Ionic and electronic properties of the topological insulator Bi\textsubscript{2}Te\textsubscript{2}Se investigated using $\beta$-detected nuclear magnetic relaxation and resonance of $^8$Li

Ryan M. L. McFadden,\textsuperscript{1,2,4} Aris Chatzichristos,\textsuperscript{2,3} Kim H. Chow,\textsuperscript{4} David L. Cortie,\textsuperscript{1,2,3,5} Martin H. Dehn,\textsuperscript{2,3} Derek Fujimoto,\textsuperscript{2,3} Masrur D. Hossain,\textsuperscript{3,5} Huw J. J.\textsuperscript{6,8} Victoria L. Karner,\textsuperscript{1,2} Robert F. Kief,\textsuperscript{2,3,5} C. D. Philip Levy,\textsuperscript{6} Ruohong Li,\textsuperscript{6} Iain McKenzie,\textsuperscript{6,7} Gerald D. Morris,\textsuperscript{6} Oren Ofer,\textsuperscript{6} Matthew R. Pearson,\textsuperscript{6} Monika Stachura,\textsuperscript{6} Robert J. Cava,\textsuperscript{5} and W. Andrew MacFarlane\textsuperscript{1,2,6,7}

\textsuperscript{1}Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z4, Canada
\textsuperscript{2}Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver, BC V6T 1Z4, Canada
\textsuperscript{3}Department of Physics and Astronomy, University of British Columbia, Vancouver, BC V6T 1Z4, Canada
\textsuperscript{4}Department of Physics, University of Alberta, 4-181 CCIS, Edmonton, AB T6G 2E1, Canada
\textsuperscript{5}Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA
\textsuperscript{6}TRIUMF, 4004 Wesbrook Mall, Vancouver, BC V6T 2A3, Canada
\textsuperscript{7}Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

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We report measurements on the high temperature ionic and low temperature electronic properties of the 3D topological insulator Bi\textsubscript{2}Te\textsubscript{2}Se using $^8$Li $\beta$-detected nuclear magnetic relaxation and resonance. At temperatures above $\sim$150 K, spin-lattice relaxation measurements reveal isolated $^8$Li\textsuperscript{6} diffusion with an activation energy $E_A = 0.185(8)$ eV and attempt frequency $\tau_0^{-1} = 8(3) \times 10^{11}$ s\textsuperscript{-1} for atomic site-to-site hopping. At lower temperature, we find a linear Korringa-like relaxation mechanism with a field dependent slope and intercept, which is 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, but that conventional theories are unable to account for the extent of the field dependence. Conventional NMR of the stable host nuclei may help elucidate their origin.

I. INTRODUCTION

Bismuth chalcogenides with the formula Bi\textsubscript{2}Ch\textsubscript{3} (Ch = S, Se, Te) are narrow gap semiconductors that have been studied for decades for their thermoelectric properties. They crystallize in the layered tetradyminate structure,\textsuperscript{1,2} consisting of stacks of strongly bound Bi-Ch-Bi-Ch quintuple layers (QLs) loosely coupled by van der Waals (vdW) interactions (see Figure 1). More recently, interest in their electronic properties has exploded\textsuperscript{3} following the realization that strong spin-orbit coupling and band inversion combine to make them 3D topological insulators (TIs),\textsuperscript{4} 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\textsubscript{2}Se\textsubscript{3} or Bi\textsubscript{2}Te\textsubscript{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\textsubscript{2}Se\textsubscript{3} with Ca doping to suppress the more usual $n$-type conductivity.\textsuperscript{5,6} On the other hand, the stoichiometric ordered\textsuperscript{7,8} ternary line compound Bi\textsubscript{2}Te\textsubscript{2}Se (BTS) exhibits a much lower conductivity thanks to its fortuitous crystal chemistry,\textsuperscript{8} with anti-site defects (e.g., bismuth substitution on a tellurium site) playing an important role.\textsuperscript{9} Indeed, BTS crystals with a characteristic bulk band gap of $\sim$0.3 eV\textsuperscript{10} have demonstrated such desired large bulk resistivities at low temperatures.\textsuperscript{8,11–13} A great deal is known about its surface properties, with angle-resolved photoemission spectroscopy (ARPES) revealing the characteristic linear dispersion about the Dirac point;\textsuperscript{9,14–18} however, the material is not an ideal TI due to the close proximity of the Dirac point to the top of the bulk valence band.\textsuperscript{2}

With the novel electronic structure of the Bi chalcogenides evident primarily in the TSS, much inquiry has focused on surface sensitive probes, such as ARPES, scanning tunnelling spectroscopy (STS), and transport. On the other hand, NMR is well-known to reveal electronic properties in metals through...
hyperfine coupling of the nucleus to surrounding electron spins that gives rise to the Knight shift, a measure of the Pauli spin susceptibility, and the Korringa spin-lattice relaxation.\textsuperscript{21,22} Theory predicts dramatic effects in such quantities for the TSS,\textsuperscript{23} but NMR is generally a bulk probe with very little sensitivity to the surface. Despite this, a considerable body of conventional NMR in the Bi\textsubscript{2}Sr\textsubscript{2}Te \textsubscript{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. The most conspicuous feature of 100\% abundant \textsuperscript{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,\textsuperscript{24} confirmed more recently by very high field NMR.\textsuperscript{25} The behavior of \(1/T_1\) is less consistent, with results ranging from \(T\)-linear to nearly \(T\)-independent\textsuperscript{24,26} at low temperature. The low abundance (\(\sim 7\%\)) pure magnetic spin 1/2 probes \textsuperscript{77}Se and \textsuperscript{125}Te show a small \(T\)-independent shift, and Korringa relaxation at low temperature in orientationally averaged powder spectra.\textsuperscript{27} This Korringa relaxation is enhanced in nanocrystals and was attributed to the TSS,\textsuperscript{28} but given the evidence for aging effects that stabilize a conventional metallic surface state,\textsuperscript{29} 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.\textsuperscript{30–32}

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 TSS, Section V. and the electronic properties of BTS giving rise to the field dependent relaxation and resonance shifts at low temperature (Section IV B). Finally, a concluding summary can be found in Section V.

II. EXPERIMENT

Since implanted ion \(\beta\)-NMR is not a widely known technique, here we summarize some of its main features. More detailed accounts can be found in Refs. \textsuperscript{33} and \textsuperscript{35}.

A. The \(\beta\)-NMR Technique

In many ways, \(\beta\)-NMR is very similar to stable isotope NMR. 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 \textsuperscript{7}\Li possesses a non-zero nuclear quadrupole moment, the nuclear spin is coupled to the local electric field gradient (EFG),\textsuperscript{22,16}

\[
eq = \frac{\hat{g}^2\nu}{\partial x_i \partial x_j},
\]

a tensor that is zero under cubic symmetry. The quadrupole interaction splits the resonance into a set of 2\(I\) satellites. The integer spin (\(I = 2\)) of \textsuperscript{8}\Li (uncommon in conventional NMR) has the important consequence that the quadrupolar spectrum has no “main line” at the Larmor frequency,

\[
\omega_0 = 2\pi v_0 = \gamma B_0,
\]
determined by the gyromagnetic ratio \(\gamma\) of the NMR nucleus and the (dominant) applied magnetic field \(B_0\). In contrast, for the more familiar case of half-integer \(I\), the \(m = \pm 1/2\) transition yields, to first order, a line at \(v_0\) unperturbed by quadrupole effects.\textsuperscript{36} While the quadrupole interaction is often the most important perturbation to the nuclear spin energy levels in nonmagnetic materials, for \textsuperscript{8}\Li it is still relatively small (in the kHz range), because its nuclear electric quadrupole moment is small, compared, for example, to \textsuperscript{209}Bi.

Distinct from conventional NMR, the probe is extrinsic to the host, and its lattice site is not known \textit{a priori}. Like the implanted positive muon in \(\mu\)SR, the \textsuperscript{8}\Li\textsuperscript{+} 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. Moreover, \textsuperscript{8}\Li\textsuperscript{+}, as a light interstitial, can often be \textit{mobile} near room temperature. In this case, the local interactions become time dependent, as the probe undergoes stochastic hopping, usually among interstitial sites. If the average hop rate is near the Larmor frequency, this will cause spin-lattice relaxation.\textsuperscript{37–39} Since this process is independent of other relaxation mechanisms due to the intrinsic fluctuations of the host, the rates simply add. At accessible beam intensities the instantaneous number of \textsuperscript{8}\Li in the sample never exceeds \(\sim 10^6\), meaning \textsuperscript{8}\Li is always present in the ultradilute limit, and interactions between \textsuperscript{8}\Li can be neglected. Any diffusive motion is thus characteristic of the \textit{isolated} interstitial.

As with conventional NMR, the spin-lattice relaxation is determined by fluctuations at the Larmor frequency in the radio-frequency (RF) range. Specific to the \(\beta\)-NMR mode
of detection, the range of measurable $T_1$ relaxation times is determined by the radioactive lifetime $\tau_i$. As a rule of thumb, measurable $T_1$ values lie in the range $0.01\tau_i$ to $100\tau_i$.\textsuperscript{35} 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.

In conventional NMR, the signal-to-noise ratio 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 $10$s 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 $^8\text{Li}$ begins to resonantly lose its spin polarization to the bath of surrounding nuclear spins. 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.

B. Measurements

$\beta$-NMR experiments were performed at TRIUMF’s ISAC facility in Vancouver, Canada. A low-energy highly polarized beam of $^8\text{Li}^+$ was implanted into a BTS single crystal (prepared as in Ref. 8) mounted in one of two dedicated spectrometers.\textsuperscript{33,40–42} The 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) that was then mounted on a cold finger cryostat. The incident $^8\text{Li}^+$ beam had a typical flux of $10^9$ ions/s over a beam spot $\sim 2$ mm in diameter. At the implantation energies $E$ used here ($5\text{ keV}$ to $28\text{ keV}$), the incident $^8\text{Li}^+$ ions typically stop on average $>30$ nm below the crystal surface, as predicted by the implantation profiles generated by SRIM Monte Carlo code\textsuperscript{43} (see Figure 10 in Appendix A). The probe nucleus, $^8\text{Li}$, has nuclear spin $I = 2$, gyromagnetic ratio $\gamma/2\pi = 6.3016\text{ MHz T}^{-1}$, nuclear electric quadrupole moment $Q = +32.6\text{ mb}$, and radioactive lifetime $\tau_i = 1.21\text{ s}$. Spin-polarization was achieved in-flight by collinear optical pumping with circularly polarized light, yielding a polarization of $\sim 70\%$,\textsuperscript{44} and monitered after ion-implantation through the anisotropic $\beta$-decay emissions of $^8\text{Li}$. Specifically, the asymmetry in two opposed scintillation counters is proportional to the average longitudinal nuclear spin-polarization.\textsuperscript{33,35} with the proportionality factor depending on the experimental geometry and the details of the $\beta$-decay.

Spin-lattice relaxation (SLR) measurements were performed by monitoring the transient decay of spin-polarization both during and following a 4 s pulse of beam.\textsuperscript{35,46} During the pulse, the polarization approaches a steady-state value, while after the pulse, it relaxes to $\sim 0$. Note that the discontinuity at $t = 4\text{ s}$ (see Figure 2) is characteristic of $\beta$-NMR SLR data. 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 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 $^8\text{Li}$.

Here, SLR rates were measured in small temperature steps from $3$–$317\text{ K}$ under applied magnetic fields between $2.20$–$6.55\text{ T}$ parallel to the trigonal $c$-axis, and with coarser temperature steps at lower magnetic fields ($2.5$–$20\text{ mT}$) perpendicular to the $c$-axis. A typical SLR measurement took $\sim 20\text{ min}$.

Resonances were acquired in a continuous $^8\text{Li}^+$ beam with a continuous wave (CW) transverse RF magnetic field stepped slowly through the $^8\text{Li}$ Larmor frequency. In this measurement mode, the spin of any on-resonance $^8\text{Li}$ is rapidly precessed by the RF field, resulting in a loss in the average time-integrated asymmetry. The evolution of the resonance was recorded over a temperature range of $3\text{ K}$ to $317\text{ K}$ in a dedicated high-field spectrometer\textsuperscript{40,42} with a highly-homogeneous magnetic field in the range of $2.20$–$6.55\text{ T}$ parallel to the BTS $c$-axis. The resonance frequency was calibrated against the position in single crystal MgO (100) at $300\text{ K}$,\textsuperscript{45} with the superconducting solenoid persistent. Resonance measurements typically took $\sim 30\text{ min}$ to acquire.

III. RESULTS AND ANALYSIS

A. Spin-Lattice Relaxation

Typical $^8\text{Li}$ SLR data at high and low magnetic field in BTS are shown in Figure 2 for several temperatures, where the spectra have been normalized by their $I = 0$ 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.\textsuperscript{33} and semimetals.\textsuperscript{48} Surprisingly, the relaxation is faster than in the normal state of the structurally similar NbSe$_2$.\textsuperscript{49} despite a very much smaller carrier density. However, it is also slower than in the 3D Ti Bi$_{1-x}$Sb$_x$.\textsuperscript{48} At all temperatures, the relaxation rate increases monotonically with decreasing magnetic field. Even at very low temperatures near $\sim 10\text{ K}$, where most excitations are frozen out, the SLR remains substantial. 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.\textsuperscript{30,31} 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; however, consistent with the approach adopted in conventional NMR in similar materials,\textsuperscript{24,27,28,32} we model the spin relaxation using a stretched exponential. Explicitly,
for a $^8$Li$^+$ ion implanted at time $t'$, the spin polarization at time $t > t'$ follows:

$$R(t, t') = \exp \left\{ -[\lambda (t - t')]^\beta \right\},$$  \hspace{1cm} (1)

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 (1) convoluted with the 4 s beam pulse,\textsuperscript{45,46} SLR spectra 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 crucial in the analysis. To find the global least-squares fit, we used custom C++ code leveraging the MINUIT\textsuperscript{53} minimization routines implemented within ROOT.\textsuperscript{54} The fit quality is good in each case ($\chi^2_{\text{global}} \approx 1.02$) and a subset of the fit results are shown in Figure 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 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.

The resulting values of $1/T_1$ are shown in Figure 3. Consistent with the qualitative behavior of the data, $1/T_1$ is relatively slow at high fields, but both temperature and field dependent. At the highest field, 6.55 T, it is extremely slow and near the measurable limit imposed by the $^8$Li lifetime (grey region in Figure 3). As the field is lowered, $1/T_1$ increases, and its temperature dependence is clearly non-monotonic. Below $\sim 150$ K, $1/T_1$ increases approximately linearly with $T$, with a field dependent slope and $T \to 0$ intercept. At higher temperatures, pronounced $1/T_1$ peaks are observed, whose maxima $T_{\text{max}}$ are field dependent. As $B_0$ is lowered, $T_{\text{max}}$ shifts to slightly lower temperatures, with a more dramatic change when the field is decreased to mT (see Figure 4).

\subsection{Modelling $T_1(T, \omega_0)$}

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 peak,\textsuperscript{37} 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.\textsuperscript{37-39} As we discuss in more detail below, we attribute this fluctuation to diffusive motion of interstitial $^8$Li$^+$ in the vdW gap between quintuple layers 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,21,22 and probably of electronic origin. Based on this, we use the following model:

\[ \frac{1}{T_1} = a + bT + c(J_1 + 4J_2). \] (2)

The first two terms in Equation (2) 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. \( \lambda_{\text{diff}} \) differs from a coupling constant, \( c \), proportional to the mean-squared transverse fluctuating field and the \( n \)-quantum NMR spectral density functions, \( J_n \).39 In this context, \( J_n \) is a frequency dependent function peaked at \( T_{\text{max}} \), which occurs when the fluctuation rate driving relaxation matches \( n\omega_0 \). While the choice of a precise form of \( J_n \) depends in detail on the dynamics, we use the empirical expression of Richards,38 which gives the correct asymptotic limits for relaxation produced by 2D fluctuations,35 originating, for example, from diffusion of \(^{8}\text{Li}^+\) confined to the vdW gap. Explicitly,38

\[ J_n \approx \tau_c \ln \left[ 1 + (n\omega_0 \tau_c)^{-2} \right], \] (3)

where \( \omega_0 \) is the Larmor frequency, and \( \tau_c \) is the correlation time, assumed to follow an Arrhenius temperature dependence:

\[ \tau_c^{-1} = \tau_0^{-1} \exp \left[ -E_A/(k_BT) \right], \] (4)

where \( \tau_0^{-1} \) and \( E_A \) are the prefactor and activation energy, respectively, with \( T \) and \( k_B \) retaining their usual meanings of the absolute temperature and Boltzmann constant.

Table I. Results from the analysis of the SLR 1/\( T_1 \) peaks in Figures 3 and 4 using Equations (2) to (4). Here, \( \omega \) denotes the orientation of the Bi\(_2\)Te\(_2\)Se trigonal \( c \)-axis with respect to the applied field \( B_0 \) and \( E \) is the \(^{8}\text{Li}^+\) 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 (4) in Figure 8 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 parameters pairs \( \tau_0^{-1} \) and \( E_A \) may be attributed to the empirical Meyer-Neldel rule.56

| \( B_0 \) (T) | \( \omega \) (keV) | \( c \) (10\(^6\) s\(^{-1}\)) | \( \tau_0^{-1} \) (10\(^{12}\) s\(^{-1}\)) | \( E_A \) (eV) |
|-------------|-------------|-------------|----------------|-------------|
| 6.55       | 28          | 1.88(2)     | 1.02(13)       | 0.156(3)    |
| 3.60       | 10          | 5.08(10)    | 0.7(2)         | 0.153(6)    |
| 2.20       | 20          | 2.86(4)     | 28(7)          | 0.235(5)    |
| 2.20       | 5           | 7.23(16)    | 1.2(5)         | 0.173(9)    |
| 0.0075     | 28          | 0.07(1)     | 1              | 0.164(3)    |
|            |             |             | 0.8(3)         | 0.185(8)    |

C. Resonance Spectra

We now turn to the \(^{8}\text{Li}\) resonance in BTS. Typical spectra at high field are shown in Figure 6. Consistent with a non-cubic crystal, the \(^{8}\text{Li}\) NMR is quadrupole split (Section II A). This is confirmed by the helicity-resolved33 spectra (Figure 11 in Appendix B) which show opposite satellites in opposite helicities. The EFG that produces the splitting is characteristic of the \(^{8}\text{Li}\) site in the crystal. From the spectra, it is relatively small, on the order of a few kHz. In addition, a second unsplitted line is evident near the midpoint of the quadrupole pattern. This line must be due to a distinct \(^{8}\text{Li}\) site with a small, unresolved quadrupolar splitting, similar to the resonance in the vdW layered NbSe\(_2\).49 This suggests that the unsplitted line corresponds to \(^{8}\text{Li}^+\) in the vdW gap in BTS, where the interstitial EFGs are minimal (see e.g., Ref. 58).

This evidence for two sites suggests that our single component relaxation model in Section III B is too simple. However, more complicated relaxation functions suffer from overparametriza-
The resonance was found to evolve substantially with temperature, as shown in Figure 6. Here, the spectra have been normalized to the off-resonance steady-state asymmetry to account for the variation of intensity due to spin-lattice relaxation.\textsuperscript{59} While it is apparent that the satellite intensities and splitting remain nearly temperature independent, the amplitude of the central line increases significantly above \(\sim100\,\text{K}\), becoming the dominant feature at 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:\textsuperscript{36}

\[
v_q = \frac{e^2 q Q}{4\hbar}.
\]  

As the splitting is small (i.e., \(v_q \ll \nu_0\)), the satellite positions are given accurately by the first-order expression:\textsuperscript{36}

\[
v_i = \nu_0 - n_i v_q f(\theta, \phi, \eta),
\]  

where \(n_i = \pm 1(\pm 3)\) for the inner (outer) satellites. The angular factor

\[
f(\theta, \phi, \eta) = \frac{1}{2} \left(3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi\right),
\]  

scales the splittings according to the polar (\(\theta\)) and azimuthal (\(\phi\)) angles between the external field and the EFG principal axis. The parameter \(\eta \in [0, 1]\) is the EFG asymmetry, which for axially symmetric sites is zero. From \(\nu_0\), we additionally calculate the frequency shift, \(\delta\), in parts per million (ppm) using:

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

where \(\nu_{\text{MgO}}\) is the reference frequency position in MgO at 300 K with \(B_0 \parallel (100)\).\textsuperscript{47}

The helicity-resolved spectra (see Figure 11) were fit using the quadrupole splitting above with \(\nu_0\) and \(v_q\) as free parameters, in addition to line widths and amplitudes. Similar to the SLR spectra in Section III A, a global fitting procedure was used by way of ROOT\textsuperscript{s} implementation of MINUIT.\textsuperscript{53} 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 6. 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, discussed further in Appendix C, all reasonable interstitial $^{6}\text{Li}^+$ sites retain the 3-fold rotation axis of the hexagonal unit cell, supporting this simplification.

The main parameters extracted from this analysis are shown in Figure 7. 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 7, above $\sim 150$ K, the shift is nearly 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, appear in the bottom panel of Figure 7. Consistent with Figure 6, 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 $T^* \approx 180$ K of the trend, as indicated in Figure 7. The other spectral parameters are nearly independent of temperature. The line widths are about $\sim 6$ kHz, with the central Lorentzian narrowing slightly with increasing $T$. This narrowing is likely the cause of its increase in amplitude. Similarly, $\nu_q \approx 7.4$ 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 $^{6}\text{Li}^+$ 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.

IV. DISCUSSION

With the main results presented in Section III, the remaining discussion is organized as follows: in Section IV A, we consider the dynamics causing the high temperature $1/T_1$ peaks, while Section IV B considers the electronic properties of BTS giving rise to relaxation and resonance shifts at low temperature.

A. High temperature lithium-ion diffusion

The most likely source of the relaxation at high temperatures is diffusive motion of $^{6}\text{Li}^+$. 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, we expect a low barrier to interstitial diffusion for any implanted $^{6}\text{Li}^+$ in the vdW gap. Stochastic motion causes the local magnetic field and EFG to become time dependent causing relaxation. From the model of $1/T_1(T)$ introduced in Equation (2) from Section III B, we obtain the kinetic parameters listed in Table I. The success of the model is demonstrated by the good self-agreement in the barrier $E_A$ and prefactor $\tau_0^{-1}$, indicating that an activated dynamic process with a 2D spectral density provides a single common source for the observed $\lambda_{\text{diff}}$. Thus, the correlation rate $\tau_c^{-1}$ in Equation (4) represents the atomic hop rate $\tau^{-1}$. The small barrier, on the order of $\sim 0.2$ 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 ~$10^{12}$ 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 Meyer-Neldel rule, where $\tau_0^{-1}$ increases exponentially with increasing $E_A$, as is often observed for related kinetic processes.

In general, the exponent appearing in $J_n$ from Equation (3) can vary from $-1$ to $-2$, 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. 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 $^7$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 $^7$Li$^+$ in rutile TiO$_2$. Finally, for each $T_{\text{max}}$ we assume $\tau_0^{-1}$ matches the Larmor frequency ($\omega_0$). The results are shown in the Arrhenius plot in Figure 8, 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 I, we take it as the best determination of the $^7$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 unsplitted 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.

Using the $^7$Li$^+$ hop rate from above, we convert $\tau_0^{-1}$ to diffusivity via the Einstein-Smolouchowski expression:

$$D = \frac{f l^2}{2d\tau},$$

where $l$ is the jump length, $d = 2$ is the dimensionality, and $f$ is the correlation factor, assumed to be unity for direct interstitial diffusion, 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 12 in Appendix C), we estimate $D$ for $^7$Li$^+$, finding a value on the order of $10^{-7}$ cm$^2$ s$^{-1}$ at 300 K. An Arrhenius plot comparing the diffusivity of $^7$Li$^+$ in BTS with other cations in structurally related materials is shown in Figure 9. It is clear that the mobility of isolated $^7$Li$^+$ is exceptional; our estimate for $D$ greatly exceeds that of lithium in the well-known fast ion conductor $h$-Li$_x$TiS$_2$. Similarly, the lithium diffusion coefficient in lithium intercalated Bi$_2$Se$_3$ is considerably slower, possibly due to Li$^+$-Li$^+$ interaction. Interestingly, the mobility of Cu in isostuctural Bi$_2$Te$_3$ is also extremely high, as revealed by Cu radiotracer and electrochemical methods. Lastly, we note that similarly large $D$ values were reported recently for $^8$Li$^+$ in the one dimensional ion conductor rutile TiO$_2$ 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.

### B. 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
They are metallic, but are poor conductors due to disorder. The origin of the linearity of the Korringa slope is thus determined by the square of the product of $A$ and $\rho(E_F)$. In fact, on inspection of the $^9\text{Li}^+$ in BTS, we find it comparable to wide band metals with vastly higher carrier densities.\textsuperscript{81–83} While the coupling $A$ for implanted $^9\text{Li}^+$ 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).\textsuperscript{85} However, in highly disordered metals, the slope is strongly enhanced.\textsuperscript{81–85} Such an enhancement may account for the substantial slope we observe. However, Equation (10) 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.\textsuperscript{84} as found, for example, near the metal-insulator transition (MIT) in doped silicon.\textsuperscript{85} 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,\textsuperscript{86} 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.\textsuperscript{87} However, in BTS (in contrast to Si), due to the high dielectric constant and low effective mass, magnetic carrier freezeout\textsuperscript{88,89} 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.\textsuperscript{12,90} Similarly, the field and temperature dependent shifts in Figure 7 may reflect a constant (diamagnetic) contribution (cf. the $^{125}\text{Te}$ shift\textsuperscript{27}), 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 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 Bi₂Se₃).

Above, we only considered bulk origins for the $\lambda_e$. While we do not expect any direct coupling to the topological surface state 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. 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. In the latter case, the acceptor band is depopulated by the surface dipole. Calculations suggest this is not the case but there is substantial evidence for time-dependent band bending from ARPES. 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 (not shown).

We have, so far, focused exclusively on the interaction between $^8$Li and the electron spins. We should also consider its interaction with their orbital currents. Note that at 100 K 1/T₁ in BTS is comparable to semimetallic bismuth, 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 $^8$Li and its concentration dependence in BiₓSbx−, solid solutions. This mechanism is due to fluctuating electronic currents, so it is naturally related to the conductivity $\sigma$. Specifically:

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

where $\sigma_\omega(q, \omega_e)$ 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 $^8$Li⁺ in a layered conductor, the hyperfine coupling $A$ for interstitial $^8$Li can be particularly weak (e.g., Bi₂Se₂). 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 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. Lee and Nagaosa have explicitly considered the case of orbital relaxation in a 2D layered metal. They find a weak logarithmic singularity in $1/T_1$ in the clean limit that is cut off by a finite mean free path. 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 Bi₁−ₓSbx. They find $T$-linear relaxation when the chemical potential is outside the gap, but within the gap, an anomalous dependence that is explicitly field dependent via the NMR frequency $\omega_e$ as $\lambda_{orb} \propto T^3 \ln(2k_B T / h\omega_e)$. 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.

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 $^8$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 $^{209}$Bi or $^7$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 whose dependence on magnetic field has largely not been explored.

V. CONCLUSION

Using temperature and field dependent ion-implanted $^8$Li β-NMR, we studied the high temperature ionic and low temperature electronic properties of Bi₂Te₂Se. Two distinct thermal regions were found; above ~150 K, the isolated $^8$Li⁺ probe undergoes ionic diffusion with an activation energy $E_A = 0.185(8)$ eV and attempt frequency $\tau^{-1}_0 = 8(3) \times 10^{11}$ 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 of the spin-lattice relaxation 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.

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Stopping distribution and range for $^8\text{Li}^+$ implanted in Bi$_2$Te$_2$Se calculated using the SRIM Monte Carlo code.\cite{SRIM} The histogram profiles, shown on the left, are generated from simulations of $10^5$ ions. The ion range and strangle at each implantation energy are shown on the right. All measurements in this study correspond to average stopping depths $\geq 30$ nm below the crystal surface, well below where the topological surface state is expected to be important.

Appendix A: Implantation profiles

As mentioned in Section II B, $^8\text{Li}^+$ implantation profiles in BTS were predicted using the SRIM Monte Carlo code.\cite{SRIM} 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 10, we calculate, in the nomenclature of ion-implantation literature, the range and strangle (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 topological surface state is expected to be important.

Appendix B: Helicity-resolved resonance spectra

Typical helicity-resolved resonance spectra are shown in Figure 11, 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,\cite{satellites} with their precise (time-average) values depending on the relaxation details.\cite{relaxation}

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$_2$.\cite{central}

Note that there is no unshifted $m_{s1/2} \leftrightarrow m_{s1/2}$ magnetic sublevel transition, in contrast to spin $I = 3/2 \ ^7\text{Li}$. The 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.\cite{overlap}

Such a feature, in a noncubic layered crystal (see Figure 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 inset in Figure 11), whose evolution with temperature is shown in Figure 6.

Appendix C: $^8\text{Li}^+$ 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 $\text{Li}^+$ obtained by chemical intercalation.

BTS is structurally similar to the transitional metal dichalcogenides (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.\cite{intercalation}

Similarly, a variety of dopants have been intercalated into the tetradymite Bi chalcogenides, such as Cu,\cite{Cu} Ag,\cite{Ag} Au,\cite{Au} and Zn.\cite{Zn} Lithium has also been inserted into Bi chalcogenides,\cite{Li} but the precise sites for $\text{Li}^+$ in the vdW gap have not been determined.\cite{Lithium}

Note that in all these cases, intercalation is at the level of atomic %, so that intercalated species certainly interact (e.g., forming “stage” compounds).\cite{intercalation}

Based on this, we expect the lowest energy site for implanted $^8\text{Li}^+$ is within the vdW gap, similar to NbSe$_2$.\cite{similar} Here, the electric field gradients should be small, yielding a small quadrupole frequency, consistent with the unsplit resonance (see e.g., Ref. 58). Within the vdW gap, several high-symmetry Wyckoff sites are available (see Figure 12): the quasi-octahedral $3b$ at $(0, 0, 1/2)$; the quasi-tetrahedral $6c$ at $(0, 0, 1/6)$; and the
BTS, the QLs in BTS account a much larger volume fraction of the crystal, which leads us to consider possible interstitial different EFGs. Noting that, in contrast to the trilayers in suggesting a nearly density functional theory calculations confirm this assignment.

As indicated in Section III C, 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 $^8$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 ~3 of the values for the 3b site in the vdW gap (~2 kHz). 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 12 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 $^8$Li$^+$ that stops at a site within the QL, where it remains static over its lifetime. Similarly, we ascribe the unsplit line to $^8$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 IV A. Note that we find no evidence for a site change transition up to 317 K, indicating a substantial energy barrier separates the two sites.

2-fold coordinated 9d at (1/2, 0, 1/2). Here, the fractional coordinates correspond to the hexagonal unit cell shown in Figure 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 $^8$Li$^+$ and it is reasonable that this is the preferred site in the vdW gap. Indeed, preliminary density functional theory calculations confirm this assignment.

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