The Initial State of Optically Polarized $^8$Li$^+$ from the $\beta$-NMR in Bismuth

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Abstract. Unlike the positive muon, $\beta$-NMR probe nuclei must be actively polarized. At the TRIUMF ISAC facility this is accomplished by in-flight collinear optical pumping with resonant circularly polarized laser light. This reliably produces a high degree of polarization, but the detailed state populations in the beam emerging from the optical polarizer are not well known. These populations are significant as they represent the initial state of the ensemble of probe spins implanted in a $\beta$-NMR experiment. Here we use the well-resolved quadrupolar split spectrum of $^8$Li$^+$ in a high purity single crystal of bismuth to extract the sublevel populations under typical polarizer operating conditions, accounting for the spin relaxation in this semimetal.

1. Introduction

Unlike the positive muon, $\beta$-NMR probe nuclei must be actively polarized. At ISAC, this is accomplished by in-flight collinear[1] optical pumping with resonant circularly polarized laser light. Optical polarization is a well-developed technique in the vapour phase[2], particularly for alkali atoms. Noble gases may be spin-exchange polarized using optically polarized alkalis[3] and these have many applications in surfaces physics[4, 5], biology[6] and quantum computation[7]. Optical pumping with polarized light is also used to polarize nuclei in many semiconductors[8, 9, 10, 11]. Optically polarized radioactive nuclei are useful as probes of the solid state analogous to $\mu$SR[12] and also have important applications in nuclear physics[13].

The ISAC optical polarizer reliably produces a high polarization $\sim 70\%$ [14], but the detailed state populations in the beam emerging from the polarizer are not well known. These populations are significant as they represent the initial state of the ensemble of probe spins used in a $\beta$-NMR experiment. Moreover, with a spin $I = 2$ nucleus, 4 parameters (rather than 1 for spin 1/2) are required to specify the spin state. Here, we use the well-resolved quadrupolar split NMR spectrum of $^8$Li$^+$ in a high purity single crystal of bismuth to extract the sublevel populations under typical polarizer operating conditions, accounting for the spin relaxation in this semimetal. The few detailed measurements of the spin states of optically polarized atoms that have been performed serve as points of comparison[15, 16, 17].
2. Experiment

A freshly cleaved plate of high purity single crystal bismuth approx 1 cm$^2$ in area was mounted on a sapphire plate in the ultrahigh vacuum high field $\beta$-NMR spectrometer. The superconducting solenoid produced a highly homogeneous magnetic field of 6.55 T along the $^8$Li$^+$ beam direction (parallel to the trigonal axis of the crystal) providing the static NMR field as well as focusing the ion beam. A continuous beam of $\sim 10^6$ $^8$Li$^+$ ions per second was implanted at 20 keV into a beam spot $\sim 2$ mm in diameter centred on the crystal. A CW RF oscillating transverse magnetic field $H_1$ was applied with frequency stepped slowly (250 Hz/s) through a range of frequencies about the Larmor frequency. The beta decay asymmetry was monitored in two scintillation detectors downstream (F) and upstream (B) of the sample. The direction of polarization was alternated by introducing a half-wave plate into the polarizing laser beam. F/B asymmetry spectra were collected in both helicities, and the results are shown in Fig. 1.

![Figure 1.](image)

*Figure 1.* The $\beta$-NMR spectrum of $^8$Li$^+$ in bismuth. Here the two helicities (polarization directions) are shown with their baselines subtracted. The single quantum satellites are labeled with the corresponding $m$ values. The three narrow resonances marked M are multiquantum. The thin blue lines are the fits that yield the satellite amplitudes.

The resonance is split into a highly resolved multiplet consisting of the expected 4 first order (primary) quadrupole satellites$^{[18, 19]}$, interlaced with 3 narrower multiquantum resonances$^{[20]}$. The multiquantum nature of these resonances is confirmed by their position midway between the single quantum satellites, their narrowness$^{[21]}$, and, most clearly, they are suppressed very strongly as the RF power is reduced (much more so than the single quantum satellites). This is not the first time multiquantum resonances have been observed with $\beta$NMR$^{[22]}$, but it is the first example at TRIUMF, likely because the pattern is much better resolved here than in other materials$^{[18, 19]}$, reflecting the very high quality Bi crystal.

A quadrupole splitting is expected as the $^8$Li$^+$ site cannot be cubic in the rhombohedral structure of Bi, hence it should experience a finite electric field gradient (EFG). The spectrum was fit with a sum of 7 Lorentzians with the splitting determined by a single parameter $\nu Q \approx 8$ kHz. In the fits, the widths of the primary satellites are the same. The amplitudes of these satellites, crucial to the analysis in this work, for the two helicities are reported in Table 1.

Finally, in the absence of the RF field, a pulsed beam of $^8$Li$^+$ was implanted to monitor the small spin-lattice relaxation rate. The detailed results will be published elsewhere$^{[23]}$, but the relaxation is single exponential, with $\lambda = 1/T_1 = 0.088(5)$ s$^{-1}$ at 294 K. Moreover the
Table 1. Lorentzian amplitudes of the single quantum quadrupole satellites of $^8$Li$^+$ in Bi from the fits shown in Fig. 1.

| $m, m-1$ | Negative  | Positive  |
|----------|-----------|-----------|
| 2, 1     | 0.0161(2) | 0.0019(2) |
| 1, 0     | 0.00715(16)| 0.0029(2) |
| 0, −1    | 0.0037(2) | 0.0085(2) |
| −1, −2   | 0.0011(2) | 0.0123(2) |

The temperature dependence of $\lambda(T)$ is linear, implying Korringa relaxation which is magnetic in origin (rather than quadrupolar), simplifying the analysis below.

3. Analysis

Most generally, the state of the $^8$Li nuclear spin ($I = 2$) is described by the density matrix $\rho_{m_1 m_2}$, with diagonal elements representing the statistical populations of the 5 magnetic sublevels $m$ and off-diagonal elements representing coherences. In particular, it is the ensemble average spin state for $\sim 10^8$ spins obtained over several minutes of data collection that is relevant to the experiment. For the optically pumped state, we expect no coherences, so we restrict ourselves to spin states described by the vector of populations $p_m = \rho_{mm}$. The spin polarization is then defined as

$$P = \frac{1}{I} \sum_{m} m p_m.$$  \hfill (1)

The polarizer produces an initial polarization $P(0)$ that we assume is transported (at a typical energy of 20 keV) to the sample and implanted without loss. Once stopped, the $^8$Li$^+$ spin state evolves, relaxing towards equilibrium $P_{eq} \approx 0$ by spin–lattice relaxation. With a continuous beam, we measure the time average polarization

$$\bar{P} = \frac{1}{\tau} \int_{0}^{\infty} e^{-s/\tau} P(s) ds,$$  \hfill (2)

where $s$ is the time after implantation and $\tau = 1.21$ s is the radioactive lifetime.

Unlike the spin 1/2 $\mu^+$, where specifying the polarization is equivalent to specifying the spin state, for higher spins, there are more degrees of freedom, and many spin states yield the same $P$. For $^8$Li$^+$ 4 parameters specify the spin state,$^1$ and specifying $P$ leaves 3. Also, unlike spin 1/2 particles, $^8$Li$^+$ has an electric quadrupole moment that couples the spin to the local EFG, which is generally non-zero at sites of lower than cubic symmetry. This coupling splits the $|\Delta m| = 1$ Zeeman transitions, which would otherwise be degenerate at the Larmor frequency $\nu_L$, into a multiplet pattern of quadrupole satellites. The scale of the coupling is given by the quadrupole frequency $\nu_Q = e^2 qQ/4h$, where $Q = +31.4$ mb is the nuclear electric quadrupole moment, $e$ the electronic charge and the principal component of the EFG tensor is $eq$. Here $\nu_Q/\nu_L \sim 10^{-4}$ so the quadrupole interaction can be treated in first order, and we expect, for the field along the EFG principal axis, satellite lines at 1/2 and 3/2 $\nu_Q$ on either side of $\nu_L$. In addition, in this experiment, the RF field is strong enough that multiquantum transitions are evident$^{20, 21, 22}$. We thus assign the satellites as shown in Fig. 1. We assume the principle direction of the EFG is the trigonal axis of the crystal, but an orientation dependence is required to confirm this.

$^1$ The fifth is determined by the normalization $\sum p_m = 1$. 


The amplitude of the primary satellites is determined by the magnitude of the RF field and the time average population difference between the two $m$ levels involved,

$$A_{m1,m2} = a_{RF} |\bar{p}_{m1} - \bar{p}_{m2}|.$$  \hspace{1cm} (3)

In the measurement, the RF amplitude is constant across the spectrum, so the factor $a_{RF}$ is common to all the satellites. Thus, the satellite amplitudes give additional information to help determine the initial spin state. If $a_{RF}$ was known, then one could simply invert these linear equations using the satellite amplitudes in Table 1, and solve for the time averaged populations $\bar{p}_m$. Instead, we take ratios of the Eqs. (3), reducing the number of constraints from 4 to 3, and treat the polarization $\mathcal{P}$ as a variable over a range near the independently estimated value of 0.7, yielding the inferred average populations as a function of $\mathcal{P}$.

The primary interest is, however, the initial values of the populations $p_m(0)$ that is characteristic of the polarized beam and independent of the sample. To extract these values from the time averages, we adopt a simple model of the relaxation – the master equation, that captures the correct transition matrix elements among the sublevels. The observed Korringa relaxation is magnetic, so the transition matrix elements follow[24]

$$W_{m \rightarrow m-1} = w_{mag}(I + m)(I - m + 1),$$  \hspace{1cm} (4)

where $w_{mag}$ is the magnetic transition rate. The master equation is a system of first order rate equations for the evolution of the populations$^3$,

$$\frac{dp_m}{dt} = W_{mn} p_n,$$  \hspace{1cm} (5)

where the matrix $W_{mn}$ encodes the transition probabilities of Eq. (4) and the thermal equilibrium state that is the asymptotic limit as $t \rightarrow \infty$, $(p_m)_{eq}$, e.g. see Ref. [25]. Because the Zeeman splitting is much less than $kT$ for all experimentally accessible conditions, $(p_m)_{eq} \approx 0.2$, for all $m$. Eq. (5) can be solved by finding the eigenvalues of $W$, which for $I = 2$ are

$$\lambda_i = 10\lambda, 6\lambda, 3\lambda, \lambda, 0,$$  \hspace{1cm} (6)

where $\lambda = 1/T_1 = 2w_{mag}$. The solution of Eq. (5) is

$$p_m(t) = E_{mi} c_i e^{-\lambda_i t},$$  \hspace{1cm} (7)

where $E_{mi}$ are the eigenvectors of $W$, and the coefficients $c_i$ are determined by the initial populations. An example of the solutions for a representative initial state and the experimental relaxation rate in Bi is shown in Fig. 2. From these solutions, we compute the time averages and arrive at the relation

$$\bar{p}_m = \frac{E_{mi} E_{ni} p_n(0)}{\lambda_i \tau + 1}.$$  \hspace{1cm} (8)

This linear set of equations can then be inverted to yield the initial populations from the time averages deduced from the satellite amplitudes. For the negative helicity values in Table 1, the results of these calculations are shown in Figs. 3 and 4 as a function of the initial polarization $\mathcal{P}(0)$. Note that Eq. (3) does not enforce the physical condition that the populations must lie in the range $[0,1]$.

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2 The time average of the $p_m$ is analogous to Eq. (2).

3 We use the convention of summation of repeated indices throughout.
4. Discussion
First we note that the results do not uniquely determine the spin state, as there is still one degree of freedom, here represented by the initial polarization. The calculated populations are not, however, strong functions of $P(0)$, and one can use the results to yield well-defined ranges. The results show that the dominant population is in the extremal $m = -2$ sublevel as expected, but that there are substantial populations in both $m = -1$ and 0 states. This will have important implications for modeling quadrupolar lineshapes in other materials, particularly where the satellites are not well-resolved. The result is also important for a detailed treatment of spin relaxation that should account for a realistic initial state. One can also see from Table 1 that the two helicities are not polarized exactly complementarily, likely due to some unintended optical effect of the half-wave plate.

Figure 2. The calculated time evolution of the sublevel populations as they approach equilibrium from Eq. (5). Note the time range shown is much longer than the $^8$Li lifetime $\tau$.

Figure 3. Time average sublevel populations deduced from the negative helicity satellite amplitudes in Table 1 using Eq. (3) as a function of the initial polarization $P(0)$.

Figure 4. The corresponding initial state sublevel populations deduced from the average populations using the measured Korringa relaxation rate and Eq. (8)

One can also consider why the polarization is not higher, as the polarizer operates well into the saturation regime, where increasing the laser power does not further increase the polarization.
In contrast, stable alkali beams can be nearly completely polarized[15, 16]. The polarizer is well aligned with the beam axis and with the experimental magnetic field, and one can anticipate a negligible reduction due to misalignment. Imperfect circular polarization (ellipticity) of the laser is a more likely candidate, but even this could only account for a small reduction of polarization (a few %). Coherent effects from the very short pumping time (the beam traverses the polarizer in about 2 µs) may be responsible. The results presented here can be used as a diagnostic for further optimization of the ISAC polarizer, and this method complements those based on optical or EPR hyperfine spectroscopy[15, 16, 17].

5. Summary
We have used the highly resolved quadrupole spectrum of $^8\text{Li}^+$ implanted into bismuth to determine the intial state of the $^8\text{Li}^+$ spin in the beams used in $\beta$-nrm at TRIUMF. The results show that populations aside from the extremal $m = \pm 2$ are non-negligible and should be taken into account. The results also give a more detailed picture of the effectiveness of the optical polarizer.

Acknowledgments
We thank D.A. Bonn and B.J. Ramshaw for providing the bismuth crystal and S. Daviel, R. Abasalti and D. Vyas for technical assistance.

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