are shown as solid coloured lines in Figure 3.2. The fit quality is good in each case (global $\chi^2 \approx 1.1$). The relaxation rates of the two components are very different with $\lambda_{\text{fast}} > 20\lambda_{\text{slow}}$, and the analysis distinguishes them clearly. Typical initial asymmetries $A_0$ of $\sim 10\%$ and $\sim 9\%$ were obtained at high and low fields, respectively.

The main fit results are shown in Figure 3.3. Consistent with the qualitative behaviour of the
Figure 3.3: Results from the analysis of the $^8$Li SLR measurements in rutile TiO$_2$ using Equation (3.1) at high- and low-field. Shown are the fraction of the slow relaxing component $f_{\text{slow}}$ (top) and the slow relaxation rate $1/T_{1\text{slow}}$ (bottom). $f_{\text{slow}}$ is surprisingly both temperature- and field-dependent, but increases towards 1 by 300 K. The qualitative features of the SLR data in Figure 3.2 can be seen clearly in the two field-dependent rate maxima in $1/T_{1\text{slow}}$. The solid red line is drawn to guide the eye. Adapted from [206]. Copyright © 2017, American Chemical Society.

spectra in Figure 3.2, the relaxation rate exhibits two maxima at each field. This is most apparent in the slow relaxing component at high magnetic field, while at low field, the low temperature peak is substantially broadened. Generally, a maximum in the relaxation rate occurs when the average fluctuation rate matches the Larmor frequency [8–11, 34–38], while the detailed temperature dependence $\lambda(T)$ depends on the character of the fluctuations.

Though the two relaxing components share similarities in their temperature dependence (see Figure 3.3 and Figure 3.9 from Section 3.6.1), we emphasize that the slow relaxing component is the more reliable. Even though the sample is much larger than the incident ion beamspot, backscattering can result in a small fraction of the $^8$Li$^+$ stopping outside the sample which typically produces a correspondingly small fast relaxing asymmetry [5]. At high field, where
$^8$Li$^+$ relaxation is generally slow, most materials show such a fast relaxing component easily distinguishable from the features of interest; however, when quadrupolar relaxation is present, which results in multiexponential relaxation for high-spin nuclei [71, 155, 156] (see Section 3.6.1), distinguishing the background contribution from an intrinsic fast component becomes difficult. At low fields, a background is even harder to isolate as $^8$Li$^+$ relaxation is typically fast under these conditions. Therefore, even though the slow component is a minority fraction at low field (see Figure 3.3), we assert that it is the more reliable.\textsuperscript{3} The fact that, as discussed in the following sections, we are able to reproduce material properties observed with other techniques is strong confirmation of the appropriateness of this choice.

3.3.2 Resonance

We now turn to the measurements of the $^8$Li resonance spectrum at $B_0 = 6.55$ T. As expected in a noncubic crystal, the NMR spectrum is split into a multiplet pattern of quadrupole satellites by the interaction between the $^8$Li nucleus and the local electric field gradient (EFG) characteristic of its crystallographic site. As seen in Figure 3.4A, the resonance lineshape changes substantially with temperature. At 10 K, it is broad with an overall linewidth of about 40 kHz, near the maximum measurable with the limited amplitude radio frequency (RF) field of this broadband spectrometer [121, 122]. Some poorly resolved satellite structure is still evident though. As the temperature increases, the intensity of the resonance increases considerably with only limited narrowing. Above 45 K, however, the resonance area decreases dramatically and is minimal near 100 K. As the temperature is raised further, the quadrupolar splitting becomes more evident, especially above 130 K. Moreover, the sharpening of these spectral features coincides with a reduction in the breadth of line, along with another increase in signal intensity. These high-temperature changes are qualitatively consistent with motional narrowing for a mobile species in a crystalline environment. By room temperature, the spectrum is clearly resolved (see Figure 3.4B) into the expected pattern of $2I$ single quantum ($|\Delta m| = 1$) quadrupole satellites interlaced with narrower double-quantum transitions occurring at the midpoint between

\textsuperscript{3}In Section 3.6.1, we consider possible origins for the strong field dependence of $f_{\text{slow}}$. 
neighbouring single quantum satellites. The well-resolved quadrupolar structure indicates a well-defined time-average EFG experienced by a large fraction of the $^8$Li at this temperature. At all temperatures, the centre of mass of the line is shifted to a lower frequency relative to $^8$Li$^+$ in MgO at 300 K. Note that the resonances in Figure 3.4 are all normalized to the off-resonance steady state asymmetry, which accounts for all the variation of signal intensity due to SLR [147].

As described in Section 2.3.1, the scale of the quadrupolar interaction is given by the quadrupole frequency $\nu_q$ in Equation (2.4). From the spectra, the splitting is on the order of a few kHz, small relative to the Larmor frequency. In this limit, the single quantum satellite positions are given accurately by first-order perturbation theory [Equations (2.5), (2.6) and (2.8)] [60, 143]. The spectrum thus consists of 4 satellites split symmetrically about $\nu_0$. Unlike the more common case of half-integer spin, there is no unshifted “main line” (the $m = \pm 1/2$ transition). The satellite intensities are also different from conventional NMR, being determined mainly by the high degree of initial polarization that increases the relative amplitude of the outer satellites [127].

We now consider a detailed analysis of the resonances. In agreement with an earlier report [134], the anti-symmetry in helicity-resolved spectra [5] reveals the resonance is quadrupole split at all temperatures; however, below 100 K the splitting is not well resolved, and an attempt to fit the spectra to a sum of quadrupole satellites proved unsuccessful. Instead, we use a single Lorentzian in this temperature region to approximate the breadth of the line. At higher temperatures, where the satellite lines become sharper, a sum of Lorentzians centred at positions given by Equations (2.5), (2.6) and (2.8) (including interlacing double-quantum transitions close to room temperature) [5] with all $m$-quanta satellites sharing the same linewidth. From the fits, we extract: the central frequency $\nu_0$; the quadrupole splittings $\nu_q$; and the overall/satellite linewidths. Note here that $\nu_q$ is the directly measured satellite splitting, following Equation (2.4), with an assumed temperature-independent angular factor $f_0 = 1$. From $\nu_0$, we calculate the frequency shift $\delta$ relative to $^8$Li$^+$ in MgO at 300 K in parts per million (ppm) using Equation (2.11). Additionally, the normalized resonance area was estimated following a procedure that removed any effect of SLR on the line intensity using a baseline estimation algorithm [223]. This allowed for a common integration scheme, independent of a particular fit model.

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4These double quantum transitions are a non-linear effect of the RF field, occurring in quadrupole split resonances when $B_1$ is relatively large ($B_1 \sim 0.5$ G for the spectra in Figure 3.4) and when $\nu_q$ relatively small (see e.g., [221, 222]).
Figure 3.4: $^8$Li resonance spectra in rutile TiO$_2$ with $B_0 = 6.55$ T $\parallel$ (100). (A) Temperature dependence of the resonance. Note that both the vertical and horizontal scales are the same for each spectra, which are offset for clarity. The zero-shifted position is taken as the resonance frequency of $^8$Li in MgO at 300 K. The lineshape changes substantially with temperature. Notice that it is most intense at 25 K, but quickly diminishes as the temperature is raised. At higher temperatures, motional narrowing is apparent and the quadrupolar structure becomes clearly visible. (B) High-resolution spectrum at 300 K. The four quadrupolar satellite transitions are clearly visible, including three narrow double-quantum transitions (DQTs) [positions indicated by DQT], each occurring at the midpoint between neighbouring single-quantum satellites (see e.g., [221, 222]). The solid orange line is a fit described in the text. Adapted from [206]. Copyright © 2017, American Chemical Society.
The results of this analysis are shown in Figure 3.5. Though the scatter in the quantities extracted are largest near 100 K, where the resonance is weakest, the qualitative trends noted above are evident. At low temperatures, the resonance is both widest and most intense, narrowing only modestly approaching 100 K. The resonance area is clearly largest around 25 K, but quickly diminishes to a minimum around 100 K. At higher temperatures where the quadrupolar structure is better resolved, the satellites have a nearly temperature independent width of $\sim 4.8$ kHz. The apparent $\nu_q$ reduces gradually from $\sim 3.8$ kHz to nearly half that value by 200 K. This reduction in splitting coincides with an increase in area, consistent with the picture of motional averaging of the quadrupolar interaction [63, 224]. This implies a fluctuation rate on the order of $\sim 2 \times 10^4$ s$^{-1}$ by $\sim 140$ K ($T_{MN}$ in Figure 3.5). The resonance shift $\delta$ is both small and negative at all temperatures, gradually increasing towards zero as the temperature is raised.

### 3.4 Discussion

The remarkably fast and strongly temperature dependent spin-lattice relaxation at high magnetic field implies an exceptional relaxation mechanism for $^8$Li in rutile distinct from other oxide insulators [146, 148, 219, 220]. The occurrence of a $T_1$ minimum indicates some spontaneous fluctuations are present that are: 1) coupled to the nuclear spin; and 2) their characteristic rate sweeps through the NMR frequency at the temperature of the minimum. Diffusive motion of $^8$Li$^+$ through the lattice provides at least one potential source of such fluctuations, as is well established in conventional NMR [8–11, 34–38]; however, without assuming anything about the particular fluctuations, we extract the temperatures $T_{\text{min}}$ of the two $T_1$ minima (see Figure 3.3), by simple parabolic fits, at several magnetic fields corresponding to NMR frequencies spanning three orders of magnitude. This approach has the advantage of not relying on any particular form of the NMR spectral density function $J(\omega_L)$ [225], which is proportional to $1/T_1$. Note that there is a clear field dependence to the high-temperature flanks of the $T_1$ minima in Figure 3.3 (i.e., they do not coalesce at high temperatures). This indicates that the fluctuations are not the result of a three-dimensional (3D) isotropic process [34], but rather one that is spatially confined to lower dimensions [35, 51]. Note that for a 1D process (as might be expected in rutile), one needs to account for the characteristic non-Debye (i.e., non-Lorentzian) fluctuation
Figure 3.5: Results for the analysis of the $^8$Li resonance measurements at high field in rutile TiO$_2$. Shown (from top to bottom) are the temperature dependence of the: linewidths, quadrupole frequency, resonance shift, and integrated area. In qualitative agreement with the normalized spectra, the resonance is broadest at low temperatures, and gradually reduces in breadth as the temperature is raised. Above 100 K the quadrupole satellites become resolved and their splitting is gradually reduced by a factor of $\sim$2 by 200 K. An estimate of the motional narrowing temperature $T_{MN}$ and an associated hop rate $\tau^{-1}(T_{MN})$ is indicated. The line is clearly most intense at low temperatures, as indicated by the resonance area, even though it is broadest here. Adapted from [206]. Copyright © 2017, American Chemical Society.
Identifying the inverse correlation time of the fluctuations $\tau^{-1}(T_{\text{min}})$ with the NMR frequency $\omega_0$ [Equation (1.11)], we construct an Arrhenius plot of the average fluctuation rate in Figure 3.6. The value of this approach is evident in the linearity of the results which indicates two independent types of fluctuations each with a characteristic activated temperature dependence. To this plot, we add the estimate of the fluctuation rate causing motional narrowing of the resonance spectra (see $v_q(T)$ in Figure 3.5), where $\tau^{-1}(T_{\text{MN}})$ matches the static splitting of the line, further expanding the range of $\tau^{-1}$. That this point lies along the steeper of the two lines is a strong confirmation that the same fluctuations responsible for the high temperature $T_1$ minimum cause the motional narrowing. Fits to a simple Arrhenius relationship given by Equation (1.3) yield: $\tau_0^{-1} = 1.23(5) \times 10^{10} \text{s}^{-1}$ and $E_A = 26.8(6) \text{meV}$ for the shallow slope, low-temperature fluctuations; and $\tau_0^{-1} = 1.0(5) \times 10^{16} \text{s}^{-1}$ and $E_A = 0.32(2) \text{eV}$ for the steep high temperature fluctuations.

The motional narrowing above 100 K is clear evidence that the corresponding fluctuations are due to long-range diffusive motion of $^8\text{Li}^+$. Unlike liquids, where motion causes the broad solid state lines to collapse to a single narrow Lorentzian, fast interstitial diffusion in a crystal averages only some of the features of the lineshape (see e.g., the $^7\text{Li}$ NMR spectra in Li$_3$N [228]). In particular, since the quadrupole splitting (the major spectral feature of the $^8\text{Li}$ resonance in rutile), is finite at every site, fast motion between sites results in an averaged lineshape consisting of quadrupole satellites split by an average EFG of reduced magnitude, see Figure 3.4. From this we conclude that the rate $\tau^{-1}$ for the steep high temperature fluctuations in Figure 3.6 should be identified with the rate of activated hopping of $^8\text{Li}^+$ between adjacent sites — the elementary atomic process of diffusion in a crystal lattice. Further confirmation of this identification comes from the excellent agreement of the activation energy with macroscopic diffusion measurements based on optical absorption (OA) [184] and impedance spectroscopy (IS) [203].

For a closer comparison with these experiments, we convert our hop rates to diffusivity via the Einstein-Smoluchowski expression, given by Equation (1.1), using $d = 1$ and $f_D = 1$. Using $l \approx 1.5$ Å, based on the ideal rutile lattice (details of the precise site of $^8\text{Li}^+$ are discussed below), we compare the results to $D$ measured by other methods in single crystal [184], thin film [229, 230], and nanocrystalline [203] rutile in Figure 3.7. The agreement in activation energy is apparent.
in the similarity of the slopes, but our $D$ is somewhat larger than the macroscopic diffusivity due to a larger prefactor. In our measurements $^8$Li$^+$ is essentially in the dilute limit, while the bulk measurements have much higher concentrations. One might expect repulsive Li$^+$–Li$^+$ interactions would inhibit ionic transport, and yield a smaller macroscopic $D$; however, the agreement in $E_A$ with the macroscopic $D$, where the (Li/Ti) concentration is as high as 30% [203], implies the barrier is very insensitive to concentration, probably due to strong screening of the Coulomb interaction by the high dielectric response of rutile [231]. Alternatively, Equation (1.1) shows that either overestimating the jump distance $l$ or the presence of correlated hopping (that reduces $f_D$ from unity) [22] would lead to an overestimate of $D$ and might account for some of the discrepancy. Note that isotopic mass effects on $D$ are expected to be negligible [232].

While our $E_A$ agrees well with macroscopic measurements using OA [184] and IS [203], it
Figure 3.7: Arrhenius plot of the Li$^+$ diffusion coefficient $D$ in rutile TiO$_2$ estimated from the $^8$Li$^+$ hop rate extracted in Figure 3.6 using the Einstein-Smoluchowski expression [Equation (1.1)] with $f = 1$, $d = 1$, and $l = 1.5$ Å. Literature values obtained from rutile single crystals [184], nanoparticles [203], and thin films [229, 230] are shown for comparison. Note that the concentration of lithium varies greatly in the reported values. While a clear deviation in the magnitude of $D$ is observed for different forms of rutile, the similarity of $E_A$ implies a common diffusion mechanism. Adapted from [206]. Copyright © 2017, American Chemical Society.

Our result is also inconsistent with the suggestion [196] that the higher barrier is characteristic
of diffusion of the Li$^+$-polaron complex instead of simply interstitial Li$^+$. We discuss this point at more length below.

We turn now to the fluctuations that predominate below 100 K and cause the low temperature $T_1$ minimum. While, we cannot be as conclusive about their origin, we delineate some interesting possibilities. In contrast to the long-range diffusive behaviour at higher temperature, the small activation energy we find is in the range of barriers obtained from molecular dynamics (MD) [196, 198, 199, 202] and DFT [192–194, 198, 200, 201] calculations for interstitial Li$^+$; however, this appears to be coincidental, since the absence of motional narrowing in this temperature range is inconsistent with long-range motion.

On the other hand, the relaxation may be caused by some highly localized Li$^+$ motion at low temperature. Local dynamics of organic molecules in solids are well-known, for example the rotation of methyl groups of molecules intercalated into crystalline hosts, where they can cause some limited dynamic averaging of the NMR lineshape [224] and relaxation [233]. Analogous effects are found for some point defects in crystals. For example, a small substitutional cation may adopt one of several equivalent off-centre sites surrounding the high symmetry site of the large missing host cation, and subsequently hop randomly among these sites within the anionic cage (e.g., Ag$^+$ in RbCl [36]).

To expand further on this possibility, we now consider the $^8$Li$^+$ site in rutile in more detail. When Li is introduced either thermally or electrochemically, it is known to occupy the open channels along the c-axis. Two high-symmetry sites are available here: the Wyckoff 4c site within a distorted oxygen octahedron; and the 4d quasi-tetrahedral site, but the precise location remains controversial and may depend on Li concentration [189, 234, 235]. Although ion implantation is far from a thermal process, the implanted ion often stops in the most energetically stable site in the unit cell. From first-principles, the lowest energy site for isolated Li$^+$ is 4c along the centre of the c-axis channel [196, 198, 200, 201], see Figure 3.1B and C. In disagreement with these calculations, an off-centre site near 4c has been predicted [192–194], but this seems unlikely given the modest size of the quasi-octahedral cage compared to the Li$^+$ ionic radius [236]. Metastable sites outside the channels (in the stacks of TiO$_6$ octahedra) have substantially higher energies [192–194, 202] and would also be characterized by much larger EFGs and quadrupole splittings (in Section 3.6.2 we consider the prospects for using the quadrupole splitting to determine the $^8$Li$^+$ site). If, on
the other hand, \(^{8}\text{Li}^+\) stops at a metastable site along the channels, such as \(4d\), it would have a very small barrier to moving to the nearest \(4c\) site. Thus, while we cannot rule out some local motion of \(^{8}\text{Li}^+\) at low temperature, we regard it as unlikely. Moreover, it is not clear how local motion could account for the temperature evolution of the resonance area, whose main feature is a peak in intensity below 50 K, see Figure 3.4.

We now consider another source of low \(T\) fluctuations, namely the electron polaron, which, for simplicity, we denote as \(\text{Ti}'_{\text{II}}\). The polaron is only slightly lower in energy (0.15 eV) than the delocalized electronic state (\(e'\)) at the bottom of the rutile conduction band \([207, 212]\). We can write the localization transition as:

\[
\text{Ti}'_{\text{II}} + e' \rightleftharpoons \text{Ti}'_{\text{II}}.
\]

Having localized, the polaron can migrate in an activated manner, with a calculated \(E_A\) that may be as low as \(\sim 30\) meV for adiabatic hopping along the \(c\)-axis stacks of \(\text{TiO}_6\) octahedra \([196, 209, 212, 213]\). Note that polaron localization also results in the formation of a local electronic magnetic moment — the polaron is a paramagnetic defect — as is clearly confirmed by EPR \([211]\). At low temperature, the polaron is likely weakly bound to other defects such as an oxygen vacancies, from which it is easily freed \([237, 238]\). If the one dimensionally mobile polaron and interstitial \(^{8}\text{Li}^+\) on adjacent sublattices come into close proximity, they may form a bound state:

\[
\text{Li}^+_i + \text{Ti}'_{\text{II}} \rightleftharpoons \text{Li}^+_i - \text{Ti}'_{\text{II}}.
\]

that is a charge-neutral paramagnetic defect complex that has been characterized by EPR and ENDOR \([215]\). The complex is predicted to be quite stable \([196]\), but its EPR signal broadens and disappears above about 50 K \([215]\). The complex is also expected to be mobile via a tandem hopping process \([196]\).

\(^{8}\text{Li}^+\) bound to a polaron will have a very different NMR spectrum than the isolated interstitial. The \(3^+\) charge of the nearby \(\text{Ti}'_{\text{II}}\) will alter the EFG and modify the quadrupole splitting, but the magnetic hyperfine field of the unpaired electron spin is an even larger perturbation, so strong in fact, that complexed \(^{8}\text{Li}^+\) will not contribute at all to the resonances in Figure 3.4, since, based on
the ENDOR [215] their resonance frequency is shifted by at least 350 kHz. For this reason we also exclude the possibility that the high temperature dynamics corresponds to motion of the Li\textsuperscript{+}−Ti\textsubscript{Ti′} complex. There is no evidence that its spin polarization is wiped out by fast relaxation which would result in a missing fraction in Figure 3.2. However, if immediately after implantation the \(^8\text{Li}\textsuperscript{+}\) is free for a time longer than the period of precession in the RF field (\(\sim 1\) kHz), it will contribute to the resonance before binding with a polaron. Similarly, if the Li\textsuperscript{+}−Ti\textsubscript{Ti′} complex undergoes cycles of binding and unbinding at higher temperature, provided it is unbound for intervals comparable to the precession period, it will participate in the resonance. In analogy with the closely related technique of radio frequency muon spin rotation (RF-\(\mu\)SR) [239], one can thus use the resonance amplitude of the diamagnetic \(^8\text{Li}\textsuperscript{+}\) in Figure 3.4 to follow kinetic processes involving the implanted ion (see e.g., the hydrogenic muonium defect in silicon [240]).

Along these lines, we suggest that the nonmonotonic changes in resonance amplitude at low temperature reflect dynamics of the Li\textsuperscript{+}-polaron complexation. The sample in our measurements is nominally undoped, and we expect the main source of polarons is oxygen substoichiometry. From its colour [217], it could have oxygen vacancies at the level of 0.1 % or less and polarons resulting from these vacancies are known to be mobile at quite low-\(T\) (i.e., below 50 K) [237, 238]. Alternatively, polarons may result from electron-hole excitations created by the implantation of \(^8\text{Li}\textsuperscript{+}\).

The large increase in resonance area between 10 and 25 K implies some form of slow dynamics on the timescale of the \(^8\text{Li}\) lifetime \(\tau_\beta\). This could be a modulation of the EFG, but more likely it is a magnetic modulation related to the polaron moment as it mobilizes. This is not motional narrowing, but rather a slow variation in the resonance condition, such that the applied RF matches the resonance frequency for many more \(^8\text{Li}\) at some point during their lifetime. The increase of intensity then corresponds to the onset of polaron motion, while the loss in intensity with increasing temperature is due to formation of the Li\textsuperscript{+}-polaron complex, and the fluctuations from this motion also become fast enough to produce the \(T_1\) minimum. The complex does not necessarily survive to high temperatures [215], though, and based on the resonance intensity, the motionally narrowed quadrupolar split resonance at high temperature corresponds to nearly all of the \(^8\text{Li}\). The \(E_A\) from the low temperature slope in Figure 3.6 is remarkably compatible with the thermal instability of the intrinsic (unbound) polaron in rutile [196, 209, 211–213, 215],
consistent with this picture.

Aside from the activation energies, the prefactors $\tau_0^{-1}$ from Equation (1.3) may provide further information on the processes involved. For atomic diffusion, the prefactor is often consistent with a vibrational frequency of the atom in the potential well characteristic of its crystalline site, typically $10^{12} - 10^{14}$ s$^{-1}$. Prefactor anomalies refer to any situation where $\tau_0^{-1}$ falls outside this range [32]. From Figure 3.6, we see that $\tau_0^{-1}$ for the high temperature dynamics is anomalously high, while for the low temperature process it is anomalously low. Within thermodynamic rate theory [25, 26], the prefactor is given by Equation (1.7). For closely related processes, $\Delta S$ is not independent of $E_A$, giving rise to the Meyer-Neldel rule (MNR) and (enthalpy-entropy) correlations between the Arrhenius slope and intercept [31, 33, 241] (see Appendix C), but independent of such correlations, a prefactor anomaly may simply result from $\Delta S_m/k_B$ being substantially different from $\sim 1$.

We first consider the high temperature prefactor, noting that the bulk diffusivity also shows an unusually large $D_0$ [184]. Prefactors of this magnitude are uncommon, but not unprecedented. For example, $^7$Li NMR in LiF at high temperature yields a comparably large $\tau_0^{-1}$ for vacancy diffusion in the “intrinsic” region [242]. Similarly, a large prefactor is observed from $^{19}$F NMR in superionic PbF$_2$ [243]. The latter case was attributed, not to motion of an isolated fluoride anion, but rather to the total effect of all the mobile interstitial $\text{F}^-$, whose concentration is also activated. This may also explain the LiF prefactor, but it clearly does not apply to the extrinsic implanted $^8$Li$^+$ in the dilute limit. With the advent of sensitive atomic resolution probes of surfaces in the past few decades, a very detailed picture of diffusion on crystal surfaces has emerged [68, 69], which can help to refine our ideas about bulk diffusion. For example, in some cases, the Arrhenius prefactor of adatoms diffusing along a step edge is significantly enhanced over a flat terrace [244]. Like the channels in rutile, step edges consist of a 1D array of vacant sites, but the direct relevance is not clear, since the adatoms are generally far from the dilute limit. We suggest that the most reasonable explanation of the high $\tau_0^{-1}$ for long-range diffusion of Li$^+$ in rutile is a large $\Delta S_m$ which can result from a ballistic picture of hopping [245, 246]. Similarly, a (Li/Ti) concentration dependence of $\Delta S_m$ may contribute to the observed concentration dependence of $D$ [184, 203].

A more common and widely discussed case is a small prefactor as we find at low temperature.
Low prefactors are often encountered in superionic conductors both in NMR [35, 247] and transport measurements, where they have been attributed to a breakdown of rate theory [248] or to low dimensionality that is often found for these structures [50] (the latter certainly applies to rutile). However, as argued above, the low temperature $^8$Li relaxation likely reflects polaron dynamics rather than $\text{Li}^+$ motion. Evidence for this comes from the low temperature evolution of the electronic conductivity of lightly deoxidized rutile that shows a resistivity minimum at about 50 K [238]. The complex low temperature behavior of rutile probably combines polaron binding to defects [237, 238] with intrinsic polaronic conductivity and the instability to delocalize [212]. Prefactors for defect-bound polarons at low temperature are significantly lower than our $\tau_0^{-1}$ [237]. It would be interesting to compare our prefactor with the activated disappearance of the EPR [211, 215] to test the connection between these two phenomena with very similar activation energies.

### 3.5 Conclusion

In summary, using low-energy ion-implanted $^8$Li $\beta$-NMR, we have studied the dynamics of isolated $^8$Li$^+$ in rutile TiO$_2$. Two sets of thermally activated dynamics were found: one below 100 K; and one at higher-temperatures. At low temperature, an activation barrier of 26.8(6) meV is measured with an associated prefactor of $1.23(5) \times 10^{10}$ s$^{-1}$. We suggest this is unrelated to $\text{Li}^+$ motion, and rather is a consequence of electron polarons in the vicinity of the implanted $^8$Li$^+$ that are known to become mobile in this temperature range. Above 100 K, Li$^+$ (not polaron complexed) undergoes long-range diffusion, characterized by an activation energy and prefactor of 0.32(2) eV and $1.0(5) \times 10^{16}$ s$^{-1}$, in agreement with macroscopic measurements. A cartoon illustrating these findings is shown in Figure 3.8. These results in the dilute limit from a microscopic probe indicate that Li$^+$ concentration does not limit the diffusivity even up to high concentrations, but that some key ingredient is missing in the calculations of the barrier. Low temperature polaronic effects may also play a role in other titanate Li$^+$ conductors, such as the perovskites [249] and spinels [250]. The present data, combined with EPR and transport studies, will further elucidate their properties.
**Figure 3.8:** Summary of the sources of dynamics in rutile TiO$_2$ revealed by $^8$Li $\beta$-NMR, shown as an Arrhenius plot of the fluctuation rate $\tau^{-1}$. Below 100 K, we suggest the low-barrier dynamics are associated with the mobility of dilute electron polarons in the vicinity of implanted $^8$Li$^+$. At higher temperatures, $^8$Li$^+$ undergoes long-range diffusion (as an uncomplexed cation) within the 1D crystallographic tunnels parallel the rutile $c$-axis. Adapted from [206]. Copyright © 2017, American Chemical Society.

### 3.6 Supplemental material

#### 3.6.1 Biexponential relaxation

Following the analysis described in Section 3.3.1, the fast relaxing component extracted from fitting the SLR measurements at high- and low-field to a biexponential relaxation function, defined in Equation (3.1), is shown in Figure 3.9. While some of the qualitative features seen in the slow component at low temperatures are apparent in $1/T_{1}^{\text{fast}}$, they are much less pronounced at high field (see Figure 3.3). The monotonic increase in $1/T_{1}^{\text{fast}}$ above $\sim150$ K contrasts the behaviour of the slow component and dominates over any local maxima that may be present. Interestingly, the ratio of relaxation times $T_{1}^{\text{fast}}/T_{1}^{\text{slow}}$ varies only weakly with temperature and remains field-independent over much of the temperature range. Deviations from a field-independent ratio occur near the local maxima in $1/T_{1}^{\text{slow}}$, clearly visible in Figure 3.3.

We now consider what might produce the biexponential relaxation $R(t, t')$ in Equation (3.1). A fraction of the implanted $^8$Li$^+$ stopping at a metastable crystallographic site at low temperature would show distinct resonance and relaxation (e.g., $^8$Li$^+$ in simple metals [147]). This would, however, be independent of applied field and would exhibit a very different temperature dependence from the in-channel diffusing site. As we find no clear evidence for multiple sites in the resonance analysis or field-independent activated modulation of the SLR rates, we conclude a secondary site cannot be the source of the biexponential relaxation.
Figure 3.9: Results from the analysis of the $^8$Li SLR measurements in rutile TiO$_2$ using Equation (3.1) at high- and low-field, described in the text. Shown are the ratio of the fast/slow relaxation times (top) and the fast relaxation rate (bottom). The ratio varies weakly with temperature and is field independent for much of it, deviating only in the vicinity of $T_{1,\text{slow}}(T_{\text{min}})$. Some of the features clearly seen in $1/T_{1,\text{slow}}$ are apparent in $1/T_{1,\text{fast}}$ (cf., Figure 3.3), but much less pronounced, especially at high field. Adapted from [206]. Copyright © 2017, American Chemical Society.

If quadrupolar fluctuations are the dominant source of relaxation, as would be expected for $^8$Li$^+$ diffusion, then on the low temperature side of the $T_1$ minimum, where the fluctuations are slow compared to $\omega_L$, the relaxation may be intrinsically biexponential for spin $I = 2$ [71, 155, 156]. However, these Redfield-theory calculations of $R(t, t')$ differ in several key assumptions from our situation, specifically: 1) the initial state of the optically polarized $^8$Li spin is quite different [127]; 2) we are not always in the extreme high field limit; and 3) one dimensional hopping yields a non-Debye fluctuation spectrum [226, 227]. Moreover, above the $T_1$ minimum, where the fluctuations are fast, the biexponential should collapse to a single exponential [156], which is certainly not the case here, particularly for the low field data. It remains to be seen whether a suitably modified theory along these lines could account for the field dependence of
the biexponential at high temperatures.

In contrast, at low temperature, we suspect the relaxation has a significant, possibly dominant, contribution from the polaron magnetic moment. Here, the spectrum of magnetic field fluctuations is naturally field dependent, yielding a strongly field dependent $\lambda$. In this case, some of the fast component at low fields would cross over to the high field slow component as $\lambda(B_0)$ decreases with increasing field. This may contribute to the pronounced change in the slow relaxing fraction $f_{\text{slow}}$ from high to low field, whose behaviour is reminiscent of longitudinal field decoupling often observed in muon spin rotation/relaxation/resonance (μSR). A detailed field dependence of the relaxation, specifically in the region of $\sim 150$ mT [215], would be necessary to confirm this.

The character of the relaxation (magnetic, quadrupolar or mixed) can also be tested by comparison with another Li isotope, such as the spin-3/2 $^9\text{Li}$ as has been recently demonstrated [251–253]. It is important to recall that the amplitude of the relaxing signal is temperature independent even at low field, meaning that we do not have a significant fraction of the signal that is so fast relaxing that it is lost (wiped out) as has been seen in $^7\text{Li}$ NMR from polarons in the perovskite $\text{Li}_3\text{La}_{2/3-x}\text{TiO}_3$ [249]. We find no evidence for a missing fraction to the level of 10% of the total signal, but can’t rule out a small missing component at the level of a few %. Thus if a significant fraction of $^8\text{Li}^+$ forms the bound complex here, then its relaxation remains measurable even at low field.

### 3.6.2 The 4$c$ site

The quadrupole splittings depend sensitively on the $^8\text{Li}^+$ site and its symmetry, and with the angular dependence of the splittings (see Section 2.3.1) combined with calculations of the EFG (including lattice relaxation), one might be able to make a site assignment. Here we set out a few properties of the most likely site (4$c$) to make some initial observations based on the site symmetry in an ideal lattice.

The 4$c$ site is coordinated by two near-neighbour and four more distant oxide ions in a shortened octahedron. As can be seen in Figure 3.10A, the axis of the two nearest-neighbour oxide ions alternates from one site to the next along $c$ by $90^\circ$. Beyond the first coordination,
there are two nearest neighbour Ti on opposite sides, and the Ti–Li–Ti direction also alternates between [100] and [010] along the channel, shown in Figure 3.10B. Overall, the site has $2/m$ symmetry with the two-fold axis parallel to $c$. This symmetry is too low to yield an axial EFG, so $\eta$ is non-zero, and may even approach $\sim 1$; however, if we consider fast hopping along the $c$-axis, and the alternating character of the adjacent sites, one expects that the time-average EFG will become (four-fold) axisymmetric. This should be the case at room temperature, where there is clear evidence for Li$^+$ diffusion, and a simple test of an axial angle dependence could confirm this.

The characteristics of this site are also important in determining properties of the Li$^+$-polaron complex. Here, one of the two neighbouring titanium is 3+, rather than 4+, which further lowers the site symmetry and alters the EFG. Calculations suggest that the polaron is mainly mobile along the stacks of adjacent edge-sharing TiO$_6$ octahedra in the $c$ direction [196, 209, 212, 213] and it is unable to move to the other Ti neighbour on the far side of the Li site. Notice that if the polaron does hop to the next Ti along the stack, it is not the near neighbour of the adjacent Li site, but of the second nearest Li site along the chain. This is easily seen by the alternation of Ti–Li–Ti mentioned above (see Figure 3.10B). If the bound complex moves in tandem, with the polaron remaining in a single TiO$_6$ stack, then fast motional averaging should not result in an axisymmetric EFG, in contrast to the case of free Li$^+$ diffusion.
Figure 3.10: View of the near-neighbour atoms to interstitial lithium (green) in the rutile TiO$_2$ 4$c$ site, showing their 90° alternating coordination axis between neighbouring 4$c$ sites along the $c$-axis channels. The nearest-neighbour atoms are indicated here by connecting grey cylinders. (A) The two nearest-neighbour oxygen (red) atoms. (B) Two nearest-neighbour titanium (blue) atoms. The structures were drawn using CrystalMaker [205]. Adapted from [206]. Copyright © 2017, American Chemical Society.
Chapter 4

Ionic and electronic properties of the topological insulator Bi$_2$Te$_2$Se

4.1 Introduction

Bismuth chalcogenides with the formula Bi$_2$Ch$_3$ (Ch = S, Se, or Te) are narrow gap semiconductors that have been studied for decades for their thermoelectric properties. They crystallize in the layered tetradyminite structure [254, 255], consisting of stacks of strongly bound Ch–Bi–Ch–Bi–Ch quintuple layers (QLs) loosely coupled by van der Waals (vdW) interactions (see Figure 4.1). More recently, interest in their electronic properties has exploded [256] following the realization that strong spin-orbit coupling and band inversion combine to make them three-dimensional (3D) topological insulators (TIs) [257], characterized by a gapless topological surface state (TSS). Electronically, this family of TIs is characterized by a relatively insulating bulk and a robustly conductive surface, with greater contrast in conductivity between the two regions significantly facilitating identification and study. The prevalence for self-doping in binary chalcogenides (e.g., Bi$_2$Se$_3$ or Bi$_2$Te$_3$) often yields crystals far from insulating in the bulk, masking the signature of the conductive surface state. This has been mitigated, for example, in the most widely studied tetradyminate TI Bi$_2$Se$_3$ with Ca doping to suppress the more usual $n$-type conductivity [258, 259]. On the other hand, the stoichiometric ordered [260, 261] ternary line compound Bi$_2$Te$_2$Se (BTS) exhibits a much lower conductivity thanks to its fortuitous crystal
Figure 4.1: Crystal structure of BTS [261], consisting of Te–Bi–Se–Bi–Te layers. These QLs are weakly coupled through vdW interactions, giving rise to a characteristic gap between adjacent Te planes. This atomic arrangement is analogous to transition metal dichalcogenides (TMDs), where it is possible to insert foreign atoms and small molecules within the vdW gap. The structure was drawn using Visualization for Electronic and StTructural Analysis (VESTA) [273]. Adapted from [274]. Copyright © 2019, American Physical Society.
Table 4.1: Properties of host nuclei in BTS relevant to NMR. For each isotope, the nuclear spin $I$, gyromagnetic ratio $\gamma/2\pi$, quadrupole moment $Q$, and natural abundance are listed. For comparison, properties of the $\beta$-detected nuclear magnetic resonance ($\beta$-NMR) probe nucleus $^8$Li are included in the bottom row.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$I$</th>
<th>$\gamma/2\pi$ (MHz T$^{-1}$)</th>
<th>$Q$ (mb)</th>
<th>Natural abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{77}$Se</td>
<td>1/2</td>
<td>+8.156 785</td>
<td>0</td>
<td>7.6</td>
</tr>
<tr>
<td>$^{123}$Te</td>
<td>1/2</td>
<td>−11.234 910</td>
<td>0</td>
<td>0.89</td>
</tr>
<tr>
<td>$^{125}$Te</td>
<td>1/2</td>
<td>−13.545 426</td>
<td>0</td>
<td>7.07</td>
</tr>
<tr>
<td>$^{209}$Bi</td>
<td>9/2</td>
<td>+6.962 477</td>
<td>−516</td>
<td>100</td>
</tr>
<tr>
<td>$^8$Li</td>
<td>2</td>
<td>+6.3016</td>
<td>+32.6</td>
<td>0</td>
</tr>
</tbody>
</table>

sensitivity to the surface. Despite this, a considerable body of conventional NMR in the Bi$_2$Ch$_3$TIs has accumulated. Since these results are closely related to the present study, we give a brief summary.

All elements in BTS have NMR-active isotopes (see Table 4.1). The most conspicuous feature of 100 % abundant $^{209}$Bi NMR is the strong quadrupolar interaction. However, the broad quadrupole pattern shows clear evidence of a shift related to carrier density, indicating a very strong hyperfine coupling [276], confirmed more recently by very high field NMR [277]. The behaviour of $1/T_1$ is less consistent, with results ranging from $T$-linear to nearly $T$-independent [276, 278] at low temperature. The low abundance ($\sim 7 \%$) pure magnetic spin 1/2 probes $^{77}$Se and $^{125}$Te show a small $T$-independent shift, and Korringa relaxation at low temperature in orientationally averaged powder spectra [279]. This Korringa relaxation is enhanced in nanocrystals and was attributed to the TSS [280], but given the evidence for aging effects that stabilize a conventional metallic surface state [281], this connection remains unclear. More recent work in single crystals has identified distinct resonances from inequivalent chalcogen planes, and a more detailed analysis of the chalcogen NMR is required [282–284].

While a great deal is known about the TSS from surface sensitive probes, little is known about how this behaviour transitions to the bulk as a function of depth below the crystal surface. We plan to address this question using highly spin-polarized radioactive ions, specifically, using depth-resolved $\beta$-NMR [5] with short-lived $^8$Li as the probe nucleus, similar to low-energy muon spin rotation (LE-$\mu$SR) [15]. As a first step, here we present results using relatively high implantation energies, 5–28 keV, corresponding to $^8$Li$^+$ implantation depths below the TSS. We
find that below $\sim 150 \text{ K}$ $^8\text{Li}$ experiences strongly field dependent relaxation and resonance shifts. The relaxation is $T$-linear and reminiscent of a Korringa mechanism, but conventional theory for NMR cannot account for its field dependence, which we suggest is due to magnetic carrier freeze out. At higher temperatures, an additional relaxation mechanism is observed, originating from ionic diffusion of isolated $^8\text{Li}^+$ in the vdw gap.

The remainder of the chapter is organized as follows: a brief description of the experiment is given in Section 4.2, followed by the results and analysis in Section 4.3. A detailed discussion is given in Section 4.4, focusing on the high temperature dynamics of the isolated $^8\text{Li}^+$ ion in the vdw gap (Section 4.4.1), and the electronic properties of BTS giving rise to the field dependent relaxation and resonance shifts at low temperature (Section 4.4.2). Finally, a concluding summary can be found in Section 4.5.

### 4.2 Experiment

A single crystal of BTS was grown as detailed by Jia et al. [261] and taken from the more insulating section of a larger boule. This insulating character was confirmed by 4-wire transport measurements, which revealed an increase in resistivity by a factor of $\sim 3$ below 100 K, characteristic of the more insulating BTS compositions [261]. At low temperature, the resistivity is maximized at $\sim 0.1 \Omega \text{ cm}$. Prior to the $\beta$-NMR experiments, the BTS crystal, with dimensions $5 \times 4 \times 0.1 \text{ mm}^3$, was cleaved in air and affixed to a sapphire plate using Ag paint (SPI Supplies, West Chester, PA) for mounting on a cold finger cryostat.

$\beta$-NMR experiments were performed at TRIUMF’s Isotope Separator and ACcelerator (ISAC) facility in Vancouver, Canada. A low-energy highly polarized beam of $^8\text{Li}^+$ was implanted into the BTS single crystal within one of two dedicated spectrometers [5, 121, 122, 124]. The incident $^8\text{Li}^+$ ion beam had a typical flux of $\sim 10^6 \text{ ions/s}$ over a beam spot $\sim 2 \text{ mm}$ in diameter. At the implantation energies $E$ used here (5 keV to 28 keV), the ions stop at average depths $>30 \text{ nm}$ (see Figure 4.14 in Section 4.6.1). Spin-polarization was achieved in-flight by collinear optical pumping with circularly polarized light, yielding a polarization of $\sim 70 \%$ [127], and monitored after ion-implantation through the anisotropic $\beta$-decay emissions of $^8\text{Li}$. Specifically, the $\beta$-count rates in two opposed scintillation counters were recorded, whose asymmetry is proportional
to the average longitudinal nuclear spin-polarization [5, 12], with the proportionality factor depending on the experimental geometry and the details of the β-decay. Details of the SLR and continuous wave (CW) resonance measurements are given in Section 2.3. A typical SLR measurement took \( \sim 20 \) min, while resonance measurements typically took \( \sim 30 \) min to acquire.

4.3 Results and analysis

4.3.1 Spin-lattice relaxation

Typical \(^8\text{Li}\) SLR data at high and low magnetic field in BTS are shown in Figure 4.2 for several temperatures, where the spectra have been normalized by their \( t = 0 \) asymmetry \((A_0)\). It is immediately evident that the SLR rates are strongly dependent on both temperature and field. In high fields, the relaxation is relatively slow, but comparable to that observed in some elemental metals [5] and semimetals [285]. Surprisingly, the relaxation is faster than in the normal state of the structurally similar NbSe\(_2\) [286], despite a very much smaller carrier density. However, it is also slower than in the 3D TI Bi\(_{1-x}\)Sb\(_x\) [285]. At all temperatures, the relaxation rate increases monotonically with decreasing magnetic field. Even at very low temperatures near \( \sim 10 \) K, where most excitations are frozen out, the SLR remains substantial, as shown in Figure 4.3. The relaxation rate at low field is orders of magnitude faster than in Tesla fields, suggesting the importance of low field relaxation from the host lattice nuclear moments [139, 152]. On top of the field dependence, there is also a strong temperature dependence; the relaxation rate increases with increasing \( T \), but this trend is non-monotonic and at least one temperature exists (per field) where the rate is maximized.

We now consider a detailed analysis to quantify these observations. First, we remark that the relaxation is non-exponential at all temperatures and fields. The precise origin for this remains unclear. While it is well-known that magnetic relaxation of quadrupolar spins is multiexponential, this is not the case here, as the initial state following optical pumping has purely vector (i.e., Zeeman) polarization,\(^1\) yielding single exponential magnetic relaxation, similar to

\(^1\)That is, the magnetic sublevel populations \( p_m \) vary linearly in \( m \), as opposed to, for example, quadratically in the case of quadrupolar alignment. This description of spin orientation (as well as other higher order terms) can be obtained by decomposing the spin system’s density matrix in terms of irreducible spherical tensor operators \( \hat{T}_{k,q} \) (see e.g., [12, 40, 41, 71, 287–289]). Specifically, vector/Zeeman polarization corresponds to the \( \hat{T}_{k=1,q=0} \) term.
**Figure 4.2**: $^8$Li SLR data in BTS at high and low magnetic fields. The characteristic kink at $t = 4$ s corresponds to the trailing edge of the $^8$Li$^+$ beam pulse. The $^8$Li SLR is strongly field-dependent, increasing with decreasing magnetic field, and increases non-monotonically with increasing temperature. The solid black lines are the result of a global fit to all spectra at a given field to a stretched exponential relaxation function, Equation (2.13), convolved with the square beam pulse [153, 154]. The spectra have been binned by a factor of 20 for clarity. Adapted from [274]. Copyright © 2019, American Physical Society.

The conventional NMR case where all the quadrupole satellites are simultaneously saturated (see e.g., [290]). If, however, the relaxation is quadrupolar (due to a fluctuating electric field gradient (EFG)), then in the slow limit for $I = 2$, the relaxation is biexponential [71, 155, 156]. In light of this, we model the spin relaxation using a stretched exponential, consistent with the approach adopted in conventional NMR in similar materials [276, 279, 280, 291]. Explicitly, for a $^8$Li$^+$ ion implanted at time $t'$, the spin polarization at time $t > t'$ follows Equation (2.13). where $\lambda \equiv 1/T_1$ is the relaxation rate and $0 < \beta \leq 1$ is the stretching exponent. We find this to be the simplest model that fits the data well across all temperatures and fields. Using Equation (2.13) convolved with the 4 s beam pulse [153, 154], SLR data grouped by magnetic field $B_0$ and implantation energy $E$ were fit simultaneously with a shared common initial asymmetry $A_0(B_0, E)$. Note the statistical uncertainties in the data are strongly time-dependent and accounting for this is
Figure 4.3: Field dependence of $^8\text{Li}$ SLR data in BTS at 10 K. The characteristic kink at $t = 4$ s corresponds to the trailing edge of the $^8\text{Li}^+$ beam pulse. Even at low temperature, where most excitations are frozen out, the $^8\text{Li}$ SLR is strongly field-dependent, increasing with decreasing magnetic field. This field dependence suggests the importance of fluctuations from host lattice nuclear moments [139, 152]. An implantation energy of 28 keV was used for each measurement, except at 2.20 T, which was recorded at 20 keV $^8\text{Li}^+$. The solid black lines are the result of a global fit to all spectra at a given field to a stretched exponential relaxation function, Equation (2.13), convolved with the square beam pulse [153, 154]. The spectra have been binned by a factor of 20 for clarity.

crucial in the analysis. To find the global least-squares fit, we used custom C++ code leveraging the MINUIT [176] minimization routines implemented within ROOT [175]. The fit quality is good in each case ($\chi^2_{\text{global}} \approx 1.02$) and a subset of the fit results is shown in Figure 4.2 as solid black lines. The large values of $A_0$ extracted from the fits ($\sim 10\%$ for $B_0 \geq 2.20$ T and $\sim 16\%$ for $B_0 \leq 20$ mT) are consistent with the full beam polarization, implying that there is no appreciable missing fraction due to a very fast relaxing component. $A_0$ extracted from these fits are used to normalize the spectra in Figure 4.2. For all the fits, the stretching exponent $\beta \approx 0.5$, with a weak temperature dependence: in high field, decreasing slightly at temperatures below $\sim 200$ K.
Figure 4.4: The SLR rate for $^{8}$Li in BTS at high magnetic fields with $B_0 \parallel (001)$ using a stretched exponential analysis. $1/T_1$ is strongly field-dependent, increasing with decreasing magnetic field, but also increases non-monotonically with temperature. At each field, a clear $1/T_1$ maximum can be identified where the average fluctuation rate of the dynamics inducing relaxation matches the $^{8}$Li Larmor frequency. The solid black lines are fits to the model in Equations (1.3), (1.15) and (4.1), consisting of a linear $T$-dependence with a non-zero intercept and a term due to ionic diffusion. The highlighted grey region denotes the lower limit of measurable $1/T_1$ due to the $^{8}$Li probe lifetime. Adapted from [274]. Copyright © 2019, American Physical Society.

4.3.2 Modelling relaxation

We now consider a model of the temperature dependence of the measured $1/T_1$. We interpret the relaxation peak as a Bloembergen-Purcell-Pound (BPP) peak [34], where the rate of a fluctuating interaction with the nuclear spin sweeps through the Larmor frequency $\omega_0 = \gamma B_0$ at the rate peak [34, 35, 225]. As we discuss in more detail below, we attribute this fluctuation to diffusive motion of interstitial $^{8}$Li$^+$ in the vdW gap between QLs in BTS. It is clear that the peaked relaxation adds to an approximately linearly temperature dependent term, reminiscent of Korringa relaxation characteristic of NMR in metals [7, 42], and probably of electronic origin.
Figure 4.5: Temperature dependence of the $^8$Li$^+$ $1/T_1$ in BTS at low magnetic field [7.5 mT $\perp$ (001)]. The relaxation rate is orders of magnitude larger than at high fields, with both a larger apparent $T$-linear slope and intercept. There is some evidence of a small $1/T_1$ peak (see inset) near $\sim$150 K superposed on the dominant linear dependence. Above 200 K, $1/T_1$ increases substantially, suggestive of another relaxation mechanism absent at higher fields. Adapted from [274]. Copyright © 2019, American Physical Society.

Based on this, we use the following model:

$$1/T_1 = a + bT + c(J_1 + 4J_2).$$

The first two terms in Equation (4.1) account for the linear $T$-dependence $\lambda_e \equiv a + bT$ and the remaining terms $\lambda_{\text{diff}} \equiv c(J_1 + 4J_2)$ describe the peak. $\lambda_{\text{diff}}$ consists of a coupling constant, $c$, proportional to the mean-squared transverse fluctuating field and the $n$-quantum NMR spectral density functions, $J_n$ [225]. In this context, $J_n$ is a frequency dependent function peaked at $T_{\text{max}}$, which occurs when the fluctuation rate driving relaxation matches $\sim n\omega_0$. While the choice of a precise form of $J_n$ depends in detail on the dynamics, we use the empirical expression of Richards [35] given by Equation (1.15), which gives the correct asymptotic limits for relaxation produced by two-dimensional (2D) fluctuations [51], originating, for example, from diffusion of
Table 4.2: Results from the analysis of the $^8$Li SLR $1/T_1$ peaks in BTS, shown in Figures 4.4 and 4.5, using Equations (1.3), (1.15) and (4.1). Here, $\Delta$ denotes the orientation of the BTS trigonal $c$-axis with respect to the applied field $B_0$ and $E$ is the $^8$Li$^+$ implantation energy. Values for the coupling constant $c$, prefactor $\tau_0^{-1}$, and activation energy $E_A$ are indicated. For comparison, the kinetic parameters extracted from fitting $\omega_0(T_{\text{max}})$ to Equation (1.3) in Figure 4.10 (described in Section 4.4.1) are shown in the bottom row. The good agreement in these values, independent of the analysis details, indicates a single common dynamic process. Differences in the parameter pairs $\tau_0^{-1}$ and $E_A$ may be attributed to the empirical Meyer-Neldel rule (MNR) [33], which is evident when plotted on a semi-logarithmic scale (see Figure 4.9). Adapted from [274]. Copyright © 2019, American Physical Society.

<table>
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<th>$B_0$ (T)</th>
<th>$\Delta$</th>
<th>$E$ (keV)</th>
<th>$c$ ($10^6$ s$^{-2}$)</th>
<th>$\tau_0^{-1}$ ($10^{12}$ s$^{-1}$)</th>
<th>$E_A$ (eV)</th>
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<tr>
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<td>5</td>
<td>7.23(16)</td>
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<td></td>
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<td>0.07(1)</td>
<td>1</td>
<td>0.164(3)</td>
</tr>
</tbody>
</table>

$^8$Li$^+$ confined to the vdW gap. As mentioned previously, we make the usual assumption that the $\tau_c$ in Equation (1.15) follows an Arrhenius temperature dependence given by Equation (1.3).

Fits of the $1/T_1$ data to the model given by Equation (4.1) with Equations (1.3) and (1.15) are shown in Figures 4.4 and 4.5 as solid black lines, clearly capturing the main features. While the kinetic parameters determining the position and shape of the SLR peaks differed somewhat at different fields (see Table 4.2), good overall agreement was found from this analysis, and we consider the details further below in Section 4.4.1. As anticipated, the slope and intercept of $\lambda_e$ were both strongly field dependent. At low fields, the intercept $a$ is quite large and varies as $\omega_0^{-2}$ (Figure 4.6), behaviour characteristic of relaxation due to host nuclear spins. Just as in the case of $^8$Li in NbSe$_2$ [139], this field dependence can be described by a simple BPP model [34] given by Equation (1.14). A fit to this model, shown as a solid red line in the upper panel in Figure 4.6, yields a coupling constant $C_0^2 = 1.5(3) \times 10^6$ s$^{-2}$ and $\tau_c = 3.2(7) \times 10^{-5}$ s. We note that the magnitude of $C_0^2$ is compatible with the observed $^8$Li resonance linewidth, discussed in Section 4.3.3, and that $\tau_c$ is remarkably close to the $^{209}$Bi NMR $T_2$ time in Bi$_2$Se$_3$ [278]. It is, however, not clear whether the intercept at 2.20 T is a remnant of this low field relaxation, or is due to an electronic mechanism [292]. In any case, it is small and we will not consider it further. In contrast, the slope $b$ varies as $\omega_0^{-1.5}$ with a pronounced anisotropy between orientations.
Figure 4.6: Field dependence of the intercept $a$ and slope $b$ describing the low temperature electronic relaxation in Equation (4.1). (Top panel): The $T \to 0$ intercept of $1/T_1$ falls with increasing field as $1/\omega_0^2$, behavior consistent with a low field relaxation due to fluctuating host lattice nuclear spins [139]. The solid red line indicates a fit to a simple BPP model [34] given by Equation (1.14), yielding a coupling constant $\tilde{C}_2^0 = 1.5(3) \times 10^6$ s$^{-2}$ and correlation time $\tau_c = 3.2(7) \times 10^{-5}$ s, the latter being remarkably close to the $^{209}$Bi NMR $T_2$ time in Bi$_2$Se$_3$ [278]. The inset shows a zoom of the small high field intercepts, at the lower limit measurable due to the $^8$Li probe lifetime highlighted in grey. (Bottom panel): Field dependence of the low temperature slope of $1/T_1$, exhibiting a strong orientation dependence, but a common field dependence $\propto \omega_0^{-1.5}$, indicated by the solid coloured lines. Adapted from [274]. Copyright © 2019, American Physical Society.

(Figure 4.6). We return to these points below in Section 4.4.2.

4.3.3 Resonance spectra

We now turn to the $^8$Li resonance in BTS. Typical spectra at high field are shown in Figure 4.7. Consistent with a non-cubic crystal, the $^8$Li NMR is quadrupole split (as described in Section 2.3). This is confirmed by the helicity-resolved spectra (see Figure 4.15 in Section 4.6.2) which show opposite satellites in opposite helicities [5]. The EFG that produces the splitting is characteristic of the $^8$Li site in the crystal. From the spectra, it is relatively small, on the order of a few kHz.
In addition, a second unsplit line is evident near the midpoint of the quadrupole pattern. This line must be due to a distinct $^8$Li site with a small, unresolved quadrupolar splitting. A similar unsplit resonance was observed in the vdW layered material NbSe$_2$ [286], which was thought to originate from implanted $^8$Li$^+$ stopped at an interstitial site within the vdW gap.

This evidence for two sites suggests that our single component relaxation model in Section 4.3.2 is too simple. However, more complicated relaxation functions suffer from over-parametrization, and we have retained the single stretched exponential to represent the overall average relaxation of $^8$Li in BTS.

The resonance was found to evolve substantially with temperature, as shown in Figure 4.7.
Here, the spectra have been normalized to the off-resonance steady-state asymmetry to account for the variation of intensity due to SLR [147]. While it is apparent that the satellite intensities and splitting remain nearly temperature independent, the amplitude of the central line increases significantly above $\sim 100$ K, becoming the dominant feature by room temperature. Additionally, a small shift in the resonance centre-of-mass frequency can be seen, increasing in magnitude with decreasing temperature.

To quantify these observations, we now consider a detailed analysis, noting first that the scale of the quadrupolar splitting is given by the quadrupole frequency $\nu_q$ [60], defined in Equation (2.4). As the splitting is small (i.e., $\nu_q \ll \nu_0$), the satellite positions are given accurately by Equation (2.5) using the first-order corrections in Equations (2.6) and (2.8) [60]. From $\nu_0$, we additionally calculate the frequency shift, $\delta$, in parts per million (ppm) using Equation (2.11) and the position in MgO at 300 K with $B_0 \parallel (100)$ as the reference [148].

The helicity-resolved spectra were fit using the quadrupole splitting above with $\nu_0$ and $\nu_q$ as free parameters, in addition to line widths and amplitudes. Similar to the SLR data in Section 4.3.1, a global fitting procedure was used by way of ROOT’s [175] implementation of MINUIT [176]. The two helicities of each spectrum were fit simultaneously with resonance positions and widths as shared parameters. The fits were constrained such that the centre-of-mass frequency $\nu_0$ was shared between the unsplit Lorentzian and quadrupole satellites. Any difference in centre of mass of the split and unsplit lines was too small to measure accurately, and the two lines shift in unison with temperature, as can be seen in Figure 4.7. In addition, we assume the EFG principal axis is along the $c$-axis and $\eta = 0$, making the angular factor unity. This assumption does not affect accurate extraction of the splitting frequency, but precludes unambiguous identification of the EFG tensor elements. Based on a simple point charge model of the lattice (see Section 4.6.3), all reasonable interstitial $^6\text{Li}^+$ sites retain the 3-fold rotation axis of the hexagonal unit cell, supporting this simplification. Changes to the satellite splitting pattern from preliminary measurements at low field with $B_0 \perp c$ are consistent with these assumptions.

The main parameters extracted from this analysis are shown in Figure 4.8. Consistent with the two main qualitative features of the spectra, both the amplitude and shift show substantial changes with temperature. In the top panel of Figure 4.8, above $\sim 150$ K, the shift is nearly
Figure 4.8: Fit results for $^8$Li resonance in BTS at high field with $B_0 \parallel (001)$, following the fitting procedure described in the text. The upper panel shows the resonance shift $\delta$ relative to MgO. Above $\sim 150$ K, the shift is nearly field independent and scattered about 0; however, at lower temperatures, the trends at each field diverge, revealing a field dependent shift whose magnitude is maximized at the lowest temperatures. The lower panel shows the change in amplitude of the central Lorentzian and quadrupole satellites (averaged over all four lines), normalized by the off-resonance baseline [147]. The amplitude of the unsplit line grows above $\sim 100$ K, contrasting the temperature independence of the quadrupole satellite amplitudes. The inflection point $T^*$ of this trend is indicated by the dashed vertical black line. The solid black lines are drawn to guide to the eye. Adapted from [274]. Copyright © 2019, American Physical Society.

field independent and centred around $\sim 0$ ppm. Shifts of this magnitude are difficult to quantify accurately and the scatter in the values is of the same order as systematic variations in the line position, making differences of this order not very meaningful. In contrast, at lower temperatures, the shift trends for each field diverge, revealing a significant field-dependent shift whose magnitude is maximized at the lowest temperature.

The changes in amplitude of central Lorentzian and quadrupole satellites (averaged over all four lines), normalized by the off-resonance baseline [147], appear in the bottom panel of Figure 4.8. Consistent with Figure 4.7, the amplitude of the unsplit line grows above $\sim 100$ K and approaches saturation near room temperature, in contrast to the temperature insensitivity
of the satellite amplitudes. From the smooth growth of the unsplit line amplitude, we identify the inflection point \( T^* \approx 180 \text{ K} \) of the trend, as indicated in Figure 4.8. The other spectral parameters are nearly independent of temperature. The line widths are about \( \sim 6 \text{ kHz} \), with the central Lorentzian narrowing slightly with increasing \( T \). This narrowing is likely the cause of its increase in amplitude. Similarly, \( v_q \approx 7.4 \text{ kHz} \) was characteristic of the splittings over the entire measured temperature range.

Based on these results at the lowest measured temperatures, where dynamic contributions to the resonance are absent, we estimate a 1:1 relative occupation for \(^8\text{Li}^+\) in the two sites. Note, however, that changes in amplitude, up to our highest measured temperature 317 K, are inconsistent with a site change, where the growth of one amplitude is at the expense of the other (see e.g., the \(^8\text{Li} \beta\text{-NMR in Ag [121] or Au [293]}\)).

### 4.4 Discussion

With the main results presented in Section 4.3, the remaining discussion is organized as follows: in Section 4.4.1, we consider the dynamics causing the high temperature \( 1/T_1 \) peaks, while Section 4.4.2 considers the electronic properties of BTS giving rise to relaxation and resonance shifts at low temperature.

#### 4.4.1 High temperature lithium-ion diffusion

The most likely source of the relaxation at high temperatures is diffusive motion of \(^8\text{Li}^+\). While we cannot rule out some local stochastic motion within a cage, or motion of another species in the lattice, given the demonstrated ability to chemically insert Li at room temperature in isostructural bismuth chalcogenides [294, 295], we expect a low barrier to interstitial diffusion for any implanted \(^8\text{Li}^+\) in the vdW gap. Stochastic motion causes the local magnetic field and EFG to become time dependent causing relaxation [34, 35]. From the SLR, we can thus obtain information on the kinetic parameters of the diffusion. From the model of \( 1/T_1(T) \) introduced in Equation (4.1) from Section 4.3.2, we obtain the kinetic parameters listed in Table 4.2. The success of the model is demonstrated by the good self-agreement in the barrier \( E_A \) and prefactor
\( \Delta_{MN} = 0.022 \pm 0.002 \text{ eV} \)
\( T_{iso} = 254 \pm 27 \text{ K} \)

**Figure 4.9:** Meyer-Neldel plot of the \(^8\text{Li}^+\) Arrhenius activation energy \( E_A \) and prefactor \( \tau_0^{-1} \) pairs from Table 4.2, showing the exponential increase in \( \tau_0^{-1} \) with increasing \( E_A \). The linearity of the data on this scale suggests a common origin for the kinetics. From the fit to the data shown in black, the compensation energy \( \Delta_{MN} \) and isokinetic temperature \( T_{iso} \) are identified and indicated in the inset.

\( \tau_0^{-1} \), indicating that an activated dynamic process with a 2D spectral density provides a single common source for the observed \( \lambda_{diff} \). Thus, the correlation rate \( \tau_c^{-1} \) in Equation (1.3) represents the atomic hop rate \( \tau^{-1} \). The small barrier, on the order of \( \sim 0.2 \text{ eV} \), is consistent with expectations for an isolated interstitial ion, where Coulomb \( \text{Li}^+–\text{Li}^+ \) repulsion is negligible. Similarly, the \( \tau_0^{-1} \)'s on the order of \( \sim 10^{12} \text{ s}^{-1} \) are compatible with typical optical phonon frequencies, as is often the case for mobile ions in a lattice. The relatively small deviations in \( E_A \) and \( \tau_0^{-1} \) obtained at different fields may be ascribed to the empirical MNR, where \( \tau_0^{-1} \) increases exponentially with increasing \( E_A \), as is often observed for related kinetic processes [33]. This relationship is evident when the values in Table 4.2 are plotted on a semi-logarithmic scale, as shown in Figure 4.9 (see also Appendix C).

In general, the exponent \( \alpha \) appearing in \( J_n \) from Equation (1.15) can vary from 1 to 2 [52], with deviations from 2 reflecting correlated dynamics that can arise from, for example, Coulomb...
interactions with other ions acting to bias the probe ion’s trajectory [45]. Such correlations affect the shape the $1/T_1$ peak, yielding a characteristic asymmetry with a shallower slope on the low-$T$ side. In contrast, the high symmetry about $T_{\text{max}}$ is consistent with uncorrelated fluctuations driving relaxation, as expected for isolated $^8$Li undergoing direct interstitial site-to-site hopping.

As further confirmation of the appropriateness of the form of $J_n$, we consider an alternative approach agnostic to these details. At each field, we determine the temperature $T_{\text{max}}$ of the $1/T_1$ peak using a simple parabolic fit (after removal of the $T$-linear contribution). This approach has the advantage that it does not rely on any particular form of $J_n$, and we recently used it to quantify diffusion of isolated $^8$Li$^+$ in rutile TiO$_2$ [206]. Finally, for each $T_{\text{max}}$ we assume $\tau_c^{-1}$ matches the Larmor frequency $\omega_0$. The results are shown in the Arrhenius plot in Figure 4.10, where the linearity of the data, spanning three orders of magnitude, demonstrates the consistency of the approach. The Arrhenius fit shown yielded an activation energy $E_A = 0.185(8)$ eV and prefactor $\tau_0^{-1} = 8(3) \times 10^{11}$ s$^{-1}$, in good agreement with the values from the analysis using the 2D $J_n$. Noting that this result lies in the middle of range reported in Table 4.2, we take it as the best determination of the $^8$Li$^+$ hop rate.

Another well-known signature of diffusion in NMR is motional narrowing. When the diffusive correlation rate exceeds the characteristic static frequency width of the line, the local broadening interactions are averaged and the line narrows. In the context of dilute interstitial diffusion in a lattice, the primary quadrupolar interaction may, however, not be averaged to zero, since, in the simplest case, each site is equivalent and characterized by the same EFG. We observe a slight narrowing and a large enhancement in the amplitude of the unsplit resonance with an onset in the range 100 K to 120 K, consistent with where the extrapolated $\tau_c^{-1}$ would be in the kHz range of the linewidth. With the CW resonance measurement, we often find the change in amplitude is more pronounced than the width [296].

Using the $^8$Li$^+$ hop rate from above, we convert $\tau^{-1}$ to diffusivity via the Einstein-Smoluchowski expression, given by Equation (1.1), where $d$ and $f_P$ are assumed to be 2 and 1, respectively, to compare with other measurements of interstitial ionic diffusion in related materials. Using $l \approx 4.307$ Å, the distance between neighbouring $3b$ sites in the vdW gap in the ideal BTS lattice (see Figure 4.16 in Section 4.6.3), we estimate $D$ for $^8$Li$^+$, finding a value on the order of $10^{-7}$ cm$^2$ s$^{-1}$ at 300 K. An Arrhenius plot comparing the diffusivity of $^8$Li$^+$ in BTS with other
Figure 4.10: Arrhenius plot of the $^8$Li fluctuation rate in BTS extracted from the NMR frequency dependent positions of $1/T_1(T_{\text{max}})$ in Figures 4.4 and 4.5. The solid red line is a fit to Equation (1.3) with the activation energy $E_A$ and prefactor $\tau_0^{-1}$ indicated in the inset and the fit’s $\pm 1\sigma$ uncertainty band is highlighted in grey. The kinetic parameters extracted from this minimally model-dependent analysis are in good agreement with those obtained from fits of the $1/T_1$ data to Equations (1.3), (1.15) and (4.1), given in Table 4.2. Adapted from [274]. Copyright © 2019, American Physical Society.

The mobility of isolated $^8$Li$^+$ is exceptional; our estimate for $D$ greatly exceeds that of lithium in the well-known fast ion conductor $h$-Li$_x$TiS$_2$ [301, 302]. Similarly, the lithium diffusion coefficient in lithium intercalated Bi$_2$Se$_3$ is considerably slower [294], possibly due to Li$^+$–Li$^+$ interaction. Interestingly, the mobility of Cu in isostructural Bi$_2$Te$_3$ is also extremely high, as revealed by $^{64}$Cu radiotracer [297] and electrochemical methods [300]. Lastly, we note that similarly large $D$ values were reported recently for $^8$Li$^+$ in the one dimensional ion conductor...
rutile TiO$_2$ [206] and we speculate that the exceptional mobility may be generic for isolated Li$^+$ (i.e., at infinitely dilute concentrations) in ion conducting solids. It would be interesting to test this conjecture against detailed ab initio calculations. Understanding the mobility of dilute intercalates, a simple theoretical situation difficult to interrogate experimentally, remains of fundamental interest [303].

### 4.4.2 Low temperature electronic properties

We turn now to the low temperature results, below the diffusion-related peak, in the range 5 K to 150 K. The diffusive contribution to the relaxation rate is falling exponentially with reduced
temperature below the peak, and the remaining low temperature relaxation must thus have a distinct origin. In this regime, the relaxation rate is linear in $T$, with a slope that is significantly field dependent. In this range there is also a $T$-dependent resonance shift that is also field dependent.

In metals, the dominant features of NMR (and β-NMR) are due to coupling between the conduction electron and nuclear spins, giving rise to the Korringa $T$-linear $1/T_1$ and a $T$-independent Knight shift proportional to the Pauli susceptibility [7, 42]. The apparent Korringa-like dependence in Figures 4.4 and 4.5 is thus surprising, since ideal BTS is a narrow gap semiconductor, with an energy gap $E_g \approx 0.3$ eV [263]. In comparison to metals, NMR in semiconductors is much less well-known, largely because the coupling to the electron spins is much less universally dominant, and often other channels, such as phonons, compete with electronic effects and complicate the interpretation (e.g., in elemental Te [304] and InSb [305], with similar $E_g$ to BTS). However, while calculations and experiments agree on $E_g$ in BTS [263, 267], it is abundantly clear from both experiment [306] and theory [262, 307] that it is unlikely to exist as an intrinsic semiconductor. Rather, it is significantly self-doped by native defects, such as chalcogenide vacancies (donor) and Bi/Te antisite defects (acceptor). Among the tetradymites, BTS is relatively highly insulating, but this does not indicate a paucity of native defects, but rather a coincidental near compensation between the $n$- and $p$-types. Brahlek et al. have made the point that these materials are, in fact, so highly doped that they are metallic, but are poor conductors due to disorder [308]. Such disorder is clearly evident in our data, contributing to the stretched exponential character of the spin relaxation and the line broadening.

The origin of the linearity of the Korringa law is evident from a derivation based on a Fermi golden rule approach to the spin-flip scattering of conduction electrons by the hyperfine interaction with the nuclear spin. The sum over electron momenta when converted to an integral over energy yields:

$$\frac{1}{T_1} = \frac{2\pi}{\hbar A^2} \int \rho^2(E)f(E) \left[1 - f(E)\right] \, dE,$$

where $A$ is the hyperfine coupling energy, $f(E)$ is the Fermi-Dirac distribution, $\rho(E)$ is the electronic density of states, and the integral is over all electron energies in the conduction band. In a broad band degenerate metal, where the Fermi level $E_F \gg k_B T$, the density of states $\rho(E)$ is
practically constant over the range where the Fermi factor is nonzero, and the integral is given to an excellent approximation by:

$$\frac{1}{T_1} = \frac{2\pi}{\hbar} A^2 \rho^2(E_F) k_B T. \tag{4.3}$$

The Korringa slope is thus determined by the square of the product of $A$ and $\rho(E_F)$. In fact, on inspection of the $^{8}\text{Li} \lambda_e$ in BTS, we find it comparable to wide band metals with vastly higher carrier densities [121, 147, 152, 286, 293, 309–311] (see Figure 4.12). While the coupling $A$ for implanted $^{8}\text{Li}^+$ in BTS is not known, it is unlikely to compensate for the much lower $\rho(E_F)$, to yield a comparable Korringa slope. Note that the Korringa law is remarkably robust to disorder and, for example, applies in the normal state of the alkali fullerides where the mean free path is comparable to the lattice constant (the Ioffe-Regel limit) [312]. However, in highly disordered metals, the slope is strongly enhanced [313–315]. Such an enhancement may account for the substantial slope we observe. However, Equation (4.2) indicates that if $\rho(E)$ has significant structure on scales comparable to $k_B T$, as it might in a narrow impurity band, its detailed form and nondegeneracy can render the $T$-dependence nonlinear [316], as found, for example, near the metal-insulator transition (MIT) in doped silicon [317]. Thus, the evident linearity is still surprising. Moreover, in metals, the Korringa slope does not depend on magnetic field.

In doped Si, near the MIT, a field dependence of the enhanced Korringa slope has been found at mK temperatures [319], where it was attributed to the occurrence of uncompensated localized electron spins, probably on some subset of more isolated neutral P donors. Such moments are also evident in the NMR of the dopant nuclei [320]. However, in BTS (in contrast to Si), due to the high dielectric constant and low effective mass, magnetic carrier freezeout [321, 322] may account for the diminished slope at high fields. In this case, the field localizes the carriers so they no longer participate in the conduction band, correspondingly reducing the Korringa slope. This may account, in part, for the significant positive magnetoresistance in BTS [265, 323]. Similarly, the field and temperature dependent shifts in Figure 4.8 may reflect a constant (diamagnetic) contribution (cf. the $^{125}\text{Te}$ shift [279]), in addition to a positive hyperfine field related to the carriers, which diminishes with localization. However, the localized electrons may well provide additional (more inhomogeneous) relaxation and resonance broadening. We know of no case
Figure 4.12: Comparison of the $^8$Li SLR rate in BTS with other materials where electronic relaxation dominates. The rates in NbSe$_2$ [286], Ag [147], and Pt [311] were reported previously, with additional estimates shown here for NbSe$_2$ obtained using the resonance baseline asymmetry [147, 286]. The solid black lines are fits to the data. The bump in the Ag $1/T_1$ around 125 K is due to $^8$Li transitioning from a metastable interstitial to a substitutional site [121, 147, 318].

The temperature dependence of the relaxation rate in BTS contrasts the structurally similar NbSe$_2$, which, in spite of a much higher carrier concentration, shows a shallower Korringa slope and the absence of diffusion-induced $1/T_1$ peak; however, common to both materials is an apparent finite $1/T_1(T = 0 \text{ K})$ intercept, even at relatively high magnetic fields. The highlighted grey region denotes where $1/T_1 \leq 10^{-2}/\tau_\beta$ and is difficult to measure during the $^8$Li probe lifetime [12].

where NMR has been used to study magnetic freezeout. In order to test this idea, it will be essential to compare results on different samples of BTS and related materials (e.g., Ca-doped Bi$_2$Se$_3$).

Above, we only considered bulk origins for the $\lambda_e$. While we do not expect any direct coupling to the TSS at the implantation energies used, it is important to consider the effects of band bending at the surface. If the bulk electronic bands are bent downward at the surface, a conventional 2D electron gas may be stabilized [281]. Metallic screening will confine this surface region to a few nm from the surface. In the opposite case, upward bending makes the surface
region more insulating, and the dielectric screening is much weaker, producing a depletion region on the scale of µm, as has been demonstrated by ionic liquid gating [324]. In the latter case, the acceptor band is depopulated by the surface dipole. Calculations suggest this is not the case [325], but there is substantial evidence for time-dependent band bending from ARPES [271]. Generally, this downward bending is found to produce a more metallic surface. With its exposure to air prior to the measurements, we assume that our sample’s surface is passivated and is metallic, typical of an “aged” surface, so we can safely neglect possible depth dependence to the carrier concentration at the implantation energies used. This is consistent with the absence of an appreciable implantation energy dependence in $\lambda_e$ at 2.20 T (see Figure 4.13).³

We have, so far, focused exclusively on the interaction between $^8\text{Li}$ and the electron spins. We should also consider its interaction with their orbital currents. Note that at 100 K $1/T_1$ in BTS is comparable to semimetallic bismuth [285], with a similar carrier density, but a much longer mean free path. In Bi, due to its strong orbital diamagnetism, we suggested that orbital fluctuations might be responsible for the fast relaxation of $^8\text{Li}$ and its concentration dependence in $\text{Bi}_x\text{Sb}_{1-x}$ solid solutions [285]. This mechanism is due to fluctuating electronic currents, so it is naturally related to the conductivity $\sigma$. Specifically [326]:

$$\left(\frac{1}{T_1}\right)_{\text{orb}} \propto k_B T \int \frac{\text{Re}\{\sigma_{\perp}(q, \omega_0)\}}{q^2} d^3q,$$

where $\sigma_{\perp}(q, \omega)$ is the generalized wavevector ($q$) and frequency dependent conductivity transverse to the nuclear spin. Clearly, this relaxation is enhanced by higher conductivity; however, in metals, it has long been recognized that orbital relaxation is usually much weaker than the spin-related Korringa relaxation discussed above.

For interstitial $^8\text{Li}^+$ in a layered conductor, the hyperfine coupling $A$ for interstitial $^8\text{Li}$ can be particularly weak (e.g., NbSe₂ [286]). In these circumstances, it is possible that orbital relaxation will dominate. Unlike the contact coupling $A$, orbital fields fall as $1/r^3$, where $r$ is the distance between the probe spin and the fluctuating current, so all nuclei in the material, and potentially

³We note that there is an apparent depth dependence in the diffusive contribution to $1/T_1$ in Figure 4.13. At lower $^8\text{Li}^+$ implantation energies, the $1/T_1$ peak appears larger, though its position remains unchanged. The precise origin for this is unclear. One possibility, however, is an enhancement in the number of structural defects close to the BTS surface, which could inflate the magnitude of the fluctuating field (i.e., the coupling term $c$ in Equation (4.1)). Note that the values of $c$ for the different data series in Figure 4.13 only differ by a factor of $\sim 2.5$ (see Table 4.2), implying the defect enhancement isn’t dramatic, consistent with the depth-independent electronic $1/T_1$. 96
**Figure 4.13:** Temperature dependence of the $^6$Li SLR rate $1/T_1$ in BTS at $B_0 = 2.20$ T || (001) for two implantation energies. The virtually identical relaxation rates below 150 K suggest the electronic contribution to $1/T_1$ is depth independent over the range of $^6$Li$^+$ implantation energies used here. However, the magnitude of the $1/T_1$ peaks are visibly depth dependent, though their positions remain unchanged. The origin for this remains unclear.

Even nuclei in close proximity, will sense spatially extended orbital fluctuations. For example, this mechanism has been studied as a proximal source of decoherence in spin based qubit devices [327]. Lee and Nagaosa have explicitly considered the case of orbital relaxation in a 2D layered metal [328]. They find a weak logarithmic singularity in $1/T_1$ in the clean limit that is cut off by a finite mean free path [329]. Similar to the Korringa rate, the orbital relaxation rate is linear in $T$ for a broad band metal. Recently, this approach was generalized to the case of massive Dirac-like electrons in 3D, appropriate to semimetallic Bi$_{1-x}$Sb$_x$ [326, 330]. They find $T$-linear relaxation when the chemical potential is outside the gap [326], but within the gap, an anomalous dependence that is explicitly field dependent via the NMR frequency $\omega_0$ as $\lambda_{\text{orb}} \propto T^3 \ln(2k_B T/\hbar \omega_0)$. While this is not what we find, it does suggest that if orbital relaxation is effective here, it may exhibit some unexpected field dependence in the inhomogeneous metallic state hypothesized for the tetradymites [331]. Similarly, the existence of orbital current
fluctuations implies additionally a fluctuating EFG. This gives rise to a quadrupolar contribution to the orbital relaxation mechanism, which has been treated in detail for 3D Dirac electron systems [326]. While it is unclear if the result applies directly to our situation, this quadrupolar contribution to $1/T_1$ was concluded to be negligible.

In fact, some features of our data do suggest the importance of orbital effects. One is the similarity of shifts of the quadrupolar split resonance and the unsplit Lorentzian. If, as seems to be reasonable, these resonances originate in different lattice sites of $^8\text{Li}^+$, then one would expect different hyperfine couplings and different (spin) shifts. If the shift is rather orbital in origin with significant contribution from long length-scale currents, one would expect the same shift for any site (and even any nucleus) in the unit cell. In general, however, one would expect both spin and orbital couplings, and nuclei of such different species, such as $^{209}\text{Bi}$ or $^8\text{Li}$, would likely differ.

We have ruled out a number of possibilities, but we do not have a conclusive explanation of the interesting features of the data at low temperatures. At this point, it is worth noting that conventional NMR in the tetradymite TIs are also characterized by highly variable power law $T$-dependent relaxation [276, 278, 332] whose dependence on magnetic field has largely not been explored.

4.5 Conclusion

Using temperature and field dependent ion-implanted $^8\text{Li} \beta$-NMR, we studied the high temperature ionic and low temperature electronic properties of BTS. Two distinct thermal regions were found; above $\sim 150 \text{ K}$, the isolated $^8\text{Li}^+$ probe undergoes ionic diffusion with an activation energy $E_A = 0.185(8) \text{ eV}$ and attempt frequency $\tau_0^{-1} = 8(3) \times 10^{11} \text{ s}^{-1}$ for atomic site-to-site hopping. A comparison of the kinetic details with other well-known Li$^+$ conductors suggests an exceptional mobility of the isolated ion. At lower temperature, field dependent relaxation and resonance shifts are observed. While the linearity in temperature of the SLR rate is reminiscent of a Korringa mechanism, existing theories are unable to account for the extent of the field dependence. We suggest that these may be related to a strong contribution from orbital currents or the magnetic freezeout of charge carriers in the heavily compensated semiconductor.
Field dependent conventional NMR of the stable host nuclei, combined with the present data, will further elucidate their origin.

4.6 Supplemental material

4.6.1 Implantation profiles

As mentioned in Section 4.2, $^8\text{Li}^+$ implantation profiles in BTS were predicted using the Stopping and Range of Ions in Matter (SRIM) Monte Carlo code [133]. At each implantation energy, stopping events were simulated for $10^5$ ions, with their resulting histogram representing the predicted implantation profile. From the profiles shown in Figure 4.14, we calculate, in the nomenclature of ion-implantation literature, the range and straggle (i.e., the mean and standard deviation) at each simulated energy. At the implantation energies used here (5 keV to 28 keV), the incident $^8\text{Li}^+$ ions typically stop on average $>30$ nm below the crystal surface, depths well below where the TSS is expected to be important.

4.6.2 Helicity-resolved resonance spectra

Typical helicity-resolved resonance spectra are shown in Figure 4.15, demonstrating the two key features in the line’s fine structure. A quadrupolar splitting on the order of several kHz, clearly evidenced by the asymmetric shape about the resonance centre-of-mass in each helicity, can be associated with the outermost satellite lines. Note that the satellite intensities are different from conventional NMR and are determined mainly by the high degree of initial polarization, which increases the relative amplitude of the outer satellites [127], with their precise (time-average) values depending on the relaxation details [147]. Secondly, another significantly smaller quadrupolar frequency can be ascribed to a “central” Lorentzian-like line, analogous to what was observed in the structurally similar NbSe$_2$ [286]. Note that there is no unshifted $m_{\pm1/2} \leftrightarrow m_{\mp1/2}$ magnetic sublevel transition, in contrast to spin $I = 3/2$ $^7\text{Li}$. The radio frequency (RF) amplitude dependence and the absence of other multiquantum lines indicate that it is also not a multiquantum transition. Instead it must originate from the overlap of the four unresolved satellites with a small quadrupole splitting [285]. Such a feature, in a noncubic...
**Figure 4.14:** Stopping distribution and range for $^8\text{Li}^+$ implanted in BTS calculated using the SRIM Monte Carlo code [133]. The histogram profiles, shown on the left, are generated from simulations of $10^5$ ions. The ion range and straggle at each implantation energy are shown on the right. All measurements in this study correspond to average stopping depths ≥30 nm below the crystal surface, well below where the TSS is expected to be important. Adapted from [274]. Copyright © 2019, American Physical Society.

layered crystal (see Figure 4.1 in Section 4.1), is suggestive that this component originates from $^8\text{Li}^+$ within the vdW gap, where the magnitude of EFGs at interstices are minimized. Resonances of the two helicities can be combined to give an overall average lineshape (see bottom panel in Figure 4.15), whose evolution with temperature is shown in Figure 4.7 from Section 4.3.3.

### 4.6.3 $^8\text{Li}^+$ sites

Here we consider the stopping sites in more detail. Generally, ion-implanted $^8\text{Li}^+$ occupies high-symmetry crystallographic sites that locally minimize its electrostatic potential. This may include metastable sites that are not the energetic minimum, but have a significant potential barrier to the nearest stable site. While these sites are characteristic of the isolated implanted ion, they may be related to the lattice location of Li$^+$ obtained by chemical intercalation.
Figure 4.15: Typical helicity-resolved $^8$Li resonance spectra in BTS with 6.55 T $\parallel$ (001), revealing the fine structure of the line. Four quadrupole satellites, split asymmetrically in each helicity about a “central” Lorentzian line are evident. Note that, in contrast to conventional NMR, the satellite amplitudes are determined primarily by the high degree of initial polarization [127]. The solid coloured lines are global fits to a sum of five Lorentzians with positions given by Equations (2.4) to (2.6) and (2.8) (see Section 4.3.3 for further details). Upon combining helicities, a nearly symmetric line about the resonance centre-of-mass, shown in the bottom panel, is obtained. Adapted from [274]. Copyright © 2019, American Physical Society.

BTS is structurally similar to the TMDs that consist of triatomic layers separated by a vdW gap between chalcogen planes. This spacious interstitial region accommodates many types of extrinsic atoms and small molecules in the form of intercalation compounds [333]. Similarly, a variety of dopants have been intercalated into the tetradymanite Bi chalcogenides, such as Cu [300], Ag [334], Au [335], and Zn [336]. Lithium has also been inserted into Bi chalcogenides [294, 295, 337, 338], but the precise sites for Li$^+$ in the vdW gap have not been determined [295]. Note that in all these cases, intercalation is at the level of atomic %, so that intercalated species certainly interact (e.g., forming “stage” compounds [333]).

Based on this, we expect the lowest energy site for implanted $^8$Li$^+$ is within the vdW gap, similar to NbSe$_2$ [286]. Here, the EFGs are likely minimized, yielding a small quadrupole
Figure 4.16: High-symmetry sites within the vdW gap of BTS, shown as coloured circles, in a plane perpendicular to the trigonal $c$-axis. The Wyckoff position is indicated for each site and the boundary of the unit cell is marked by solid black lines. Neighbouring $3b$ (blue) sites, enclosed by Te quasi-octahedra, are connected indirectly through $6c$ (green) sites with quasi-tetrahedral Te coordination, and directly through $9d$ (pink) sites of lower symmetry. The structure was drawn using VESTA [273]. Adapted from [274]. Copyright © 2019, American Physical Society.

frequency, consistent with the unsplit component of the resonance in Figure 4.15. Within the vdW gap, several high-symmetry Wyckoff sites are available (see Figure 4.16): the quasi-octahedral $3b$ at $(0, 0, 1/2)$; the quasi-tetrahedral $6c$ at $(0, 0, 1/6)$; and the 2-fold coordinated $9d$ at $(1/2, 0, 1/2)$. Here, the fractional coordinates correspond to the hexagonal unit cell in Figure 4.1 from Section 4.1. Neighbouring $3b$ sites are connected by direct paths through the $9d$ sites and indirect paths (i.e., dog-leg trajectories) passing through $6c$ sites. The $3b$ site offers by far the largest coordination volume for interstitial $^8\text{Li}^+$ and it is reasonable that this is the preferred site in the vdW gap. Indeed, preliminary density functional theory calculations confirm this assignment.

As indicated in Section 4.3.3, the low temperature resonances suggest a nearly 1:1 relative occupation of two sites with different EFGs. Noting that, in contrast to the trilayers in TMDs, the QLs in BTS account a much larger volume fraction of the crystal, which leads us to consider possible interstitial sites therein. While interstitial sites within the QL will be characterized by
lower-symmetry and much larger EFGs, the most likely sites retain the trigonal rotation axis (e.g., 6c at (0, 0, 1/3)). A simple point-charge model of isolated $^8\text{Li}^+$ in the BTS lattice, using ionic charges of +0.3 for Bi and −0.2 for Se/Te (1/10 their nominal values), gives $\nu_q$ for these sites that are within a factor $\sim 3$ of the values for the 3b site in the vdw gap ($\sim 2$ kHz), consistent with the difference required to explain the experimental spectra. Note that, while the point charge model predicts nearly identical $|\nu_q|$ for all sites in the vdw gap, sites on the edges of the hexagons in Figure 4.16 have the opposite sign.

From the helicity-resolved resonances, the sign of the EFG does not change with temperature and, based on the $T$-independent $\nu_q$ and satellite amplitudes, we suggest that this component corresponds to a fraction of implanted $^8\text{Li}^+$ that stops at a site within the QL, where it remains static over its lifetime. Similarly, we ascribe the unsplit line to $^8\text{Li}^+$ stopped in the vdw gap, likely in the 3b site. This component, in contrast, is dynamic above 100 K, accounting for the growth in resonance amplitude and the $1/T_1$ maxima, which we consider in more detail in Section 4.4.1. Note that we find no evidence for a site change transition up to 317 K, indicating a substantial energy barrier separates the two sites.
Chapter 5

Local ionic, electronic, and magnetic properties of the doped topological insulators Bi$_2$Se$_3$:Ca and Bi$_2$Te$_3$:Mn

5.1 Introduction

The bismuth chalcogenides Bi$_2$Ch$_3$ (Ch = S, Se, or Te) of the layered tetradymite structure are an interesting class of highly two dimensional narrow bandgap semiconductors. Strong spin-orbit coupling inverts the energy ordering of their bands, making them bulk topological insulators (TIs) characterized by a single Dirac cone at the Brillouin zone centre and a topologically protected metallic surface state [259, 339]. This has augmented longstanding interest in their thermoelectric properties with significant efforts (theoretical and experimental) to understand their electronic properties in detail [254, 255]. Consisting of weakly interacting Ch–Bi–Ch–Bi–Ch atomic quintuple layers (QLs) (see e.g., Figure 4.1), they can also accommodate intercalant species such as Li$^+$ in the van der Waals (vdW) gap between QLs [294, 295, 340], similar to the layered transition metal dichalcogenides (TMDs) [341, 342]. Although their bandgaps are $\sim$150 meV, doping by intrinsic defects, such as Ch vacancies, yields crystals that are far from insulating. To increase the contrast in conductivity between the bulk and the metallic topological surface state (TSS), they can be compensated extrinsically. For example, Ca substitution for Bi suppresses the self-doped $n$-type conductivity in Bi$_2$Se$_3$ [258, 259]. Doping can also be used to
modulate their magnetic properties, yielding magnetic TIs where the TSS is gapped [343], for example, by substitution of Bi with a paramagnetic transition metal [344, 345].

The intriguing electronic properties of the tetradyminate TIs have predominantly been investigated using surface sensitive probes in real and reciprocal space (e.g., scanning tunnelling spectroscopy (STS) and angle-resolved photoemission spectroscopy (ARPES)), as well as other bulk methods. In complement to these studies, nuclear magnetic resonance (NMR) offers the ability to probe their electronic ground state and low-energy excitations through the hyperfine coupling of the nuclear spin probe to the surrounding electrons. Such a local probe is especially useful when disorder masks sharp reciprocal space features, as is the case in Bi$_2$Ch$_3$. The availability of a useful NMR nucleus, however, is usually determined by elemental composition and natural (or enriched) isotopic abundance, as well as the specific nuclear properties such as the gyromagnetic ratio $\gamma$ and, for spin $> 1/2$, the nuclear electric quadrupole moment $Q$. While the Bi$_2$Ch$_3$ family naturally contain several NMR nuclei [276, 279, 291], they are either low-abundance or have a large $Q$. As an alternative, here we use an ion-implanted NMR probe at ultratrace concentrations, with detection based on the asymmetric property of radioactive $\beta$-decay [5].

Using $\beta$-detected nuclear magnetic resonance ($\beta$-NMR), we study two single crystals of doped Bi$_2$Ch$_3$ — compensated Bi$_2$Se$_3$:Ca (BSC) and magnetic Bi$_2$Te$_3$:Mn (BTM) — each with a beam of highly polarized $^8$Li$^+$. In many respects, $\beta$-NMR is closely related to muon spin rotation/relaxation/resonance ($\mu$SR), but the radioactive lifetime is much longer, making the frequency range of dynamics it is sensitive to more comparable to conventional NMR. In addition to purely electronic phenomena, in solids containing mobile species, NMR is also well known for its sensitivity to low frequency diffusive fluctuations [34, 36, 346], as are often encountered in intercalation compounds. At ion-implantation energies sufficient to probe the bulk of BSC and BTM, we find evidence for ionic mobility of $^8$Li$^+$ above $\sim$200 K, likely due to two-dimensional (2D) diffusion in the vdW gap. At low temperature, we find Korringa relaxation and a small temperature dependent negative Knight shift in BSC, allowing a detailed comparison with $^8$Li in the structurally similar Bi$_2$Te$_2$Se (BTS) [274]. In BTM, the effects of the Mn moments predominate, but remarkably the signal can be followed through the magnetic transition. At low temperature, we find a prominent critical peak in the relaxation that is suppressed in
a high applied field, and a broad, intense resonance that is strongly shifted. This detailed characterization of the $^8\text{Li}$ NMR response is an important step towards using depth-resolved $\beta$-NMR to study the low-energy properties of the chiral TSS.

5.2 Experiment

Doped TI single crystals BSC and BTM with nominal stoichiometries Bi$_{1.99}$Ca$_{0.01}$Se$_3$ and Bi$_{1.9}$Mn$_{0.1}$Te$_3$ were grown as described in Refs. [258, 344] and magnetically characterized using a Quantum Design magnetic property measurement system (MPMS). In the BTM, a ferromagnetic transition was identified at $T_C \approx 13 \text{ K}$, consistent with similar Mn concentrations [344, 347–349]. In contrast, the susceptibility of the BSC crystal was too weak to measure accurately, but the data show no evidence for a Curie tail at low-$T$ that could originate from dilute paramagnetic defects.

$\beta$-NMR experiments were performed at TRIUMF’s Isotope Separator and ACcelerator (ISAC) facility in Vancouver, Canada. Detailed accounts of the technique can be found in Refs. [5, 274]. A low-energy highly polarized beam of $^8\text{Li}^+$ was implanted into the samples mounted in one of two dedicated spectrometers [5, 122]. Prior to mounting, the crystals were cleaved in air and affixed to sapphire plates using Ag paint (SPI Supplies, West Chester, PA). The approximate crystal dimensions were 7.8 mm $\times$ 2.5 mm $\times$ 0.5 mm (BSC) and 5.3 mm $\times$ 4.8 mm $\times$ 0.5 mm (BTM). With the crystals attached, the plates were then clamped to an aluminum holder threaded into an ultra-high vacuum (UHV) helium coldfinger cryostat. The incident $^8\text{Li}^+$ ion beam had a typical flux of $\sim 10^6$ ions/s over a beam spot $\sim 2$ mm in diameter. At the implantation energies $E$ used here (between 1 keV to 25 keV), $^8\text{Li}^+$ stopping profiles were simulated for $10^5$ ions using the Stopping and Range of Ions in Matter (SRIM) Monte Carlo code (see Section 5.6.1) [133]. For $E > 1$ keV, a negligible fraction of the $^8\text{Li}^+$ stop near enough to the crystal surface to sense the TSS. Most of the data is taken at 20 keV, where the implantation depth is $\sim 100$ nm, and the results thus reflect the bulk behaviour. A typical spin-lattice relaxation (SLR) measurement took $\sim 20$ min. A single resonance spectrum typically took $\sim 30$ min to acquire.
Figure 5.1: Typical $^8$Li SLR data in Ca doped Bi$_2$Se$_3$ at high (left) and low (right) magnetic field with $^8$Li$^+$ implanted at 20 keV. The shaded region indicates the duration of the $^8$Li$^+$ beam pulse. The relaxation is strongly field dependent, increasing at lower fields, and it increases non-monotonically with increasing temperature. The solid black lines show fits to a stretched exponential described in the text. The initial asymmetry $A_0$ from the fits is used to normalize the data which are binned by a factor of 20 for clarity.

5.3 Results and analysis

5.3.1 Bi$_2$Se$_3$:Ca

Typical $^8$Li SLR data in BSC, at both high and low magnetic field, are shown in Figure 5.1. To aid comparison, $A(t)$ has been normalized by its initial value $A_0$ determined from fits described below. Clearly, the SLR is strongly temperature and field dependent. At low field, the SLR is very much faster, due to additional relaxation from fluctuations of the host lattice nuclear spins [139]. The temperature dependence of the relaxation is non-monotonic, indicating that some of the low frequency fluctuations at $\omega_0$ are frozen out at low temperature.

The relaxation is non-exponential at all temperatures and fields, so the data were fit with the phenomenological stretched exponential. This approach was also used for $^8$Li in BTS [274] and
in conventional NMR of related materials [276, 279, 291]. Explicitly, for a $^8$Li$^+$ implanted at time $t'$, the spin polarization at time $t > t'$ follows Equation (2.13). This is the simplest model that fits the data well with the minimal number of free parameters, for the entire Bi$_2$Ch$_3$ tetradyminite family of TIs.

Using Equation (2.13) convolved with the beam pulse, the SLR data in BSC, grouped by magnetic field $B_0$ and implantation energy $E$, were fit simultaneously with a shared common initial asymmetry $A_0(B_0, E)$. Note that the statistical uncertainties in the data are strongly time-dependent (see e.g., Figure 5.1), which must be accounted for in the analysis. Using custom C++ code incorporating the MINUIT minimization routines [176] implemented within the ROOT data analysis framework [175], we find the global least-squares fit for each dataset. The fit quality is good ($\chi^2_{\text{global}} \approx 1.02$) and a subset of the results are shown in Figure 5.1 as solid black lines. The large values of $A_0$ extracted from the fits ($\sim 10\%$ for $B_0 = 6.55$ T and $\sim 15\%$ for $B_0 = 15$ mT) are consistent with the full beam polarization, with no missing fraction. The fit parameters are plotted in Figure 5.2, showing agreement with the qualitative observations above.

We now consider a model for the temperature and field dependence of $1/T_1$. We interpret the local maxima in $1/T_1$ in Figure 5.2 as Bloembergen-Purcell-Pound (BPP) peaks [34], caused by a fluctuating field coupled to the $^8$Li nuclear spin with a characteristic rate that sweeps through $\omega_0$ at the peak temperature [34, 35, 225]. Potential sources of the fluctuations are discussed below. The rate peaks are superposed on a smooth background that is approximately linear, reminiscent of Korringa relaxation in metals [7, 42]. This is surprising, since BSC is a semiconductor, but it is similar to BTS [274]. We discuss this point further in Section 5.4.2.

From this, we adopt the following model for the total SLR rate:

$$1/T_1 = a + bT + \sum_i c_i \left(J_{1,i} + 4J_{2,i}\right).$$

In Equation (5.1), the first two terms account for the $T$-linear contribution with a finite intercept $a$, while the remaining terms describe the $i$th $1/T_1$ peak in terms of a coupling constant $c_i$ (proportional to the mean-squared transverse fluctuating field) and the $n$-quantum NMR spectral density functions $J_{n,i}$ [225]. In general, $J_{n,i}$ is frequency dependent and peaked at a temperature where the fluctuation rate matches $\sim n\omega_0$. While the precise form of $J_{n,i}$ is not known a priori,
Figure 5.2: Temperature and field dependence of the $^8\text{Li}$ SLR rate $1/T_1$ and stretching exponent $\beta$ in Ca doped Bi$_2$Se$_3$. $\beta$ is nearly independent of temperature and field at $\sim 0.6$ (dotted line), except at low field around the large $1/T_1$ peak seen in the bottom panel. The solid and dashed black lines are global fits to Equation (5.1), consisting of a linear $T$-dependence with a non-zero intercept and two SLR rate peaks, labelled with index $i$. Independent of the choice of $J_n$ used in the analysis, the model captures all the main features of the data.

The simplest expression, obtained for isotropic three-dimensional (3D) fluctuations, has a Debye (Lorentzian) form of Equation (1.14) [34, 225]. Alternatively, when the fluctuations are 2D in character, as might be anticipated for such a layered crystal, $J_n$ may be described by the empirical expression in Equation (1.15) [35, 52]. For both Equations (1.14) and (1.15), we assume that $\tau_c$ is thermally activated, following an Arrhenius dependence analogous to Equation (1.3). If the fluctuations are due to $^8\text{Li}^+$ hopping, $\tau_c^{-1}$ is the site-to-site hop rate $\tau^{-1}$.

Using the above expressions, we fit the $1/T_1$ data using a global procedure wherein the kinetic parameters (i.e., $E_{A,i}$ and $\tau_0^{-1,i}$) are shared at all the different $\omega_0$. This was necessary to fit the data.
Table 5.1: Arrhenius parameters in Equation (1.3) obtained from the analysis of the temperature dependence of $1/T_1$ in Ca doped Bi$_2$Se$_3$ shown in Figure 5.2. The two processes giving rise to the rate peaks are labelled with index $i$. Good agreement is found between the $E_A$s determined using the spectral density functions $J_n$ for 2D and 3D fluctuations [Equations (1.14) and (1.15)].

<table>
<thead>
<tr>
<th>$J_n$</th>
<th>$\tau_0^{-1} \times 10^{10}$ s$^{-1}$</th>
<th>$i = 1$</th>
<th>$E_A$ (eV)</th>
<th>$\tau_0^{-1} \times 10^{14}$ s$^{-1}$</th>
<th>$i = 2$</th>
<th>$E_A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D</td>
<td>8.4(27)</td>
<td>0.113(5)</td>
<td>7(5)</td>
<td>0.395(15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2D</td>
<td>9(3)</td>
<td>0.106(5)</td>
<td>110(90)</td>
<td>0.430(16)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

at 6.55 T where the relaxation is very slow. For comparison, we applied this procedure using both $J_n^{3D}$ and $J_n^{2D}$ and the fit results are shown in Figure 5.2 as solid ($J_n^{3D}$) and dashed ($J_n^{2D}$) lines, clearly capturing the main features of the data. The analysis distinguishes two processes, $i = 1, 2$ in Equation (5.1): one ($i = 1$) that onsets at lower temperature with a shallow Arrhenius slope of $\sim 0.1$ eV that yields the weaker peaks in $1/T_1$ at both fields; and a higher barrier process ($i = 2$) with an $E_A$ of $\sim 0.4$ eV that yields the more prominent peak in the low field relaxation, while the corresponding high field peak must lie above the accessible temperature range. The resulting fit parameters are given in Table 5.1. We discuss the results in Section 5.4.1.

We now turn to the $^8$Li resonances, with typical spectra shown in Figure 5.3. As anticipated in a non-cubic crystal, the spectrum is quadrupole split, confirmed unambiguously by the helicity-resolved spectra, which show opposite satellites in opposite helicities of polarization (see Section 5.6.2). This splitting, on the order of a few kHz, is determined by the electric field gradient (EFG) and is a signature of the crystallographic $^8$Li site. Besides this, an unsplit component is also apparent, very close to (within $\sim 100$ Hz) the centre-of-mass of the four satellites. At low temperature, the “central” and split components are nearly equal, but as the temperature is raised, the unsplit line grows to dominate the spectrum, accompanied by a slight narrowing.

The scale of the quadrupole splitting is determined by the product of the principal component of the EFG tensor $e_Q$ with the nuclear electric quadrupole moment $e_Q$. We quantify this with a conventional definition of the quadrupole frequency (for $I = 2$), given in Equation (2.4) [60]. In high field, a first order perturbation treatment of the quadrupole interaction, given by Equations (2.5), (2.6) and (2.8), is sufficient to obtain accurate satellite positions. However, at low field, where $v_q/v_0 \approx 6\%$, second order is necessary, defined in Equations (2.7), (2.9) and (2.10) [60, 143]. Based on the change in satellite splittings by a factor 2 in going from $B_0 \parallel c$ to $B_0 \perp c$, we
Figure 5.3: $^8$Li resonance spectra in BSC at low magnetic field. The vertical scale is the same for all spectra; they have been normalized to account for changes in intensity due to SLR [147], with their baselines (shown as dashed grey lines) shifted to match the temperature. The spectra consist of a small and nearly temperature-independent quadrupole split pattern, centred about an unsplit Lorentzian line, whose amplitude grows above $\sim 150$ K. Note the quadrupole pattern of an integer spin nucleus like $^8$Li, has no central satellite (main line). The solid black lines are fits to a sum of this Lorentzian and $2I = 4$ quadrupole satellites (see text).

assume the asymmetry parameter of the EFG $\eta = 0$ (i.e., the EFG is axially symmetric). This is reasonable based on likely interstitial sites for $^8$Li$^+$ (see Section 4.6.3) [274]. Pairs of helicity-resolved spectra were fit with $\nu_0$ and $\nu_q$ as shared free parameters, in addition to linewidths and amplitudes. As the difference between the frequency of the unsplit line and the center of the quadrupole split pattern was too small to measure accurately, the fits were additionally constrained to have the same central frequency $\nu_0$. This is identical to the approach used for BTS (see Section 4.3.3) [274]. A subset of the results (after recombining the two helicities) are shown in Figure 5.3 as solid black lines.
Figure 5.4: The resonance amplitude as a function of temperature in Ca doped Bi$_2$Se$_3$ at 15 mT. While the amplitude of the satellite lines are nearly temperature independent, the central component increases substantially above 150 K, plateauing on the high-$T$ side of the $1/T_1$ maximum (grey band). The solid line is a guide, while the dashed line indicates the estimated saturation value for the Lorentzian component.

The main result is the strong temperature dependence of the resonance amplitude shown in Figure 5.4. While the satellite amplitudes are nearly temperature independent, the central component increases substantially above 150 K, tending to plateau above the $1/T_1$ peak. The other parameters are quite insensitive to temperature. Typical linewidths (i.e., full width at half maximum) are $\sim$2.2 kHz for the satellites and $\sim$3.8 kHz for the central component. The quadrupole frequency $\nu_q \approx 5.5$ kHz varies weakly, increasing slightly as temperature is lowered.

We also measured resonances at room and base temperature in high field (6.55 T) where $^8$Li is sensitive to small magnetic shifts. From the fits, we use $\nu_0$ to calculate the raw relative frequency shift $\delta$ in parts per million (ppm) using Equation (2.11). The shifts are small: $+12(2)$ ppm at room temperature and $-17(3)$ ppm at 5 K, the latter considerably smaller in magnitude than in BTS [274]. Because $^8$Li NMR shifts are generally so small, it is essential to account for the demagnetization field of the sample itself. From $\delta$, the corrected shift $K$ is obtained by the
centimetre-gram-second system of units (CGS) expression [151]:

\[ K = \delta + 4\pi \left( N - \frac{1}{3} \right) \chi_v \]  

(5.2)

where \( N \) is the dimensionless demagnetization factor that depends only on the shape of the sample and \( \chi_v \) is the dimensionless (volume) susceptibility. For a thin film, \( N = 1 \) [151], but for the thin platelet crystals used here, we estimate \( N \) is on the order of \( \sim 0.8 \), treating them as oblate ellipsoids [350]. For the susceptibility, we take the average of literature values reported for pure \( \text{Bi}_2\text{Se}_3 \) [351–354], giving \( \chi_v^{\text{CGS}} \approx -2.4 \times 10^{-6} \text{ emu cm}^{-3} \). Note that we have excluded several reports [278, 355, 356] whose results disagree by an order of magnitude from those predicted by Pascal’s constants [357]. Applying the correction for BSC yields \( K \)s of \( -2(2) \text{ ppm} \) and \( -31(3) \text{ ppm} \) at room and base temperature, respectively. We discuss this below in Section 5.4.2.

5.3.2 Bi\(_2\)Te\(_3\):Mn

Typical \(^8\)Li SLR data at high and low field in the magnetically doped BTM are shown in Figure 5.5. In contrast to nonmagnetic BSC, the relaxation at high field is fast, typical of paramagnets with unpaired electron spins [154, 358, 359]. The fast high field rate produces a much less pronounced field dependence. At low field, the SLR rate is peaked at low temperature. The relaxation is also non-exponential and fits well using Equation (2.13), with a stretching exponent systematically smaller than in the nonmagnetic BSC or BTS [274]. We analyzed the data with the same global approach, obtaining good quality fits \( (\chi^2_{\text{global}} \approx 1.01) \) demonstrated by the solid black lines in Figure 5.5. The shared values of \( A_0 \) from the fits are large (\( \sim 10\% \) for \( B_0 = 6.55 \text{ T} \) and \( \sim 15\% \) for \( B_0 = 20 \text{ mT} \)), consistent with the full beam polarization, implying that there is remarkably no magnetic wipeout from very fast relaxation [154], even at low field.

The fit parameters are shown in Figure 5.6. At all temperatures, especially at high field, the SLR rate \( 1/T_1 \) is orders of magnitude larger than in the nonmagnetic analogs. No clear \( 1/T_1 \) BPP peaks can be identified between 100–300 K; however, in the low field data, a critical divergence is evident at the magnetometric transition at about 13 K. In high field, this feature is largely washed out, with a remnant peak near 50 K. Above 200 K, the SLR rate increases very rapidly and is well-described by \( 1/T_1 \propto \exp[-E_A/(k_B T)] \), with \( E_A \approx 0.2 \text{ eV} \) at both fields. We discuss
**Figure 5.5:** Typical $^8$Li SLR data in Mn doped Bi$_2$Te$_3$ at high (left) and low (right) magnetic field for $^8$Li$^+$ implantation energies of 20 keV and 8 keV, respectively. The shaded region denotes the duration of the $^8$Li$^+$ beam pulse. The SLR is substantial and orders of magnitude faster than in BSC (see Figure 5.1) at high field. The field dependence to the SLR is much weaker than in the nonmagnetic tetradymites. The solid black lines are fits to a stretched exponential convolved with the $^8$Li$^+$ beam pulse as described in the text. The initial asymmetry $A_0$ from the fit is used to normalize the spectra. The high and low field spectra have been binned for by factors of 20 and 5.

In contrast to BSC and BTS [274], the resonance in BTM consists of a single broad Lorentzian with none of the resolved fine structure (see Figure 5.7). Surprisingly, the very broad line has significant intensity, dwarfing the quadrupole pattern in BSC in both width and amplitude. In addition, there is a large negative shift at base temperature. At room temperature, the line is somewhat narrower, and the shift is reduced in magnitude. Quantitative results from Lorentzian fits are summarized in Table 5.2.
Figure 5.6: Temperature dependence of the $^8\text{Li}$ SLR rate $1/T_1$ in Mn doped Bi$_2$Te$_3$ at high and low field. At low field, $1/T_1$ shows a critical peak at the ferromagnetic transition at $T_C \approx 13 \text{ K}$, as the Mn spin fluctuations freeze out. Above 200 K, the SLR rate increases exponentially in manner nearly independent of applied field. The solid grey lines are drawn to guide the eye.

Table 5.2: Results from the analysis of the $^8\text{Li}$ resonance in BTM at high and low temperature with $B_0 = 6.55 \text{ T} \parallel (001)$. The (bulk) magnetization $M$ measured with 1.0 T $\parallel (001)$ is included for comparison.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\bar{A}$ (%)</th>
<th>FWHM (kHz)</th>
<th>$\delta$ (ppm)</th>
<th>$M$ (emu cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>294</td>
<td>33(5)</td>
<td>16.2(12)</td>
<td>+10(9)</td>
<td>0.076</td>
</tr>
<tr>
<td>10</td>
<td>14.4(8)</td>
<td>41.7(16)</td>
<td>−206(12)</td>
<td>7.698</td>
</tr>
</tbody>
</table>

5.4 Discussion

The $^8\text{Li}$ NMR properties of nonmagnetic BSC are quite similar to previous measurements in BTS [274]. The resonance spectra show a similar splitting ($v_q$ is about 25% smaller in BSC), indicating a similar site for $^8\text{Li}$. The resemblance of the spectra extends to the detailed temperature dependence, including the growth of the unsplit line approaching room temperature. Surprisingly, the BSC spectra are better resolved than BTS, implying a higher degree of order,
Figure 5.7: Typical $^8$Li resonances in Mn doped Bi$_2$Te$_3$ and Ca doped Bi$_2$Se$_3$ at high magnetic field. The vertical scale is the same for all spectra; they have been normalized to account for changes in intensity and baseline [147]. The lineshape in the magnetic BTM is well-described by a broad Lorentzian (solid black line) with no quadrupolar splitting. A large negative shift is also apparent for BTM with respect to the reference frequency in MgO (vertical dashed line). The dotted vertical line indicates the expected resonance position due to demagnetization, revealing a large positive hyperfine field (∼38 G) at 5 K in the magnetic state.

Despite the Ca doping. This is also evident in the SLR, with a stretching exponent $β$ closer to unity in BSC than in BTS. This likely reflects additional disorder in BTS from Bi/Te anti-site defects [262] that are much more prevalent than for Bi/Se, due to the difference in radii and electronegativity. The sharp quadrupolar pattern indicates a well-defined crystallographic $^8$Li$^+$ site, and the corresponding small EFG suggests it is in the vdW gap. Density functional theory (DFT) calculations of the EFG may enable a precise site assignment. The high field SLR is also similar to BTS: it is slow and near the lower limit measurable due to the finite $^8$Li lifetime $τ_β$ and comparable to the vdW metal NbSe$_2$ [286], where the carrier concentration is much higher, but significantly slower than the TI alloy Bi$_{1-x}$Sb$_x$ [285]. The low field enhancement of $1/T_1$ is also similar, so it cannot be essentially related to the dilute $^{125}$Te moments that are absent in BSC, but probably determined primarily by the 100% abundant $^{209}$Bi. From such a detailed similarity, it is clear that a quantitative comparison with BTS and other vdW materials will be useful.
With these similarities in mind, the rest of the discussion is organized as follows: in Section 5.4.1, we consider evidence of mobility of the $^{8}$Li$^{+}$ ion; in Section 5.4.2, electronic effects at low temperature in BSC; and the magnetic properties of BTM in Section 5.4.3.

### 5.4.1 Dynamics of the Li$^{+}$ ion

In BTS, we considered if the evolution of the spectrum with temperature (similar to Figure 5.3) was the result of a site change transition from a meta-stable quadrupolar $^{8}$Li$^{+}$ site to a lower energy site with very small EFG at higher temperature [274], similar to elemental Nb [360]. We now consider an alternative explanation; namely, dynamic averaging of the quadrupolar interaction due to $^{8}$Li$^{+}$ motion. Examples of this are found in conventional $^{7}$Li NMR, where, unlike $^{8}$Li, the $I = 3/2$ quadrupole spectrum has a main line (the $m = \pm 1/2$ satellite) overlapping the averaged resonance [361, 362]. Dynamic averaging is suggested by the onset near, but below, the SLR rate peak (see Figure 5.4). However, for hopping between equivalent interstitial sites (probably the quasi-octahedral Wyckoff 3$b$ site in the vdW gap), one does not expect that the EFG will average to a value near zero (required to explain the unsplit line). A point charge estimate reveals the quasi-tetrahedral (Wyckoff 6$c$) site, thought to be the saddle point in the potential for Li$^{+}$ between adjacent 3$b$ sites [363], has an EFG of opposite sign to the 3$b$ site. If 6$c$ is instead a shallow minimum, the $^{8}$Li$^{+}$ residence time there may be long enough that the EFG averages to near zero. In the fast motion limit at higher temperatures, one would then expect the quadrupole splitting to re-emerge when the residence time in the 6$c$ “transition” site becomes much shorter [362].

We now examine the two kinetic processes causing the $1/T_1$ peaks in BSC. It is surprising to find two distinct thermally activated processes sweeping through the NMR frequency, especially since only a single process was found in BTS [274]. First, we consider the weaker feature, the low temperature ($i = 1$) peaks. In layered materials, small intercalates can undergo highly localized motion at relatively low temperatures below the onset of free diffusion [36, 346]. Such local motion may be the source of the SLR rate peak, but it is quite ineffective at narrowing the resonance, consistent with the absence of any lineshape changes in the vicinity of the $i = 1$ peaks. Caged local motion is usually characterized by a small activation barrier, comparable
to the ∼0.1 eV observed here. Similar phenomena have been observed at low temperature, for example, in neutron activated $^8\text{Li} \beta$-NMR of Li intercalated graphite, LiC$_{12}$ [77, 79]. It is not clear why such motion would be absent in BTS [274], which has a larger vdW gap than BSC (2.698 Å vs. 2.568 Å). Alternatively, this feature in the relaxation may have an electronic origin, perhaps related to the emergent low-$T$ magnetism in MoTe$_2$ observed by μSR [364] and $^8\text{Li} \beta$-NMR [365].

In contrast, the SLR rate peak above 200 K ($i = 2$) is almost certainly due to EFG fluctuations caused by stochastic $^8\text{Li}^+$ motion. From the data, we cannot conclude that this is long-range diffusion, but the room temperature Li$^+$ intercalability of Bi$_2$Se$_3$ [294, 295, 340] suggests it is. Its barrier, on the order of ∼0.4 eV, is comparable to other vdW gap layered ion conductors, but it is about twice as high as in BTS [274], possibly a result of the Se (rather than Te) bounded vdW gap, which provides less space between neighbouring QLs.

We now consider the Arrhenius law prefactors $\tau_0^{-1}$, that, for ionic diffusion, are typically in the range $10^{12}$–$10^{14}$ s$^{-1}$. For the low-$T$ process ($i = 1$), independent of the form of $J_n$ (see Table 5.1), $\tau_0^{-1} \approx 9 \times 10^{10}$ s$^{-1}$ is unusually low. In contrast, for the high-$T$ ($i = 2$) process, it is much larger and depends strongly on $J_n$. For 3D diffusion, it is in the expected range, while the 2D model yields an extremely large value, $\sim10^{16}$ s$^{-1}$, in the realm of prefactor anomalies [32] and opposite to the small value expected for low dimensional diffusion [50]. Similar behaviour was observed recently in $^7\text{Li}$ NMR of LiC$_6$ [88], where surprisingly, $J_n^{2D}$ was concluded to be less appropriate than $J_n^{3D}$, suggesting that Li motion in the vdW gap is not as ideally 2D as might be expected. In BSC, the anomaly may be related to local dynamics that onset at lower $T$, imparting some 3D character to the motion.

Given the evidence for Li$^+$ motion in BSC and BTS [274], the absence of a relaxation peak in BTM may seem unexpected. Both Ca$^{2+}$ and Mn$^{2+}$ dopants (substitutional for Bi$^{3+}$) have an effective $-1$ charge yielding an attractive trapping potential for the positive interstitial $^8\text{Li}^+$, but the Mn concentration is an order of magnitude larger. The high trap density in BTM will suppress Li$^+$ mobility. The exponential increase in $1/T_1$ above 200 K may be the onset of a diffusive BPP peak, but, in this case, one does not expect it to be so similar between the two very different magnetic fields. This may reflect a trade-off between the increase in $\omega_0$ that shifts the peak to higher temperature, slowing the relaxation on its low-$T$ flank, and the increased polarization of the Mn moments by the field that amplifies local magnetic inhomogeneities. A motional
origin for this increase is consistent with the apparent $E_A \sim 0.2$ eV, similar to $^8$Li$^+$ in BTS [274], which also has a Te bounded vdW gap of similar size to BTM (2.620 Å). However, it may have a different explanation, see below in Section 5.4.3.

5.4.2 Electronic effects at low temperature

Bismuth chalcogenide (Bi$_2$Ch$_3$) crystals exhibit substantial bulk conductivity, despite a narrow gap in the 3D band structure, making it difficult to distinguish effects of the metallic TSS. This is due to native defects (e.g., Ch vacancies) that are difficult or impossible to avoid [254]. Extrinsic dopants, such as substitutional Ca/Bi, can be used to compensate the spontaneous $n$-type doping. Brahlek et al. have argued [308] that, even for the most insulating compensated samples, the carrier densities far exceed the Mott criterion, making them heavily doped semiconductors in the metallic regime. In this case, we expect metallic NMR characteristics [366], namely a magnetic Knight shift $K$, proportional to the carrier spin susceptibility $\chi_s$. In the simplest (isotropic) case,

$$K = A\chi_s,$$

where $A$ is the hyperfine coupling constant, which is accompanied by a SLR rate following the Korringa law [7, 42],

$$\frac{1}{T_1} = 4\pi\hbar A^2\gamma_n^2 \left( \frac{\chi_s}{g^*\mu_B} \right)^2 k_B T.$$  (5.4)

Here, $\gamma_n$ is the nuclear gyromagnetic ratio, $g^*$ is the carrier $g$-factor, and $\mu_B$ is the Bohr magneton. Combining Equations (5.3) and (5.4), we obtain the Korringa product, which is independent of the value of $A$,

$$T_1TK^2 = \frac{\hbar(g^*\mu_B)^2}{4\pi k_B\gamma_n} = S(g^*).$$  (5.5)

For $^8$Li,

$$S(g^*) \approx 1.20 \times 10^{-5} \left( \frac{g^*}{g_0} \right)^2 \text{ s K},$$

where, unlike in metals, we have allowed for an effective $g$-factor that may be far from its free electron value $g_0 \approx 2$ [367]. Indeed, recent electron paramagnetic resonance (EPR) measurements in Bi$_2$Se$_3$ find $g^* \approx 30$ [368].
According to Ref. [308], BTS and BSC lie on opposite sides of the Ioffe-Regel limit, where the carrier mean free path is equal to its Fermi wavelength, with BSC having a higher carrier density and mobility. A comparative Korringa analysis could test this assertion and, to this end, using Equation (5.5) we define the dimensionless Korringa ratio as

\[ \mathcal{K} = \frac{T_1 T K^2}{S(g^*)} \]  

(5.6)

Below the Ioffe-Regel limit, the autocorrelation function of the local hyperfine field at the nucleus, due to the carriers (that determines \( T_1 \)) becomes limited by the diffusive transport correlation time. This has been shown to enhance the Korringa rate (i.e., shortening \( T_1 \)) [313, 314]. From this, one expects \( \mathcal{K} \) would be smaller in BTS than in BSC.

There are, however, significant difficulties in determining the experimental \( \mathcal{K} \). First, the Korringa slope depends on magnetic field. At low fields, this is due to coupling with the host nuclear spins, a phenomenon that is quenched in high fields where the \(^8\text{Li} \) NMR has no spectral overlap with the NMR of host nuclei. For example, in simple metals, we find the expected field-independent Korringa slope at high fields in the Tesla range [5]. In contrast, in BTS, the slope decreases substantially with increasing field, even at high fields [274]. We suggested this could be the result of magnetic carrier freeze-out. While we do not have comparably extensive data in BSC, we can compare the slope at the same field, 6.55 T (see Table 5.3). Here, in both materials, the relaxation is extremely slow, exhibiting no curvature in the SLR during the \(^8\text{Li} \) lifetime (Figure 5.1), so the uncertainties in \( 1/T_1 T \) are likely underestimates. The larger slope is, however, consistent with a higher carrier density \( n \) in BSC. The Korringa slopes should scale [367] as \( n^{2/3} \). Using \( n \sim 1 \times 10^{19} \text{ cm}^{-3} \) in BSC [258] and \( \sim 2 \times 10^{17} \text{ cm}^{-3} \) in BTS [261], the slopes should differ by a factor of \( \sim 14 \), while experimentally the ratio is \( \sim 5 \).

The next difficulty is accurately quantifying the shift \( K \), which is quite small with a relatively large demagnetization correction. Experimentally, the zero of shift, defined by the calibration in MgO, differs from the true zero (where \( \chi_s = 0 \)) by the difference in chemical (orbital) shifts between MgO and the chalcogenide. However, because Li chemical shifts are universally very small, this should not be a large difference, perhaps a few ppm. The negative low temperature shift is also somewhat surprising. The hyperfine coupling \( A \) for Li is usually determined by a
Table 5.3: Korringa analysis of BSC and BTS [274] at 6.55 T and low temperature. To calculate $\mathcal{K}$, we take $S(g^*)$ in Equation (5.6) to be $2.69 \times 10^{-3}$ s K, using the $g_\parallel$ from EPR [368].

<table>
<thead>
<tr>
<th>Material</th>
<th>$1/(T_1 T)$ ($10^{-6}$ s$^{-1}$ K$^{-1}$)</th>
<th>$K$ (ppm)</th>
<th>$\mathcal{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Se$_3$:Ca</td>
<td>9.5(8)</td>
<td>−31(3)</td>
<td>0.038(8)</td>
</tr>
<tr>
<td>Bi$_2$Te$_2$Se</td>
<td>1.79(7)</td>
<td>−115(3)</td>
<td>2.78(18)</td>
</tr>
</tbody>
</table>

slight hybridization of the vacant 2s orbital with the host conduction band. As the s orbital has density at the nucleus, the resulting coupling is usually positive, with the d band metals Pd and Pt being exceptional [5]. For a positive $\mathcal{A}$, the sign of $K$ is determined by the sign of $g^*$, which has not yet been conclusively measured in either BSC or BTS. A more serious concern is that $K$ depends on temperature (in contrast to simple metals) and, at least in BTS, also on applied field [274]. To avoid ambiguity from the field dependence, we similarly restrict comparison to the same field, 6.55 T. A similarly temperature dependent shift (for the $^{207}$Pb NMR) was found in the narrow band semiconductor PbTe [369], where it was explained by the temperature dependence of the Fermi level $E_F$ [370]. At low-$T$ in the heavily $p$-type PbTe, $E_F$ occurs in the valence (or a nearby impurity) band, but with increasing temperature, moves upward into the gap, causing a reduction in $|K|$. With this in mind, we assume the low temperature shift is the most relevant for a Korringa comparison. Without a measured $g^*$ in BTS, we simply assume it is the same as BSC, and use the $g_\parallel$ from EPR [368] to calculate the values of $\mathcal{K}$ in Table 5.3.

The values of $\mathcal{K}$ are just opposite to the expectation of faster relaxation for diffusive BTS compared to metallic BSC [308]. Electronic correlations can, however, significantly alter the Korringa ratio to an extent that depends on disorder [315]. There should be no significant correlations in the broad bulk bands of the chalcogenides, but in narrow impurity bands, this is certainly a possibility. We note that $\mathcal{K}$ is also less than 1 in PbTe [371], similar to BSC. At this stage, without more data and a better understanding of the considerations mentioned above, it is premature to draw further conclusions.

5.4.3 Magnetism in Bi$_2$Te$_3$:Mn

In the Mn doped Bi$_2$Te$_3$ at low field, the relaxation from magnetic Mn$^{2+}$ becomes faster as the spin fluctuations slow down on cooling towards $T_C$. In particular, the low-$T$ increase in
$1/T_1$ occurs near where correlations among the Mn spins become evident in EPR [348, 372]. In remarkable contrast to ferromagnetic EuO [154], the signal is not wiped out in the vicinity of $T_C$, but $1/T_1$ does become very fast. This is likely a consequence of a relatively small hyperfine coupling consistent with a Li site in the vdW gap.

High applied field slows the Mn spins more continuously starting from a higher temperature, suppressing the critical peak and reducing $1/T_1$ significantly, a well-known phenomenon in NMR and $\mu$SR at magnetic transitions (see e.g., Ref. [373]). This also explains the small critical peak in the $^8$Li SLR in the dilute magnetic semiconductor, Ga$_{1-x}$Mn$_x$As [359]. As in GaAs, Mn in Bi$_2$Te$_3$ is both a magnetic and electronic dopant. At this concentration, BTM is $p$-type with a metallic carrier density of $\sim 7 \times 10^{19}$ cm$^{-3}$ [344, 348]. However, the difference in scale of $1/T_1$ at high field between Figures 5.2 and 5.6 shows that the Mn spins completely dominate the carrier relaxation.

It is also remarkable that the resonance is so clear in the magnetic state, which is in contrast to Ga$_{1-x}$Mn$_x$As [359]. The difference is not the linewidth, but rather the enhanced amplitude. This may be due to slow $^8$Li spectral dynamics occurring on the timescale of $\tau_p$ that effectively enhance the amplitude, for example, slow fluctuations of the ordered Mn moments, not far below $T_C$. Similar behavior was found in rutile TiO$_2$ at low temperature, where it was attributed to field fluctuations due to a nearby electron polaron [206]. Enhancement of the radio frequency (RF) field at nuclei in a ferromagnet [374] may also play a role.

Above 200 K, the activated increase in $1/T_1$ may indicate the onset of diffusive $^8$Li$^+$ motion, similar to the nonmagnetic analogs, with the additional effect that the local magnetic field from the Mn spins is also modulated by $^8$Li hopping (not just the EFG), similar to the ordered magnetic vdW layered CrSe$_2$ [375]. However, it may instead mark the onset of thermal excitation of electrons across the bandgap that is narrowed by Mn doping [344]. Thermally excited carriers may also explain the increase in $1/T_1$ at comparable temperatures in Ga$_{1-x}$Mn$_x$As [359], a very different medium for Li$^+$ diffusion. Thermally increased carrier density would strengthen interaction between the Mn moments, extend their effects via Ruderman–Kittel–Kasuya–Yosida (RKKY) polarization, and increase $1/T_1$. Measurements at higher temperatures may be able to discriminate these possibilities, but it is likely that both processes will contribute.

Having established the effects of Mn magnetism in the bulk, it would be interesting to use
lower implantation energies to study how they may be altered in the surface region by coupling to the TSS.

5.5 Conclusion

Using implanted $^8$Li β-NMR, we have studied the ionic, electronic, and magnetic properties of the doped TIs BSC and BTM. From SLR measurements, we find evidence at temperatures above $\sim 200$ K for site-to-site hopping of isolated $\text{Li}^+$ with Arrhenius activation energy of $\sim 0.4$ eV in BSC. At lower temperature the electronic properties dominate, giving rise to Korringa-like relaxation and negative Knight shifts, similar to isostructural BTS. A quantitative comparison reveals Korringa ratios opposite to expectations across the Ioffe-Regel limit. In BTM, the magnetism from dilute Mn moments dominates all other spin interactions, but the β-NMR signal remains measurable through the magnetic transition at $T_C$, where a critical peak in the SLR rate is observed. The activation energy from the high temperature increase $\sim 0.2$ eV may be related to Li mobility or to thermal carrier excitations.

With these new results, a more complete picture of the implanted $^8$Li NMR probe of the tetradymite Bi chalcogenides (and other vdW chalcogenides) is beginning to emerge. At high temperatures, isolated $^8\text{Li}^+$ has a tendency to mobilize, providing unique access to the kinetic parameters governing $\text{Li}^+$ diffusion in the ultra-dilute limit. At low temperature, $^8\text{Li}$ is sensitive to the local metallic and magnetic properties of the host. With the bulk NMR response now established in Bi$_2$Ch$_3$ TIs, the prospect of directly probing the chiral TSS with the depth resolution provided by β-NMR remains promising.

5.6 Supplemental material

5.6.1 $^8\text{Li}^+$ implantation profiles

The SRIM Monte Carlo code [133] was used to predict the $^8\text{Li}^+$ implantation profiles in BSC and BTM. At a given implantation energy, stopping events were simulated for $10^5$ ions, which were histogrammed to represent the predicted implantation profile shown in Figure 5.8. From
Figure 5.8: Stopping distribution for $^8\text{Li}^+$ implanted in the doped TIs BSC and BTM, calculated using the SRIM Monte Carlo code [133] using $10^5$ ions. The implanted probe ions stop principally within $\sim 250$ nm from the crystal surface, with only a minor “tail” penetrating further. Only at the lowest $^8\text{Li}^+$ implantation energy 1 keV does an appreciable fraction ($\sim 15\%$) stop in the region where surface effects are expected to be important.

In contrast to conventional NMR, note that the satellite intensities are chiefly determined by the

5.6.2 Helicity-resolved resonances

A typical helicity-resolved $^8\text{Li}$ resonance spectrum in BSC is shown in Figure 5.10. Besides the well-resolved fine structure, the spectra unambiguously reveal the multi-component nature of the line. A quadrupolar splitting, giving the anti-symmetric shape about the resonance centre-of-mass in each helicity, on the order of several kHz, can be identified from the outermost satellites. In contrast to conventional NMR, note that the satellite intensities are chiefly determined by the
**Figure 5.9:** Stopping details for $^8\text{Li}^+$ implanted in BSC calculated using the SRIM Monte Carlo code [133]. The ion stopping range and straggle (i.e., mean and standard deviation) at each implantation energy are shown in the top panel. The bottom panel shows the predicted fraction of $^8\text{Li}^+$ that are backscattered and those that stop within the first $\sim 6$ nm, where surface effects are expected. Except at the lowest implantation energy, this latter fraction is negligible. The solid grey lines are drawn to guide the eye.

High initial polarization, causing an increase in the relative amplitude of the outer satellites [127], but also depend on the SLR. Apart from the quadrupolar component, another contribution at the resonance “centre”, with no resolved splitting, is discernible. This is consistent with the $^8\text{Li}$ resonances observed in other vdW materials [274, 286, 375]. Unlike the more common case encountered for the spin $I = 3/2$ $^7\text{Li}$ nucleus, there is no $m_{\pm1/2} \leftrightarrow m_{\mp1/2}$ main line transition that is unshifted in first-order by the quadrupolar interaction. The absence of any peaks interlacing the $m_{\pm2} \leftrightarrow m_{\pm1}$ transitions suggest this “central” line cannot be multi-quantum (cf. the spectrum in Bi [127, 285]). For presentation, we combined the helicity-resolved spectra to give an overall average lineshape (see Figure 5.3 in Section 5.3.1).
Figure 5.10: Typical helicity-resolved $^8$Li spectra in BSC, revealing the fine structure of the line. Four quadrupole satellites, split asymmetrically in each helicity about a "central" Lorentzian (marked by a vertical dashed line) are evident. Note that, in contrast to conventional NMR, the satellite amplitudes are determined primarily by the highly polarized initial state. The solid black lines are the fits described in the text and the vertical dashed line marks the resonance central frequency $\nu_0$. 
Chapter 6

Summary & outlook

We have used ion-implanted $^8\text{Li}$ β-detected nuclear magnetic resonance ($\beta$-NMR) to study the dynamics of isolated $\text{Li}^+$ in several single crystalline materials: rutile $\text{TiO}_2$, $\text{Bi}_2\text{Te}_2\text{Se}$ (BTS), $\text{Bi}_2\text{Se}_3$:Ca (BSC), and $\text{Bi}_2\text{Te}_3$:Mn (BTM). While none of these compounds natively contain lithium, their crystal structures are amenable to $\text{Li}^+$ intercalation, thanks to a connected sublattice of interstitial sites in the form of a tunnel or plane. Besides the structural properties that make them amenable to ionic diffusion, the electronic properties of the materials are also of interest, manifesting as the dominant feature of the $\beta$-NMR data at low temperature, where atomic motion is minimal. Each of these examples are clear cases where understanding the $^8\text{Li}$ probe’s coupling to the host’s electronic properties, along with its propensity to migrate at elevated temperatures, are important. The characterization of both behaviours provided here broadens the knowledge of the capabilities of the ion-implanted $\beta$-NMR technique, as well as the scope of materials it may be applied to study.

Using a combination of spin-lattice relaxation (SLR) and resonance measurements, we find evidence for motion of implanted $^8\text{Li}^+$ below 300 K, manifesting as Bloembergen-Purcell-Pound (BPP) peaks in the SLR rate $1/T_1$ and motional narrowing. From these signatures, the Arrhenius parameters governing the $\text{Li}^+$ hop rate were identified and compared with results from theory, as well as other experiments in the literature. The rate of motion inferred in this temperature range, often on the order of MHz, is rather exceptional for solid-state ion conductors. In several cases, anomalously large Arrhenius prefactors were found, opposite to
the usual case for spatially constrained ionic motion. Similarly, an instance of the empirical Meyer-Neldel rule (MNR) was observed. These observations, from unique experiments on isolated Li$^+$: suggest that the mobility of the isolated ion may be quite significant compared to more concentrated cases; challenge conventional interpretations of Arrhenius prefactors when large attempt frequencies are involved; and provide further evidence that the MNR is generic, occurring even in conceptually simple circumstances.

In the one-dimensional (1D) ion conductor rutile TiO$_2$, two sets of thermally activated dynamics were identified: one below 100 K, ascribed to electron polarons (i.e., Ti$^{3+}$ electronic defects); and another at higher temperatures, associated with $^8$Li$^+$ diffusion. The agreement of the diffusive activation energy with macroscopic measurements implies a single, common migration mechanism across all length scales. This was not clear at the outset, given the rather large disagreement between theory and experiment for the ionic hopping barrier. The results presented here suggest that a key ingredient is missing in the calculation of the diffusion barrier. Recent measurements using a beam of $^8$Li$^+$ as an online radiotracer confirm this assertion [253, 376], but reveal that some of the low-temperature dynamics are due to lithium diffusion, indicating there is further complexity to the dynamics discussed in Chapter 3.

Two types of dynamics are possible for the polaron: one associated with its unpaired spin; and another associated with its translational motion. Due to its charge, its motion is coupled to the nearby Li$^+$, but since we are sensing the nuclear magnetic resonance (NMR), the magnetic effect of the spin may dominate. The interstitial Li$^+$ may migrate as an ion or as part of mobile Li$^+$–Ti$^{3+}$ complex, which may also have its own internal motion (e.g., from binding/unbinding cycles). It has long been recognized that polaronic electron transport may be extremely important in some materials, especially mixed (ionic/electronic) conductors that are electrodes in a solid-state ionic device. Here we can study the isolated polaron-Li interaction — an ideal situation much simpler than the high density limit.

The $^6$-NMR measurements presented here suggest the low-temperature response is dominated by the proximal coupling to polarons in vicinity of the implantation site, but it is not known what fraction of the implanted probes this affects. Key to improving the understanding of Li$^+$ in rutile is further investigation of these “polaronic” interactions. A detailed characterization of the $^8$Li resonance below 100 K, in conjunction with resonant SLR hole-burning (HB) measure-
ments (see e.g., [148]), may help further elucidate the binding/migration details of the polaron. Similarly, it may be possible to use the NMR “isotope effect” to (e.g., by comparing $^8$Li and $^9$Li SLR rates [251–253]) to identify the nature of the fluctuating field at the probe implantation site.

With the results on BTS, BSC, and BTM present in Chapters 4 and 5, we have significantly advanced the understanding of how $^8$Li $\beta$-NMR may be used to study van der Waals (vdW) layered materials. The renaissance of studying materials with two-dimensional (2D) structural characteristics began with graphene (2010 Nobel Prize in Physics), which instigated a renewal of interest in other vdW materials like transition metal dichalcogenides (TMDs) that were studied extensively in the 1970s. These investigations on TMDs focused largely on electronic properties; however, the importance of their ability to accommodate foreign ions in the vdW gap, especially Li$^+$, was also realized (2019 Nobel Prize in Chemistry). More recently, interest in tetradymite bismuth chalcogenides, structurally related to the TMDs, exploded owing to their electronic structures manifesting a robustly conductive topological surface state (TSS). In all materials containing a vdW gap, developing a microscopic understanding of the mobility of foreign ions, as well as their local electronic properties, is of interest and this work establishes how implanted $^8$Li “works” in such structural motifs.

In BTS and BSC, significant thermally activated dynamics onset above $\sim$150 K. The dramatic changes to the $^8$Li resonance lineshape, similar in both materials, suggest the process is long-range diffusion of $^8$Li$^+$ in the vdW gap, consistent with the SLR BPP peaks and the ability to intercalate Li$^+$ at room temperature; however, in order to be more conclusive, higher temperatures are required, where, based on the discussion in Chapter 5, we anticipate sharper resonance fine structure from (complete) motional averaging. Our estimates of the Li$^+$ diffusivity, especially in BTS, are substantial compared to some other well-known lithium-ion conductors (e.g., Li$_x$TiS$_2$). At lower temperatures, the electronic properties of the non-magnetic topological insulators (TIs) dominate, giving rise to Korringa-like relaxation and negative Knight shifts. The metallic NMR response reflects that these materials are not really bulk insulators, with their behaviour dominated by (unwanted) defect properties. This feature may be unavoidable in all but exemplary circumstances (see e.g., Bi$_2$Te$_3$ films [377]) and is therefore important to understand. The observation of the strong field dependence to the SLR slope and resonance shift in BTS was surprising, with similar behaviour found in BSC, but from a more limited
dataset. While a detailed understanding is lacking, several possible origins were discussed in Chapter 4. Field dependent conventional NMR, using the (stable) host nuclei in Bi$_2$Ch$_3$, may provide a useful confirmation. In the magnetic BTM, coupling to the dopant Mn spins dominates all other interactions, but the $\beta$-NMR remains measurable, even in the magnetic state and at low field. This was not obvious at the outset and suggests the applicability of $\beta$-NMR to study (dilute) magnetic vdW materials, which have been scarcely explored by the technique. This ability may be related to the weakness of $^7$Li’s hyperfine coupling. With the bulk NMR response now established in Bi$_2$Ch$_3$ TIs, one can consider attempting to study directly the chiral TSS with the depth resolution provided by $\beta$-NMR; however, one first needs to carefully understand background signals at the very low implantation energies required [378].

With the ability to study Li$^+$ dynamics with ion-implanted $\beta$-NMR now firmly established, we believe the technique will become an effective means for studying solid-state lithium diffusion, especially in situations where conventional NMR isn’t feasible. The information extracted from such experiments can further be complemented by the recently developed online radiotracer method [253, 376], which uses the same $^7$Li$^+$ beam. Key to the general applicability of both approaches is access to higher temperatures; one really needs a couple orders of magnitude dynamic range in $\tau^{-1}(T)$ to extract convincing values of $\tau^{-1}_0$ and $E_A$. For $\beta$-NMR, we generally need $\tau^{-1}$ in the range of 50 kHz to 50 MHz, requiring that the temperature is high enough for fast hopping with residence times <1 ms. Plans for upgrading the maximum operating temperatures of the spectrometers discussed in Chapter 2 are underway.

Finally, with the unique depth resolution provided by ion-implanted $\beta$-NMR, it should be possible to study interface effects in ionic diffusion (e.g., the suppression or enhancement of mobility near a surface or heterocontact). Note that, in practical devices, such as rechargeable batteries, ion diffusion to and traversal across material interfaces (e.g., electrode-electrolyte contacts) is implicitly required for functionality. In particular, directly probing Li$^+$ motion in a depth-resolved manner at space charge regions [379] (e.g., near heterocontacts) is intriguing, but difficult to do with (ionic) conductivity measurements. LiF/TiO$_2$ thin films, where an interfacial enhancement to Li$^+$ diffusivity in LiF has been observed [380, 381], may be an ideal case to start with.
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Appendix A

β-NMR probe ion concentration

A characteristic feature of ion-implanted β-detected nuclear magnetic resonance (β-NMR) is the ability to study the dynamical behaviour ultra-dilute probe ions (e.g., $^8\text{Li}^+$ [89, 169, 206, 274] or $^{31}\text{Mg}^+$ [382]) in condensed phases. This is, in many respects, similar to the use of muon spin rotation/relaxation/resonance (μSR) to simulate the behaviour of hydrogen inside materials [383]. An important consideration, however, is just how dilute are the implanted probe ions? For an implanted probe $X^+$, its concentration in a sample can be written as:

$$[X^+](t) = \frac{n_X(t)}{V(t)},$$

where $n_X(t)$ is the number of implanted ions at any given time, and $V(t)$ is the volume in the sample they occupy. Clearly, estimating $[X^+](t)$ reduces to achieving good estimates for $n_X(t)$ and $V(t)$. The precise answer for either quantity, however, depends largely on the conditions of the β-NMR experiment (e.g., beam focus, isotope production efficiency, etc. — see Chapter 2). Here we consider the quantification of $[X^+]$ and provide estimates for typical values during an experiment.

For a constant (average) beam rate $R_X$ the number of implanted ions during a beam pulse is:

$$n_X(t) = R_X \int_0^t \exp \left( \frac{-t'}{\tau_\beta} \right) dt' = R_X \tau_\beta \left[ 1 - \exp \left( \frac{-t}{\tau_\beta} \right) \right],$$

where $\tau_\beta$ is the mean decay time of the β-ray.
where $\tau_\beta$ is the nuclear lifetime of X. For a sufficiently long beam pulse, we obtain the steady-state condition (i.e., radiochemical equilibrium):

$$\bar{n}_X = \lim_{t \gg \tau_\beta} n_X(t) \approx R_X \tau_\beta.$$  \hfill (A.3)

This is the usual situation during a continuous wave (CW) resonance measurement, but is typically not achieved during a spin-lattice relaxation (SLR) measurement using a short beam pulse (see Section 2.3.1). As such, $\bar{n}_X$ is the upper limit for the number of implanted probes at any given time. Our detected rate $R_X$ is only a fraction of the total rate $R^t_X$ due to finite detector solid angle, the steady-state number of ions can be estimated as:

$$\bar{n}_X \approx \epsilon^{-1} R_X \tau_\beta,$$  \hfill (A.4)

where $\epsilon$ is the scaling factor for our detection efficiency. In an experiment using $^8$Li, $R_X \approx 10^6 \text{ ions/s}$, $\tau_\beta = 1.21 \text{ ms}$ [18], and, assuming $\epsilon$ is on the order of ~10% in the high field spectrometer [121–123], this puts $\bar{n}_X$ at about $\sim 10^7$ ions.

Estimating $V(t)$ is somewhat trickier than estimating $\bar{n}_X$, since it requires some assumptions regarding the mobility of the ions in the sample. In a liquid, the diffusivity of $X^+$ may be high enough such that, to a reasonable approximation, the probe ions quickly homogenize over the volume of the sample within their lifetime. By contrast, in a solid whose structure is not amenable to ionic diffusion, the implanted probes will be effectively immobile and the relevant volume reduces to that of the implantation profile. In cases of intermediate mobility, knowledge of the probe's diffusion coefficient is required and the stopping profile must be evolved in time.\footnote{Note that this also necessary when using $^6$Li as an online radiotracer (see e.g., [253, 376]).}

We forgo dealing with this more complicated situation here, in favour of exploring the other two limiting cases. These can be used to give upper/lower bounds on acceptable values.

In the limit of very slow diffusion, it is possible to estimate $V$ using information from stopping profile generated from a Stopping and Range of Ions in Matter (SRIM) Monte Carlo calculation [133] (see e.g., Figure A.1); From the charge-coupled device (CCD) images of typical beamspots at high magnetic field (e.g., from scintillating sapphire [141] — see Figure 2.9 in
Figure A.1: Scaled three-dimensional (3D) $^8\text{Li}^+$ implantation profile used to determine the typical (peak) $^8\text{Li}^+$ concentration in a $\beta$-NMR experiment. (A) Cartoon of the $^8\text{Li}^+$ implantation process in rutile TiO$_2$. (B) One-dimensional (1D) histogram of the stopping probability $\rho(z)$ as a function of depth $z$ below the surface. (C) Two-dimensional (2D) histogram of the implantation profile in the lateral directions $x$ and $y$, spread to correspond to a beamspot full width at half maximum (FWHM) of 2 mm. (D) 2D histogram of the implantation profile in the $x$ and $z$ directions, scaled to correspond to a beamspot FWHM of 2 mm. This scaling corresponds to a convex hull [384] of $\sim1 \times 10^{-7}$ cm$^{-3}$ and, assuming a typical $^8\text{Li}^+$ beam rate, a (peak) concentration of $\sim1.8 \times 10^{13}$ cm$^{-3}$ (cf. $3.2 \times 10^{22}$ cm$^{-3}$ for Ti in TiO$_2$). The cividis colourmap [27] is used for the 2D histograms.

Chapter 2), we know the beamspot is roughly $\sim2$ mm in diameter. In a back-of-the-envelope approach, we could assume that the beamspot is perfectly circular and use the mean stopping depth from the SRIM calculation to compute $V$. This “cylindrical” approximation is simply:

$$V \approx \pi r^2 \bar{z},$$

(A.5)

where $r$ is the radius of the beamspot and $\bar{z}$ is the mean stopping depth. Using typical values of $r \sim 1$ mm and $\bar{z} \sim 100$ nm for, a $V$ on the order of $\sim3 \times 10^{-7}$ cm$^3$ is obtained.
To improve upon this estimate, we must consider the details of the full 3D stopping profile; however, this on its own is insufficient, as the SRIM calculation assumes a point source for the incident ions. To better account for the macroscopic profile of the beam, a simple approach is to spread the incident lateral (i.e., \(x\) and \(y\)) components of incoming ions such that the FWHM of the new lateral profile matches the beampot diameter observed in the CCD images. For this, we use a 2D Gaussian distribution of arrival positions and set the FWHM in the \(x\) and \(y\) directions to 2 mm. Select projections from this “scaling” procedure are shown in Figure A.1.

With these modifications to the implantation profile, \(V\) can be estimated by considering the total volume occupied by all simulated ions. That is, one needs to determine the minimum volume that encloses all possible stopping positions. This can be done by computing the convex hull \([384]\) of the 3D stopping profile (e.g., using the Python library SciPy \([385]\)). For a typical implantation profile, this approach gives a volume of \(\sim 7 \times 10^{-6} \text{ cm}^3\). This is somewhat larger, but still within an order of magnitude, of the much cruder “cylindrical” approximation.

In the limit of very fast 3D probe diffusion, like one might expect in liquid, the appropriate volume is simply that of the sample under investigation. For example, in \(^{8}\text{Li}\) or \(^{31}\text{Mg}\) \(\beta\)-NMR experiments on ionic liquid droplets \([169, 382]\), \(V\) is on the order of a few \(\mu\text{L}\), which is considerably larger than either estimate in the static limit. In most solids below \(\sim 320 \text{ K}\), however, \(D\) is unlikely to large enough to disperse the implanted probes over its full volume.

Using the assumptions outlined above, we can now make three estimates for (steady-state) probe ion concentrations. In the limit where all of the implanted ions are effectively static, the “cylindrical” approximation gives: \([X] \sim 4 \times 10^{14} \text{ cm}^{-3}\). The more robust estimate using the convex hull \([384]\) of the (scaled) 3D stopping profile gives: \([X] \sim 2 \times 10^{13} \text{ cm}^{-3}\). For comparison, in the limit of very fast probe diffusion (i.e., in a liquid at high temperature): \([X] \sim 6 \times 10^{10} \text{ cm}^{-3}\). This is the lower limit for the concentration in the ionic liquid experiments \([169, 382]\). For comparison, in the example shown in Figure A.1 for rutile \(\text{TiO}_2\), \([\text{Ti}] = 3.2 \times 10^{22} \text{ cm}^{-3}\), clearly dwarfing the above estimates by no less than \(\sim 10^8\)! It is surprising, however, to find that \([X]\) differs by only three decades between the fast-diffusion and convex hull approaches. This may be due to the fact that the hull volume is biased by outliers in the stopping profile and it does not account for the spatial inhomogeneity of the ions within the enclosed volume. Undoubtedly, there are regions within this volume where the concentration is higher and these regions will be...
where most of the detected signal in the $\beta$-NMR experiment comes from.

As a simple check, we may consider that a smaller fraction of the hull volume (e.g., $\sim 0.5$) may include the vast majority (e.g., $\sim 0.875$) of all implanted ions; however, this implies our estimate using the full volume is only off by a relatively small factor, not several orders of magnitude, suggesting that the method gives a reasonable estimate.

These considerations are clearly in the dilute limit and we anticipate no measurable effects of interactions among $^8$Li. It is a different question about the damage $^8$Li leaves behind which may have a significantly longer lifetime than 1.2 s. This would yield a rate dependence and evolution of the data with overall exposure.
Appendix B

Continuum diffusion

In the limit of many small steps, the theory of discrete random walks (see Section 1.1.1) crosses over to continuum diffusion, familiar for fluid phases. Even in solids, when diffusion over macroscopic length scales are probed (e.g., from ionic conductivity or tracer diffusivity measurements), the continuum approximation is generally good. Here, we recall its basic properties.

The phenomenological description of continuum diffusion was first expressed by Fick, who noted that particles tend to disperse from regions of high to low concentrations. That is, the flux of particles $J$ at a concentration $c$ is related by:

$$J = -D \nabla c,$$

where the proportionality constant $D$ is the diffusion coefficient. Generally, the diffusivity can be anisotropic (i.e., $D$ is a second-rank real tensor), but often in isotropic phases (most fluids) it can be treated as a scalar quantity. Equation (B.1) is commonly referred to as Fick’s 1st law. Dimensional analysis of Equation (B.1) reveals the expected units of $D$; $J$ is the number of particles passing per unit area per unit time (e.g., cm$^{-2}$ s$^{-1}$) and $c$ has units of particles per unit volume (e.g., cm$^{-3}$), giving $D$ units of area per unit time (e.g., cm$^2$ s$^{-1}$).

As a consequence of the conservation of matter, time-dependent changes in concentration
must follow the negative of the divergence of flux (i.e., we have the continuity relation):

$$\frac{\partial c}{\partial t} = -\nabla \cdot J.$$ \hspace{1cm} (B.2)

Hence, the full time dependence of this behaviour is captured by Fick’s 2\textsuperscript{nd} law:

$$\frac{\partial c}{\partial t} = D\nabla^2 c,$$ \hspace{1cm} (B.3)

where \( t \) is time. Equation (B.3) is an elliptic second-order homogeneous partial differential equation with constant coefficients, sometimes called the diffusion equation. It is very similar to an equation for heat transport and it has been studied extensively [386]. Generally, \( D \) is taken to be a constant independent of both time and space. While solutions to Equation (B.3) depend on both the initial and boundary conditions [387], they are generally related to a Gaussian function, equivalent to expressions derived from the microscopic theory of random walks [19]. Solving Equation (B.3) allows one to determine \( D \) from concentration profiles \( c(r, t) \), where \( r \) and \( t \) are spatial and temporal coordinates. This is sketched in Figure B.1 for a (radio)tracer diffusion experiment.

**Figure B.1:** Sketch of a (radio)tracer diffusion measurement. Tracer atoms are first deposited on the surface of a solid, after which the material is annealed at fixed temperature for a time \( t \), facilitating the penetration of the tracers into the solid. The material is then quickly cooled, suppressing further migration, and partitioned into sections, wherein the concentration of the tracers is measured. The spatial extent of the concentration of tracer atoms after time \( t \) is proportional to their diffusivity \( D \). Adapted from [388]. Copyright © 2005, Springer-Verlag Berlin Heidelberg.
Appendix C

Empirical compensation “laws”

In the study of rate processes, it is an empirical fact that the results from many experiments are well-described by a simple Arrhenius expression [33], analogous to that given by Equation (1.3). What is then extracted from an experiment are two parameters — an activation energy and a prefactor — which are capable of describing the full temperature dependence of the rate constant (e.g., $\tau^{-1}$ or $D$). A breakthrough in explaining this Arrhenius form came in the development of transition state theory (TST) (see e.g., [24]) to describe how rate constants for chemical reactions depend on temperature. A measured barrier $E_A$ is thus related to the difference in the thermodynamic potentials between the transition and initial states of the reactive partners. Indeed, these same ideas have been extended to migration of atoms in solids [26] and, so long as no curvature is observed on an Arrhenius plot (e.g., from a strong temperature dependence to $\Delta G_m$), the Arrhenius parameters are also available for comparison with results from theory; however, the conventional interpretation of these quantities can be challenging in light of their high degree of correlation.

With only two degrees of freedom in an Arrhenius expression (see e.g., Equation (1.3)), changes in one parameter are highly correlated with changes in the other, even for measurements of the same kinetic process, particularly if the measured dynamic range is relatively small. Empirically, this correlation results in an exponential relationship between $\tau_0^{-1}$ and $E_A$, colloquially referred to as the Meyer-Neldel rule (MNR) in solid-state sciences after the work of
Figure C.1: Illustration of the MNR for a kinetic process. (A) Meyer-Neldel plot of the exponential relationship between the measured Arrhenius prefactor $\tau_0^{-1}$ and activation energy $E_A$ for related kinetic processes [Equation (C.1)]. The Meyer-Neldel energy $\Delta_{MN}$ can be identified from the slope of the dashed grey line in the semi-logarithmic plot. (B) Arrhenius plot of the related rate processes following the MNR. The isokinetic temperature $T_{iso}$ [Equation (C.2)] can be identified at the equivalence point (i.e., the crossing temperature) of all related rate processes, indicated by the vertical dashed grey line.

Meyer and Neldel [389]. Explicitly, it is often found that [33]:

$$\tau_0^{-1} \approx \tau_{MN}^{-1} \exp\left(\frac{E_A}{\Delta_{MN}}\right),$$  \hspace{1cm} (C.1)

where $\tau_{MN}^{-1}$ and $\Delta_{MN}$ are the MNR prefactor and energy, respectively. The temperature where all related kinetic processes are equal, known as the isokinetic point $T_{iso}$, is identified as:

$$T_{iso} = \frac{\Delta_{MN}}{k_B}.$$  \hspace{1cm} (C.2)

These empirical relationships are illustrated in Figure C.1.

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1In other disciplines, the MNR is synonymously referred to as enthalpy-entropy correlations, the isokinetic rule, or the compensation law (see e.g., [33]).
This thesis was typeset with LuaLaTeX using 11 pt Scientific and Technical Information eXchange (STIX) fonts. BibLaTeX and Biber were used for the bibliography management. The data analysis described herein was achieved using a mix of C, C++, and Python code. Data fitting was done almost exclusively using the functionality built into ROOT [175], especially the implementation of the MINUIT [176] minimization algorithms. Post-processing of the results benefited from the facilities implemented in NumPy [390] and SciPy [385], with many of the figures in this thesis produced using Matplotlib [391]. Crystal structures appearing in this work were drawn using either CrystalMaker [205] or Visualization for Electronic and STructural Analysis (VESTA) [273].