**β-NMR of Isolated $^8\text{Li}^+$ Implanted into a Thin Copper Film**

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Depth-controlled β-NMR was used to study highly spin-polarized $^8\text{Li}^+$ in a Cu film of thickness 100 nm deposited onto a MgO substrate. The positive Knight Shifts and spin relaxation data show that $^8\text{Li}^+$ occupies two sites at low temperatures, assigned to be the substitutional ($S$) and octahedral ($O$) interstitial sites. Between 50 to 100 K, there is a site change from $O$ to $S$. The temperature dependence of the Knight shifts and spin-lattice relaxation rates at high temperatures, i.e. when all the Li are in the $S$ site, is consistent with the Korringsa Law for a simple metal.

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Nuclear magnetic resonance (NMR) is a powerful tool for investigating the microscopic magnetic behavior in solid state systems. However, conventional NMR is often not sensitive enough to investigate thin film structures and generally cannot be used to study thick conducting samples. Recently, a high field, beta-detected $^8\text{Li}^+$ nuclear magnetic resonance (β-NMR) spectrometer with depth control was developed at TRIUMF in Vancouver, Canada. This novel instrument utilizes $^8\text{Li}^+$ (spin 2, lifetime 1.21 s) as the radioactive nuclear spin probe and provides enough sensitivity to allow NMR studies of thin metal structures to be carried out. These measurements are aimed at better characterizing the behavior of $^8\text{Li}^+$ as a prototypical impurity in metals and to enable investigations of finite-size effects in these materials. Furthermore, they establish the basis for future studies of other systems consisting of metal layers such as magnetic multilayers.

Using the TRIUMF β-NMR spectrometer, we recently carried out a detailed high field, depth resolved, $^8\text{Li}^+$ β-NMR study of a 50 nm Ag film. Two β-NMR resonances were observed at low temperatures which had Knight Shifts of +120(12) ppm and +212(15) ppm, implying that $^8\text{Li}^+$ sits in two different high symmetry sites in the FCC lattice. Although these shifts are small, the ability to apply high magnetic fields allowed the two signals to be easily resolved at all temperatures. Above $\approx 100$ K, the $^8\text{Li}^+$ makes a transition from the 212 ppm site to the 120 ppm site, suggesting that the 212 ppm signal is due to $^8\text{Li}^+$ residing in the octahedral ($O$) site and the 120 ppm signal is due to $^8\text{Li}^+$ in the substitutional ($S$) site. The site assignments were based on comparing the temperature dependence of the $S$ and $O$ signals with other β-NMR and channeling experiments in similar systems. For example, for $^{12}\text{B}$ in Cu, β-NMR cross-relaxation measurements clearly show that boron occupies the $O$ site at low temperatures, but moves to the $S$ site at high temperatures. The temperature dependences of the Knight Shifts and spin-lattice relaxation rates (i.e. $1/T_1$) were consistent with the Korringsa Law, implying that the $^8\text{Li}^+$ senses a free-electron like local electronic susceptibility in the thin Ag film.

Will similar behavior be observed for $^8\text{Li}^+$ implanted into thin films of other “simple” FCC elemental metals such as Cu? In this paper, we experimentally investigate if such expectations are valid by carrying out β-NMR studies of isolated $^8\text{Li}^+$ in a thin Cu film. In addition, since the host atoms in Cu have nuclear spin 3/2 and a relatively large quadrupole moment, this study lays down groundwork for the development of general techniques that can provide information on the local structure of the $^8\text{Li}^+$ site in thin films and near interfaces, such as “cross-relaxation” and (a preliminary study in) Au. $^8\text{Li}^+$ occupies two sites in Cu at low temperatures with Knight Shifts of +120(3) and +182(3) ppm, attributed to the $S$ and $O$ sites respectively. A transition from the 182 ppm site to the 120 ppm site occurs between 50 and 150 K. The spin lattice relaxation rate at high temperatures follows a Korringa law as expected for a simple metal. These measurements will provide a useful reference for future β-NMR and β-NQR experiments on samples that use Cu as a thin capping layer, a substrate, or as part of a multilayered structure.

In the NMR of metals, an important experimental quantity is the relative shift $\delta$ of the resonance frequency $\nu$ with respect to the Larmor frequency $\nu_0$ of the nucleus in an external magnetic field $H_0$, i.e. $\delta = (\nu - \nu_0)/\nu_0$. In many “simple” metals, $\delta$ is the Knight shift ($K$); it is independent of temperature and is a consequence of the Fermi contact interaction of the nuclear spin with the weak Pauli spin paramagnetism of the conduction
electrons. A second important experimental quantity is the spin-lattice relaxation rate $1/T_1$ of the nucleus. Under the aforementioned conditions where the contact hyperfine interaction dominates, the random spin-flip scattering of the conduction electrons from the nucleus leads to a linear temperature dependence of the $1/T_1$ rate, and hence a product $T_1 T$ that is independent of temperature. Furthermore, the so-called Korringa Law is satisfied: $(T_1 T K^2)/X = 1$ where $X = (\gamma_e/\gamma_n)^2(\hbar/8\pi^2 k_B)$, with $\gamma_e$ and $\gamma_n$ denoting the gyromagnetic ratios of the electron and nucleus respectively. In the case of $^8\text{Li}^+$, the nuclear probe that is of relevance in this paper, $\gamma_n = 8 \gamma = 6.3015 \text{ MHz/T}$, and hence $X = 1.2022 \times 10^{-5}$ s K.

Our current $\beta$-NMR studies are on a Cu film of thickness 100 nm grown via thermal evaporation at a rate of 0.7 nm/s from a 99.999% purity Cu source in a pressure of $10^{-7}$ Torr onto a MgO substrate. A low energy (30.6 keV) beam of highly polarized $^8\text{Li}^+$ is produced at the Isotope Separator and Accelerator (ISAC) facility at TRIUMF and implanted into the sample\cite{10,11}. A large nuclear polarization ($\approx 70\%$) of the $^8\text{Li}^+$ is generated in-flight using a collinear optical pumping method. The $\beta$-NMR spectrometer resides on a high voltage platform which allows the implantation energy of the $^8\text{Li}^+$ to be varied between 1 − 30 keV when a suitable positive bias is applied to the platform. These implantation energies correspond to an average depth from 3 to 100 nm, as calculated using TRIM.SP\cite{12}. In $\beta$-NMR the nuclear polarization, i.e. the quantity of interest, is monitored by detecting the $\beta$s that are emitted preferentially opposite to the direction of the $^8\text{Li}^+$ polarization at the time of decay (i.e. parity violation). The emitted betas are detected using plastic scintillation counters forward and backward to the initial $^8\text{Li}^+$ polarization. The experimentally observed asymmetry $A(t)$ of the $\beta$ countrates is proportional to the $^8\text{Li}^+$ nuclear spin polarization. In our experiment, we are interested in measuring the magnetic resonance signal and the spin-lattice relaxation rate $1/T_1$:

1. The magnetic resonance is detected by monitoring the time-averaged nuclear polarization as a function of the frequency $\nu$ of a small perpendicular radiofrequency (RF) magnetic field ($\sim 10^{-4}$ T). The resonance condition is satisfied when $\nu$ is equal to the Larmor frequency of $^8\text{Li}^+$ in the internal field. On resonance, there is a reduction in the nuclear spin polarization; hence, $A(t)$ and consequently $A(\nu) = (A(t))$ decreases.
2. The spin-lattice relaxation rate $1/T_1$ is measured with the RF off. The beam is admitted for 0.5 s every 15 s, and the evolution of the asymmetry $A(t)$ is measured. Recall that $1/T_1$ is the rate at which the asymmetry relaxes from its initial value at $t = 0$ to its equilibrium value (i.e. zero polarization).

First, we discuss the resonance data. By implanting at the full energy (30.6 keV), a significant fraction of the $^8\text{Li}^+$ stops in the cubic insulator MgO, providing an in-situ reference of its Larmor frequency in the applied field $\nu_{\text{MgO}}$ (see Fig. 1). This is true because the Knight shift of the $^8\text{Li}^+$ in an insulator should be zero, and we also expect the chemical shift to be small\cite{13}. In Fig. 1 the zero frequency shift corresponds to $\nu_{\text{MgO}} = 25.83994(5)$ MHz. Then, at each temperature, the implantation energy is reduced to 10.6 keV, a value chosen so that all of the $^8\text{Li}^+$ stops in the Cu film; representative spectra at a number of temperatures in an applied field of 4.1 T are shown in Fig. 1. The following qualitative features are apparent: At all temperatures, resonances are observed that are positively shifted from zero, demonstrating that we are able to detect the Knight Shifts due to $^8\text{Li}^+$ in the thin Cu film. At low temperatures, the lineshape is noticeably asymmetric. In order to better understand the origin of this asymmetry, we examined the shapes of the signal with the $^8\text{Li}^+$ forward and backward polarized, i.e. with $^8\text{Li}^+$ initially (primarily) in the $m = +2$ and $m = -2$ state (in our instrument, this can be done by changing the sense of rotation of the circularly polarized pumping light). We find that the lineshape is skewed towards higher frequencies in both situations. This establishes that the asymmetric lineshape is not due to unresolved quadrupole effects since the existence of such interactions would result in a skewness towards high frequencies in one instance and a skewness towards lower

![FIG. 1: (color online) Representative resonance signals of $^8\text{Li}^+$ in the Cu/MgO sample in an applied field of 4.1 T. Each spectrum was obtained at an implantation energy of 10.6 keV, except the bottommost one, which was obtained at the full implantation energy of 30.6 keV. The three vertical dashed lines indicate the peak frequencies of the MgO, S and O signals. The zero shift in frequency is taken to be that in MgO at room temperature. The long-dashed lines indicate the S and O contributions of the signal at each temperature.](image-url)
frequencies in the other instance\cite{14}. Hence, these measurements rule out a model where the resonance is due to $^8\text{Li}^+$ stopping in a single non-cubic site since such a center should experience a significant quadrupole interaction. Therefore, the asymmetric line at low temperatures indicates that $^8\text{Li}^+$ occupies two inequivalent cubic sites, and each site is characterized by a different positive Knight shift. However, the shifts are not large enough to be clearly resolved. As the temperature is raised, the line becomes more symmetric and the peak frequency shifts to lower values. This indicates that a change in site has occurred.

The resonance signals at all temperatures can be fit to a sum of two Gaussians:

$$A(\nu) = A_b + \frac{A_S}{W_S \sqrt{\pi}} \exp\left[\frac{-2(\nu - \nu_S)^2}{W_S^2}\right] + \frac{A_O}{W_O \sqrt{\pi}} \exp\left[\frac{-2(\nu - \nu_O)^2}{W_O^2}\right], \quad (1)$$

where $W_S$ and $W_O$ are the widths and $\nu_S$ and $\nu_O$ are the peak frequencies. These four parameters are assumed to be the same at all temperatures. The remaining parameters $A_b$ (baseline term), $A_S$, and $A_O$ were allowed to vary with temperature. In anticipation of our assignment of the sites, discussed below, the subscripts $S$ and $O$ are used to denote the substitutional and octahedral sites respectively. The fitted widths are $W_S = 3.205 \pm 0.006$ kHz and $W_O = 4.33 \pm 0.02$ kHz (the error estimates are entirely statistical\cite{15}). The Knight Shifts\cite{16} can be obtained from the fitted values of $\nu_S$ and $\nu_O$, as well as $\nu_{MgO}$, to be $K_S = +120 \pm 3$ ppm and $K_O = +182 \pm 3$ ppm. These values are indicated as vertical dashed lines in Fig. 1. The normalized amplitudes are shown in Fig. 2 demonstrating that, as the temperature is increased, there is a thermally activated transition from the $O$ to the $S$ site. Note that the amplitudes do not add up to unity. Possible explanations include: (i) insufficient RF power to saturate the $S$ and $O$ lines and (ii) the existence of very broad lines due to $^8\text{Li}^+$ stopping in sites of non-cubic symmetry, and would hence have significant quadrupole interaction.

Our results for $^8\text{Li}^+$ in Cu are similar to that obtained in the Ag film studied recently\cite{1}. For example, the measured low temperature Knight Shifts in Cu are similar to those in the Ag film\cite{1} of 120 ppm and 212 ppm. There, the sites were attributed to $^8\text{Li}^+$ located in the substitutional ($S$) and octahedral ($O$) sites respectively. As discussed in the introduction, such an assignment was made by comparing the data with the “typical” temperature dependence seen for light radioactive impurities in metals, and for $^{12}\text{B}$ in Cu in particular\cite{2}. By analogy, in Cu, we make an assignment of the 120 ppm signal to the $S$ site and the 182 ppm signal to the $O$ site. As Fig. 2 indicates, $^8\text{Li}^+$ makes a transition from the 182 ppm site to the 120 ppm site between $\approx 50$ to 100 K. This is likely a consequence of a thermally activated transition of the interstitial $^8\text{Li}^+$ to a nearby vacancy created during the implantation process. It is worthwhile pointing out that Ohsumi et al. \cite{17} also assigned their high temperature site to the $S$ site after considering the $\beta$-NMR linewidths of $^8\text{Li}^+$ in a single crystal of Cu\cite{17}. However, some of their conclusions are different from ours. They propose that $\approx 30\%$ of the $^8\text{Li}^+$ stops in an $O$ site. In addition, they were not able to detect any changes from 11 K to 300 K that could be attributed to a site change. The reasons for the discrepancies with our observations are not clear, but could partly be due to the fact that their studies were conducted at significantly lower applied field, and hence are even less able to resolve two closely spaced lines. It would require the development of powerful spectroscopic techniques such as cross-relaxation to unambiguously establish the location of $^8\text{Li}^+$ at all temperatures.

The linewidths of the $^8\text{Li}^+$ resonance signals in Cu are significantly larger than those in Ag\cite{1}. The dominant broadening mechanism of the $\beta$-NMR signals is from the dipolar broadening by the host spins\cite{18}. Hence, the larger linewidths in Cu compared to Ag are expected since the nuclear moments of the Cu host atoms are about an order of magnitude greater than those of Ag\cite{19}. Furthermore, the lattice constant of Cu (0.361 nm) is smaller than that of Ag (0.408 nm). The fitted linewidths to Eq. 1 imply that the second moments of the lines are 3.08 kHz$^2$ and 5.63 kHz$^2$ for the $S$ and the $O$ sites respectively. The former is comparable to the prediction of 1.44 kHz$^2$ for $^8\text{Li}^+$ in an undistorted $S$ site\cite{17}. The extra broadening may be partly due to the higher RF power used\cite{20} here compared to Ref. 17 ($\sim 3$ times higher).

We now discuss the spin relaxation data of $^8\text{Li}^+$ in the Cu film. The inset in Fig. 3 shows examples of the asymmetry $A(t)$; it is phenomenologically well-described at all temperatures by a single exponential relaxation function with decay rate $1/T_1$. The temperature dependence of the $1/T_1$ rates are shown in Fig. 3 and are obtained in applied magnetic fields of 4.1 T and 6.5 T. The $1/T_1$ values are the same at these two fields, as expected if
the dominant relaxation mechanism at these fields is Korringa relaxation. The resonance data described above have shown that at high temperatures (above \(\approx 100\) K), all the \(^6\text{Li}^+\) are in the \(S\) site; here, the \(1/T_1\) rates are due to the \(S\) site only. They are linear with temperature, and are described by \((T_1 T)^{-1} = (1.059 \pm 0.026) \times 10^{-3}\) \(s^{-1}K^{-1}\). By combining this value with the experimentally determined \(K_S\) of +120 ppm we obtain a Korringa ratio of \(T_1TK^2/X = 1.13 \pm 0.05\), close to the value of unity expected from the Korringa law. This agreement implies that \(^6\text{Li}^+\) senses a local susceptibility that is free-electron like. Note that at low temperatures, there is significant occupation of both the \(S\) and \(O\) sites and the effective \(1/T_1\) rates consist of contributions from \(^6\text{Li}^+\) in both these locations. For comparison, the dashed line in Fig. 3 shows the calculated effective rates obtained by using the resonance amplitudes from Fig. 2: the relaxation rates of the \(S\) site at high temperatures, and the Knight shifts of the \(S\) and \(O\) sites. The calculations are in reasonable agreement with the measured results. The deviation at low temperature is most probably due to an additional site with a broad line that was not observed in our resonance measurements, but contributes to \(A(t)\).

By comparison, Ohsumi et al.\(^{17}\) have reported the \((T_1 T)^{-1}\) values for \(^8\text{Li}^+\) in Cu at 20 K, 100 K, and 280 K. They found that this quantity is nearly independent of temperature with an average value of \((2.4 \pm 0.1) \times 10^{-3}\) \(s^{-1}K^{-1}\). They did not report a value for the Korringa ratio since measurements of the Knight Shifts were not carried out. Our value of the Korringa ratio of 1.13 \(\pm 0.05\) is somewhat smaller than that of \(^{63,65}\text{Cu}\) in Cu of 1.9 \(^{21}\).

We briefly point out that our preliminary studies in a Cu crystal have shown that \(1/T_1\) is independent of the magnetic field above \(\approx 0.07\) T, but is highly field dependent below this value. For example, at 200 K, the phenomenological \(1/T_1\) rates change from the constant value at \(\approx 0.2\) \(s^{-1}\) at higher fields to \(\approx 0.7\) \(s^{-1}\) near zero field. We believe that in this regime, the dipole-dipole interactions between the \(^8\text{Li}^+\) and the Cu nuclei contribute significantly to the \(1/T_1\) rates. The qualitative explanation for these effects are discussed in numerous references, including Ref. \(^{4,22,24}\). We defer the quantitative discussion of the low field behavior of the \(^8\text{Li}^+\) relaxation in Cu, as well as other simple metals such as Ag, Au and Al, to a future publication.

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**Fig. 3:** (color online) The temperature dependence of \(1/T_1\) at 4.1 T (black circles) and 6.55 T (red stars). The straight line is a best fit to the data above 100 K through the origin while the dashed line is the calculated effective relaxation rate (see text).

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gyromagnetic ratios 11.33 MHz/T and 12.10 MHz/T respectively. By contrast, Ag has two isotopes with a nuclear spin $I = 1/2$: $^{107}$Ag (abundance 51.8%) and $^{109}$Ag (abundance 48.2%) with gyromagnetic ratios $-0.173$ MHz/T and $-0.1992$ MHz/T respectively.

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