\(^8\)Li\(^+\) Knight shift and Resonance in the Enhanced Paramagnet Platinum studied by \(\beta\)NMR

Oren Ofer\(^a\), K.H. Chow\(^b\), I. Fan\(^b,c\), M. Egilmez\(^h,d\), T.J. Parolin\(^e\), M.D. Hossain\(^f\), J. Jung\(^h\), Z. Salman\(^g\), R.F. Kiefl\(^f,h\), C.D.P. Levy\(^a\), G.D. Morris\(^a\), M.R. Pearson\(^a\), H. Saadaoui\(^g\), Q. Song\(^f\), D. Wang\(^f\), W.A. MacFarlane\(^e\)

\(^a\)TRIUMF, 4004 Wesbrook Mall, Vancouver, BC, V6T 2A3 Canada
\(^b\)Department of Physics, University of Alberta, Edmonton, AB, T6G 2G7 Canada
\(^c\)Department of Physics, National Tsing Hua University, Hsinchu, Taiwan, R.O.C. 30013
\(^d\)Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, England, CB2 3QZ
\(^e\)Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z1 Canada
\(^f\)Department of Physics and Astronomy, University of British Columbia, Vancouver, BC V6T 1Z1 Canada
\(^g\)Paul Scherrer Institute, Laboratory for Muon Spin Spectroscopy, 5232 Villigen PSI, Switzerland
\(^h\)Canadian Institute for Advanced Research, CIFAR

Abstract

We report the behavior of \(\^8\)Li\(^+\) implanted into Platinum foil as revealed by \(\beta\)-detected Nuclear Magnetic Resonance (\(\beta\)-NMR). At an applied field of 4.1 T, a single resonance is observed, which is attributed to Li in an octahedral interstitial site. The temperature dependence of the Knight shift for this resonance is monitored at temperatures ranging from 4 to 300 K. Over this range the Knight shift is found to be linearly dependent on the temperature.

Keywords: Pt, \(\beta\)NMR, Knight shift

1. Introduction

Here we report the results of \(\beta\)NMR studies of \(\^8\)Li\(^+\) in a high purity Platinum (Pt) foil (5N). Pt is an enhanced paramagnet which differs from other noble metals such as Au, Ag or Cu. Instead it is closely related to Palladium. Pt has a strong electron exchange interaction that results in an enhanced paramagnetic susceptibility, which is often observed as a large temperature-dependent paramagnetic susceptibility. The measurements presented here can provide a useful reference for future \(\beta\)NMR experiments on heterostructures with Pt overlayers, finite size effects of low-dimensional Pt, as well as depth-controlled experiments on samples which use Pt as a substrate, multilayer or part of a monolayer.

2. Experiment

The experiments were conducted at the TRIUMF ISAC facility, which provides a low energy (\(\approx\) 30 keV) beam of hyperpolarized \(\^8\)Li\(^+\), at a typical rate of 10\(^7\) ions/s. Here, we briefly describe the resonance experiment and the...
corresponding calculation of the Knight-shift. The $^8\text{Li}^+$ probe has a spin $I = 2$, a quadrupolar moment $Q/e = +31 \text{ mb}$, a nuclear gyromagnetic ratio $g = 6.3015 \text{ MHz/T}$, and a lifetime of $\tau = 1.2 \text{ s}$. About 70% spin polarization of the $^8\text{Li}^+$ nuclei is produced by optical pumping and the sense of circular polarization (helicity) of the pumping laser is selected such that the spin polarization direction is either parallel or antiparallel to the applied magnetic field. Data is collected under both polarizations repeatedly for accurate baseline determination. The $^8\text{Li}^+$ penetrate the sample mounted on a coldfinger cryostat in an ultra-high vacuum chamber situated in the bore of a superconducting magnet producing homogenous magnetic field, $H_0$. The measurements described here were done with applied $H_0 = 4.1\text{ T}$. The ion beam is focused to a 3-mm diameter beamspot.

The resonance measurements were performed when a small radio-frequency magnetic field, $H_1 \approx 100 \mu\text{T}$, is applied transverse to the spin polarization and $H_0$. The $H_1$ frequency, $\nu$, is randomly swept within a given interval and the resonance is achieved when the Larmor condition is satisfied, $\nu = gB_{\text{int}}$, where $B_{\text{int}}$ is the internal field experienced by the $^8\text{Li}^+$ ion. It is then identified by the loss of the time-averaged asymmetry, $A(\nu)$. The resonance spectra are well described by a Lorentzian lineshape,

$$ A(\nu) = \frac{A_0}{\nu} \frac{w}{(\nu - \nu_{\text{Pt}})^2 + w^2} $$

where $A_0$ is the amplitude, $\nu_{\text{Pt}}$ is the Pt resonance with a width $w$ (FWHM). We find that $w$ has no temperature dependence with a mean 1.2(1) MHz, supporting a single site occupancy. For the calculation of the Knight-shift, a reference sample was also measured. An ideal reference sample would be an insulating compound which does not exhibit any frequency shift, particularly in the temperature range measured with the Pt sample. Moreover, the resonance of the reference sample indicates the true value of the field at the sample position. Therefore, measurements of the cubic insulator MgO were performed before and after the Pt sample. The MgO reference measurements revealed $\nu_{\text{MgO}} = 25.834738(3) \text{ MHz}$.

### 3. Results

Figure 1a depicts the typical resonance spectra of $^8\text{Li}^+$ in Pt taken at 295 K and 6 K. A single resonance is observed in contrast to previous $\beta$NMR studies on other nobel metals such as Au[1], Ag[2], Cu[3] and Pd[4], where a double site occupancy is observed indicated by a closely spaced but distinct resonances. The single resonance peak with a temperature independent $w$ suggests a single site occupancy of the $^8\text{Li}^+$ in the FCC structure of Pt. Moreover, since the resonance measured close to the Larmor frequency of the applied field establishes that $^8\text{Li}^+$ is located in a cubic-
symmetric site, which in a FCC structure could be substitutional, octahedral or tetrahedral. The tetrahedral site could be ruled-out due to the relatively small lattice constant of Pt.

The frequency shift, \( \delta = \nu_{\text{Pt}} - \nu_{\text{MgO}} \), is shown in Fig. 1b. We find that \( \delta \) is negative and decreases monotonically with decreasing \( T \). This is analogous to Pd[1] but different from other noble metals, where a positive shift is observed. The frequency shift \( \delta \) corrected for demagnetization effects, by assuming that the Pt foil acts as a thin slab[6], using

\[
K(T) = \delta(T) + \frac{8\pi}{3} \frac{\rho}{M_r} \chi
\]  

where, for Pt, the density \( \rho = 21.45 \text{ g/cm}^3 \), the molar mass \( M_r = 195.1 \text{ g/mol} \) and \( \chi \) is the measured bulk susceptibility. The calculated \( K(T) \) is shown in Fig. 1b and the bulk susceptibility, measured using Quantum Design Magnetic Property Measurement System with 4.1 T applied field, is depicted in Fig.2a. \( \chi(T) \) is almost \( T \) independent, it has only \( \approx 10\% \) difference in this temperature range, indicating the dominance of the Pauli-like susceptibility. Hence the correction to \( \delta \) is nearly a constant, which can be seen by comparing \( \delta \) and \( K \), both shown in Fig. 1b.

In Fig. 2b we plot the Knight shift versus the bulk susceptibility \( \chi \) with \( T \) as an implicit parameter. A linear dependence is found at high \( T \), however a sudden increase in \( K(\chi) \) is observed below \( \chi \leq 2.31 \times 10^{-4} \text{ emu/mol} \). The observed temperature dependence of \( \chi \) exhibits an anomalous increase below 80 K (see Fig. 2a), which is usually attributed to impurities[5]. Hence, we can associate the drop in \( K(\chi) \) to the impurity contribution originating from the bulk \( \chi \) data. It should be noted, that in the early work of Ref.[5], a deviation from linearity in the \( K - \chi \) was seen at the lowest \( T \) measured, however the \( T \) was not given. The inset of Fig. 2b, shows the \( ^{195}\text{Pt Knight-shift (}K_{\text{Pt}}, \text{ from Ref. [5]) versus the } ^{8}\text{Li} \ K(T) \) where a linear dependence is seen with the exception of the lowest measured point of \( K_{\text{Pt}} \). The Knight-shift \( K \) is expected to follow the linear Jaccarino relation, \( K = A\chi \), where \( A \) is the hyperfine coupling. The slope from a linear fit to the experimental data, shown as the solid line, yields the hyperfine coupling constant \( A = -13.1 \pm 0.1 \text{ kG}/\mu\text{B for } ^{8}\text{Li}^+ \text{ in Pt.} \)

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5. References

[1] T. J. Parolin, Z. Salman, K. H. Chow, Q. Song, J. Valiani, H. Saadaoui, A. O’Halloran, M. D. Hossain, T. A. Keeler, R. F. Kiefl, S. R. Kreitzman, C. D. P. Levy, R. I. Miller, G. D. Morris, M. R. Pearson, M. Smadella, D. Wang, M. Xu and W. A. MacFarlane, Phys. Rev. B 77, 214107 (2008).

[2] G. D. Morris, W. A. MacFarlane, K. H. Chow, Z. Salman, D. J. Arseneau, S. Daviel, A. Hatakeyama, S. R. Kreitzman, C. D. P. Levy, R. Poutissou, R. H. Heffner, J. E. Elenewski, L. H. Greene and R. F. Kiefl, Phys. Rev. Lett. 93, 157601, (2004).

[3] Z. Salman, A. I. Mansour, K. H. Chow, M. Beaudoin, I. Fan, J. Jung, T. A. Keeler, R. F. Kiefl, C. D. P. Levy, R. C. Ma, G. D. Morris, T. J. Parolin, D. Wang and W. A. MacFarlane, Phys. Rev. B 75, 073405 (2007).

[4] T. J. Parolin, Z. Salman, J. Chakhalian, Q. Song, K. H. Chow, M. D. Hossain, T. A. Keeler, R. F. Kiefl, S. R. Kreitzman, C. D. P. Levy, R. I. Miller, G. D. Morris, M. R. Pearson, H. Saadaoui, D. Wang and W. A. MacFarlane, Phys. Rev. Lett. 98, 047601 (2007).

[5] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).

[6] M. Xu, M. D. Hossain, H. Saadaoui, T. J. Parolin, K. H. Chow, T. A. Keeler, R. F. Kiefl, G. D. Morris, Z. Salman, Q. Song, D. Wang, W. A. MacFarlane, J. Magn. Res. 191, 47 (2008).