Abstract

Using low energy beta-detected nuclear magnetic resonance ($\beta$NMR), the Knight shift and spin-lattice relaxation rate of dilute $^7$Li$^+$ implanted into a 28 nm Pd film on a MgO substrate were studied as a function of temperature. The shift of the resonance is negative, but much smaller in magnitude than observed in two other much thicker samples. The corresponding spin-lattice relaxation rates are found to be linear with temperature $T$, but are roughly 50% slower than the rates measured in a Pd foil. Potential explanations are discussed.

Key words: $\beta$NMR, Palladium, Knight shift, Spin-lattice relaxation, thin film

1. Introduction

Recently, we reported the $\beta$NMR of $^7$Li$^+$ implanted into a 100 nm thick Pd film deposited on a SrTiO$_3$ (STO) substrate[1]. We found a large negative shift of the resonance that scaled with the temperature dependent magnetic susceptibility of the conduction electrons ($\chi$) down to about 100 K, i.e. a Knight shift $K$ in the sense of NMR in metals[2]. We attributed the deviation of the temperature dependence below 100 K to a scattering effect due to the $^7$Li itself. This behaviour was consistent with other measurements on a (much thicker) Pd foil[3].

Correcting the measured shift for the demagnetization field reduces the magnitude of the shift by about half, but the corrected shift remains large, negative and temperature dependent, in contrast to the group 11 metals Ag[4], Cu[5] and Au[6].

Finite size effects have been studied in the conventional NMR of small particles[7], but with low energy $\beta$NMR we can study metals that do not have a favourable NMR nucleus such as Pd, and study single thin films instead of polydisperse randomly oriented nanoscopic powders. Because of the large $K$ in Pd, we should be quite sensitive to finite size effects which manifest themselves as an asymmetric broadening of the NMR towards zero shift due to a depth-dependent local electronic environment near free surfaces.
Here we report initial measurements in a thinner film of Pd. In contrast to the expected line broadening, we find the position of the line shifts substantially towards zero shift without broadening. We then discuss the possible origins of this remarkable effect.

2. Experimental

In these experiments an optically, spin-polarized beam of $^8\text{Li}^+$ ($\tau = 1.2$ s, $I = 2$, $^8\gamma = 6.3015$ MHz/T) of energy 28 keV is focussed onto a sample mounted on a coldfinger UHV cryostat in a static homogeneous longitudinal magnetic field $H_0$. The ions are implanted at a rate of $\sim 10^6$/s into a beamspot a few mm in diameter. Plastic scintillators are mounted forward and backward to the initial $^8\text{Li}$ spin. The asymmetry $A$ in the count rates for the anisotropic beta decay is thus a direct measure of the $^8\text{Li}$ spin polarization. The spectrometer may be biased to a high positive voltage enabling electrostatic deceleration of the ion beam, and variable implantation energies.

For these measurements, resonances were collected using two distinct modes. In the first, a continuous ion beam is used and a transverse, continuous-wave (CW) oscillating RF magnetic field $H_1$ is applied; the frequency $\nu$ is slowly stepped through a given range. On resonance, the nuclear polarization is destroyed resulting in a decrease in $A$. In the second mode, a continuous beam is introduced, but a series of pulses of modulated RF is introduced effectively scanning randomly over a range of frequency. $A$ is measured before and after the RF pulse, and the difference of the $A$ values is monitored as a function of the RF frequency. RF power broadening and possible spin dynamic effects generally make the CW resonances broader than their pulsed counterparts. To measure the spin-lattice relaxation rate $\lambda \equiv T_{1}^{-1}$, a 4 s pulse of beam is admitted and the evolution of polarization $A(t)$ is monitored as a function of time in the absence of $H_1$.

The sample is a 28 nm film of Pd grown from the same source, under similar conditions as that of the Au-capped 100 nm film reported in Ref. [1]. However, this thinner film was deposited onto a single crystal (001) MgO substrate and left bare rather than Au capped. Similar to the 100 nm film, this film is polycrystalline with a preferred orientation along the (111) direction as determined by x-ray diffraction.

3. Results

![Fig. 1.](image_url)

(a) Representative spectra recorded in the 28 nm Pd film on MgO for $H_0 = 4.1$ T at an implantation energy of 2.1 keV using pulsed RF mode fit to two Lorentzians. (b) Spectra in the 28 nm film for $H_0 = 6.55$ T at an implantation energy of 0.9 keV using CW RF mode. A spectrum recorded in the Au-capped 100 nm/STO film for $H_0 = 4.1$ T at a similar $T$[1] is shown for comparison.

Resonances were recorded using reduced implantation energies to maximize the signal from the Pd film (and minimize that of the substrate). Spectra from the high and low $T$ regions are shown in Fig. 1a where the RF frequency scale has been converted into “shift” using $K = (\nu - \nu_0)/\nu_0$, where $\nu_0$ is the resonance frequency of $^8\text{Li}$ in the MgO substrate at full implantation energy, a convenient in-situ reference for the applied field[8]. The shift is substantially smaller in magnitude than previous Pd samples[1,3], but still negative. It is also more weakly temperature dependent, but still shows the largest negative shift for the lowest temperatures. The dramatic difference between the shift in this and previous samples is illustrated in Fig. 1b where a resonance in the Au(10 nm)/Pd(100 nm)/STO film[1] is shown along with a spectrum from the 28 nm film. The latter was recorded using a larger $H_0$; however, we have confirmed that $K$ is independent of $H_0$, as expected for a magnetic (rather than quadrupolar) shift.

The spectra were fit using two Lorentzians with one fixed at $K = 0$ ppm to account for a small amplitude shoulder that does not shift with $T$. At present,
the origin of this signal is unknown, but it is not unique to Pd films on MgO as it is also observed in the resonances of bare Pd films on STO[10].

We now correct $K(T)$ for the macroscopic demagnetization, treating the film as a homogeneously magnetized slab with a demagnetization factor of $N = 4\pi$. The corrected shift $K^c(T)$ is thus given by

$$K^c(T) = K(T) + \frac{8\pi}{3} \chi_{Pd}(T),$$

where $\chi_{Pd}(T)$ is the volume susceptibility of the host. In the absence of a better estimate, since the magnetic moment of the film itself is much too small to measure, we assume $\chi_{Pd}(T)$ is simply that of pure bulk Pd. Calculations indicate that bulk $\chi$ can be expected for crystalline films thicker than $\sim 16$ monolayers (8 nm)[9]. Under this assumption, the corrected shift for two values of $H_0$ is shown in Fig. 2 with the similarly corrected shift measured in the 100 nm/STO film. We note that $K^c(T)$ for the 28 nm/MgO film is of comparable magnitude to the 100 nm/STO film, but the values are opposite in sign (however, see the discussion below).

For both Pd films, $K^c$ is proportional to $\chi_{Pd}$ at high $T$. The dashed lines in Fig. 1 illustrate the trend in $K^c$ with $T$ if this linearity were to hold to the lowest temperature. The slope of the $K^c$ vs. $\chi_{Pd}$ plot, a measure of the hyperfine coupling, for the 28 nm film is about 40% larger (and positive) than that for the 100 nm film. Also $K^c(T)$ for the 28 nm/MgO film scales with $\chi_{Pd}(T)$ more closely than the 100 nm/STO film, especially at lower $T$.

The spin-lattice relaxation rate $\lambda$ measured in the 28 nm/MgO film for $H_0 = 4.1$ T and a 2.1 keV implantation energy. The low-$T$ linear region of the $T_1^{-1}$ measured in Pd foil[1] is shown for comparison. The inset displays a representative time spectrum from the film at 140 K.

Fig. 2. Temperature dependence of the demagnetization-corrected Knight shifts recorded for $H_0 = 4.1$ T (circles) and for $H_0 = 6.55$ T (triangles). $K^c(T)$ measured in a 100 nm/STO film[1] is also shown. The dashed lines represent the shifts for $K^c$ linear with $\chi_{Pd}$.

4. Discussion

We now consider what may account for the substantial differences in this sample compared to the other two thicker ones. While we do anticipate a thickness dependent broadening in films as thin as 28 nm, we do not expect a change in the net shift. If we assume the hyperfine coupling of the implanted $^8$Li to the Pd conduction band is not sample dependent, then the smaller shift implies the susceptibility of the Pd is reduced for the 28 nm film. In this
case the demagnetization correction in the previous section will be substantially overestimated. For very thin metal films, quantum confinement may reduce the density of states at the Fermi level, thus reducing $\chi$, but there are also other possibilities.

First, there may be substantial structural differences in Pd films grown on STO and MgO substrates, with good lattice matching only for the former. It is well known that magnetism in Pd is very sensitive to its atomic arrangement[14]. In epitaxially grown films, a regular network of misfit dislocations is formed near the interface due to strain relaxation on MgO at room $T$[15]. Such dislocations are not found for Pd films on STO[16]. However, for this film, the growth rate may have prevented the film from relaxing significantly to a structure correlated with the substrate, except possibly very close to the interface.

Second, Pd is well known for its ability to absorb large quantities of hydrogen, accounting for its use in hydrogen purification. High concentration interstitial hydrides PdH$_x$ ($x \sim 1$) have much smaller, temperature-independent $\chi$ than pure Pd, since H acts as a donor, pushing the Fermi level above the d-band peak into the broad sp-band[17]. Molecular hydrogen (H$_2$) readily adsorbs on Pd, dissociating and absorbing to form a hydride layer immediately below the surface followed by diffusion of H into the bulk[18]. H$_2$ is a very minor atmospheric gas (concentrations of a few hundred ppb) and thus is not likely a source of significant contamination. However, H$_2$ is one of the few residual gases in UHV systems and has been found to contaminate metals such as Nb in high temperature UHV annealing[19]. One objection to this explanation is that there is no evidence of similar H contamination of the bare Pd foil, even at low implantation energy [3], but a subsurface hydride layer does provide an appealing explanation for the small resonance at $K = 0$.

To decide between these different (and possibly other) explanations, more measurements, particularly looking for a systematic thickness dependence, are required.

5. Conclusion

In conclusion, we have observed a dramatic difference in the Knight shift and spin-lattice relaxation rate of $^6$Li implanted in a 28 nm Pd film on MgO compared to two other thicker samples of Pd. We have identified some possible explanations, but none of them are fully satisfactory. More measurements are required to conclusively identify the origin of this remarkable effect.

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References

[7] e.g. J.J. van der Klink and H.B. Brom, Prog. NMR. Spectrosc. 36 (2000) 89.
[12] M.D. Hossain et al., these proceedings.