β-NMR of Palladium Foil

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Abstract

Beta-detected NMR (β-NMR) of low energy implanted ^{8}Li$^+$ was studied in metallic Palladium. The resonance was found to have a large negative shift with respect to the reference signal in the cubic insulator MgO. This shift exhibited significant temperature dependence on cooling below room temperature, approximately proportionate to the temperature dependent spin susceptibility of pure Pd. Thus it is tentatively attributed to a Knight shift (K) caused by a large negative hyperfine coupling; a phenomenon common in transition metal ions, but not in alkalis. However, the spin lattice relaxation of ^{8}Li is much slower than expected from the Korringa law for such a large K. We compare results from samples of very different thicknesses: 12.5 μm foil and a 100 nm thin film.

Key words: β-NMR, Palladium, Knight shift, Nuclear probes.

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1. Introduction

Long known to be a strongly exchange-enhanced paramagnet, the properties of Pd films are of interest both theoretically and experimentally. On account of its large Stoner parameter ($s \simeq 10$), ferromagnetic ordering can be induced in Pd for very dilute concentrations of $3d$ impurities[1]. Examples of other properties reported for Pd films include the observation of a large increase in the susceptibility of Pd layers sandwiched between Au[2], and superconductivity following low temperature irradiation with He$^+$[3]. For metals with large s, changes in structure are expected to produce significant changes in the electronic and magnetic properties[2], and as such, Pd may be an excellent candidate in which to look for confinement effects. A μSR study of metallic Pd found a room temperature Knight shift (K) for μ^+ of -223(80) ppm[4]. Here we report on analogous measurements of $K(T)$ for ^{8}Li in Pd foil using the complementary technique of β-NMR.

In these experiments an optically spin-polarized, 30 keV, beam of ^{8}Li$^+$ ($\tau = 1.2$ s, $I = 2$) is focussed onto a sample mounted on a coldfinger cryostat in a UHV chamber. A static longitudinal magnetic field

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is applied by a superconducting solenoid. Plastic scintillators are mounted forward and backward to the initial Li spin direction (the ion beam passes through a hole in the back detector). At the time of decay (^{8}Li$\rightarrow$^{8}Be + e$^-$ + ν_e) the β electron is preferentially emitted in a direction parallel to the Li spin. The anisotropy in the decay results in an observed asymmetry between the two detector rates. A continuous-wave oscillating RF magnetic field is introduced perpendicular to the static field. This field is slowly stepped through a chosen frequency range, and on resonance, destroys the Li polarization resulting in a loss of asymmetry. The asymmetry versus applied RF frequency yields the β-NMR spectrum. The spectrometer may be biased enabling electrostatic deceleration of the ion beam, and variable implantation energies of 0.5–30 keV.

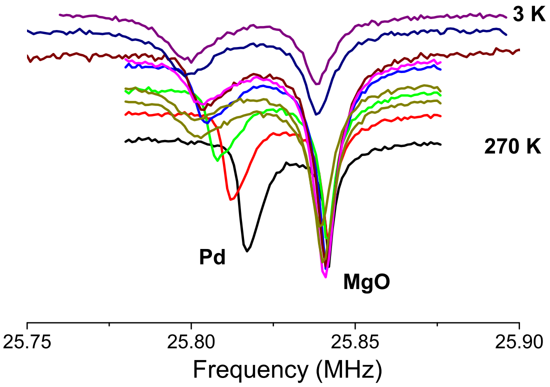

Fig. 1. Temperature dependence of the β-NMR spectrum in Pd foil at 4.1 T. In these composite spectra a narrow MgO line moves little with temperature, while the Pd signal shifts to lower frequencies and becomes significantly broader with decreasing T.

2. Experimental results

A piece of 99.95% Pd foil (Alfa Aesar) was wrapped around a single crystal of MgO. A small pinhole was used to pierce the foil and expose the MgO backing. Centering the beam onto this hole allowed for the simultaneous collection of a signal from both materials at 4.1 T (See Fig. 1). The signal from ^{8}Li$^+$ stopping in insulators like MgO is expected to be little shifted from the Larmor frequency ($\nu_L \approx$25.836 MHz at the nominal field). The high frequency signal close to this value is assigned to the MgO backing. It is immediately apparent that the shift of the Pd signal is quite large and negative relative to the MgO reference (ν_r). Indeed the observed Knight shift $K = (\nu - \nu_r)/\nu_r$ is as large as -900 ppm at room temperature; -1500 ppm at 3 K.

Pd is one of the few metals whose Pauli susceptibility varies with temperature. The temperature dependence of K was shown to track χ in a study that was the first to observe the NMR of ^{105}Pd[5]. The variation of K with T is not surprising; however, the large magnitude of the shifts is unexpected for the small alkali. A second unexpected result is the negative shift in the Pd. Perhaps not coincidently, large, negative intrinsic Knight shifts ($\sim -3 \times 10^4$ ppm) have been observed in the conventional NMR of Pt and Pd where core polarization plays a role. However, *a priori* such behavior is not expected to be observed in the NMR of alkali metals[6].

The signal from the Pd is also quite broad, even at room T, requiring relatively high RF power ($\sim$10 W) to obtain a reasonable amplitude. The broadening is likely a result of inhomogeneity of the local field; due mostly to the magnetization induced in the Pd by dilute magnetic impurities. As seen in Fig. 1 the Pd lines broaden by a factor of $\sim$4 as T is lowered.

Less evident in Fig. 1 are the small amplitude shoulders that appear at lower T; suggestive of multiple overlapping peaks. The peaks are too broad to be resolved, but the resonances can be reasonably fit by two overlapping Gaussians. There are two possibilities for the stopping sites: an interstitial site, and a substitutional site. It is consistently found that for light implanted ions the octahedral interstitial sites are favored in FCC metals[7], while at sufficiently high temperatures often only the substitutional sites can be detected[8]. This data does not allow for a definitive assignment of signals; however, the absence of quadrupole splitting indicates both sites are cubic. It is expected that the interstitial site will increase in amplitude as T is reduced, and as a result of being a more confined, will have the larger $|K|$[8].

Thin film samples can experience *de*magnetization effects due to their shape. The larger than expected K is obviously not related to such an effect. Another possible explanation for such large values is the influence of the stray field from the foil on Li in the MgO. This field could result in a shift of ν_r to higher frequency, artificially increasing K. However, if this were the case, a significant temperature dependence of the absolute MgO position would be expected, in contrast to the temperature independence seen in Fig. 1. It is reasonable to conclude that the magnetization of the foil is not influencing the resonance frequency in MgO. Finally, the large K can not be due to the foil-with-pinhole geometry as a similar sample constructed of Nb foil and crystalline MgO gave rise to a small, positive K[9].

The relation between the observed $K(T)$ and $\chi(T)$ is best illustrated by the plot shown in Fig. 2 (cf. Fig. 5 of Ref. [5]). The χ values were determined from SQUID measurements on the same foil sample used in the β-NMR. In this plot, temperature is an implicit variable; decreasing from left to right. A linear relationship is apparent between the values at high T. A best-fit line to these points yields $K = -1.88(8) \times 10^{-6}\chi - 4(5) \times 10^{-5}$. The slope of this line gives a measure of the hyperfine coupling constant (A_{hf}) for ^{8}Li in Pd, and the intercept yields the orbital shift. This orbital contribution is a measure of the ^{8}Li chemical shift: -40(50) ppm. Although the uncertainty in this value is rather large, the chemical shift of Li in Pd is consistent with ^{6,7}Li chemical shifts in ionic solutions (typically ranging from -3 to +3 ppm)[10]. At low T any dilute paramagnetic impurities in the foil will affect the measured χ significantly while, due to their low concentration, will not affect the resonance position. Thus, the measured $K(T)$ no longer tracks $\chi(T)$ in the low T region of the plot.

To verify that the results obtained from the foil were not unique to that sample, a 100 nm thin film was studied. The sample was grown via e-beam deposition from a 99.99% source onto a 60-80 °C single crystal SrTiO$_3$ (STO) substrate at a rate of 0.5Å/s under a pressure of $\sim 10^{-8}$ Torr, and subsequently capped with 10 nm of Au. Monte Carlo simulations of the stopping distribution for this sample indicated that an incident beam energy of 11 keV would result in the majority of ions stopping in the metal layers. Two typical spectra are displayed in Fig. 3. The signal from ^{8}Li in STO is quadrupole-split[11], so ν_r was inferred from the signal in the Au overlayer. The ^{8}Li K is known to be +60 ppm in Au relative to MgO[12]. The large, negative K observed in the foil is reproduced in the film. Furthermore, the multiple peak structure suggested in the foil is better resolved. Two lines are distinguishable even at room T, and we tentatively assign the two lines to 2 Li sites in Pd. In a manner similar to the foil, the highest frequency line loses amplitude on cooling. For the higher(lower) frequency site $K =$ -780 ppm(-920 ppm) at 270 K, increasing to -1100 ppm(-1300 ppm) at 8.5 K. It is interesting to note that the Au resonance here is much broader than that seen in other Au samples[12,15]. This is probably an effect of its proximity to the Pd layer, and not the Au thickness[12].

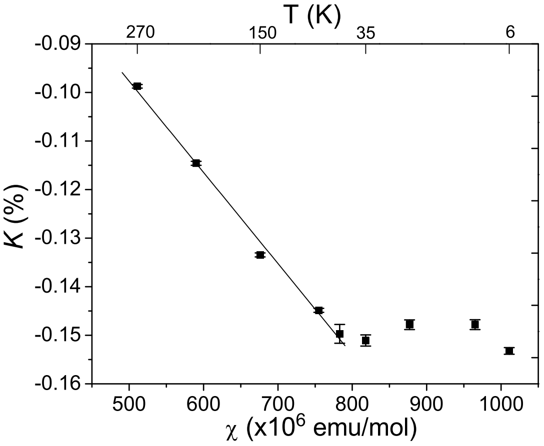

Fig. 2. A 'Jaccarino-Clogston' plot of the ^{8}Li Knight shift versus χ of the Pd foil. Temperature is an implicit variable.

In metals, the spin-lattice relaxation rate (T_1) is dominated by random spin-flip scattering by the conduction electrons. $1/T_1$ varies linearly with temperature, as expressed by the Korringa relation:

$$K^2 T_1 T = S \qquad (1)$$

For ^{8}Li, $S = 1.2 \times 10^{-5}$s K. The ratio $\mathcal{K} = K^2 T_1 T/S$ is, in the ideal case, equal to unity. Deviations from unity may occur for a number of reasons, in particular electron-electron interac-

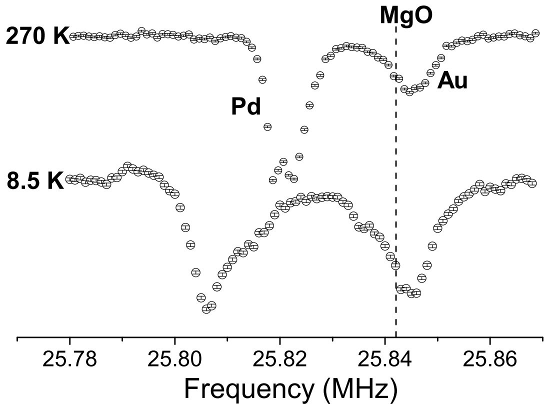

Fig. 3. High and low T spectra collected at 4.1 T in a 100 nm thin Pd film deposited on $SrTiO_3$ and capped with Au. Since no reference MgO is present, the frequency of ^{8}Li in MgO was estimated from the known K in Au; given by the dotted line. Two sites are evident in the Pd.

tions[13]. From conventional NMR of ^{105}Pd, $\mathcal{K} = 9.4$ at 4 K[13].

The Korringa relation can be used to predict values of K given T_1, and vice versa. A previous measurement for the relaxation time of ^{8}Li in room temperature Pd foil was 3.0(7) s[14]. If $\mathcal{K}$ is assumed to be unity, for 270 K Eq. (1) predicts $|K| \approx 110$ ppm. Similarly, the foil $K = -9.8 \times 10^{-4} - (-4 \times 10^{-5})$ leads to a calculated $T_1 = 0.05$ s, significantly faster than was observed. This K and $T_1 = 3$ s give an unrealistic $\mathcal{K} = 60$. Thus, even the smallest observed K in Pd is much larger than expected.

3. Conclusion

In conclusion, we have observed a giant K of ^{8}Li in Pd– much larger than any other known shift in β-NMR. Further experimental and theoretical studies are needed to clarify its origin. Of particular interest are results from techniques that employ nuclear probes, as they can provide details about the *local* magnetic properties of Pd films and heterostructures. As well, the β-NMR technique presents unique possibilties for magnetic resonance studies of size-dependent effects in metals.

4. Acknowledgements

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References

[1] L. Cheng, et al., Phys. Rev. B 69 (2004) 144403, and references therein.

[2] M.B. Brodsky, A.J. Freeman, Phys. Rev. Lett. 45 (1980) 133.

[3] B. Stritzker, Phys. Rev. Lett. 42 (1979) 1769.

[4] J. Imazato, et al., J. Phys. Soc. Jpn. 48 (1980) 1153.

[5] J.A. Seitchik, A.C. Gossard, V. Jaccarino, Phys. Rev. 136 (1964) A1119.

[6] e.g., C.H. Pennington, V.A. Stenger, Rev. Mod. Phys. 68 (1996) 855.

[7] e.g., E. Jäger, et al., Phys. Lett. 123A (1987) 39.

[8] G.D. Morris, et al., Phys. Rev. Lett. 93 (2004) 157601.

[9] T.J. Parolin, et al. (unpublished).

[10] H. Günther, in: Encyclopedia of Nuclear Magnetic Resonance, eds. D.M. Grant and R.K. Harris (Wiley & Sons, West Sussex, 1996) Vol. 5.

[11] W.A. MacFarlane, et al., Physica B 326 (2003) 209.

[12] Z. Salman, et al. (unpublished).

[13] G.C. Carter, L.H. Bennett, D.J. Kahan, in: Metallic Shifts in NMR, eds. B. Chalmers, J.W. Christian, and T.B. Massalski, Progress in Materials Science Vol. 20 (Pergamon Press, Oxford, 1977).

[14] I. Koenig, et al., Z. Phys. A 318 (1984) 135.

[15] W.A. MacFarlane, et al., Physica B 326 (2003) 213.