The spin lattice relaxation of $^8$Li in simple metals


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Abstract

We report the modification to the linear temperature dependence of the Korringa nuclear spin-lattice relaxation rate of an implanted NMR probe in silver, as it makes a thermally activated site change. We develop a simple model of this phenomenon, which is found in a number of metals including Au and Nb.

Key words: Korringa law, spin relaxation in metals

1. Introduction

The nuclear spin lattice relaxation rate $\lambda = 1/T_1$ in non-magnetic metals is often due primarily to spin flip scattering from the conduction electrons, the so-called Korringa relaxation [1], with its characteristic linear temperature dependence

$$\lambda = \frac{\pi A_{hf}^2}{\hbar} \rho^2(E_F)kT,$$

where, in the simplest model, $A_{hf}$ is the contact hyperfine coupling of the conduction electrons (having density of states at the Fermi Energy $\rho(E_F)$) to the nucleus. For light implanted “nuclei” like the muon and $^8$Li the coupling is generally small and $\lambda$ is consequently almost always too slow to measure with $\mu$SR; however, this is not the case with the much longer lived $\beta$-NMR probes ($^8$Li has a mean lifetime $\tau = 1.21$ s), where Korringa $\lambda$ has been measured in a number of metals, including some where the conventional host lattice NMR is difficult or impossible due to the lack of a sensitive (high gyromagnetic ratio, $\gamma = 630.15$ Hz/G) nucleus, e.g. Pd and Au [2,3]. Korringa relaxation is an important means of characterizing a metal and deviations from it have been very useful in the study of metals. For example, the Hebel-Slichter coherence peak in $\lambda$ that occurs at the superconducting transition can be used to distinguish a conventional $s$-wave superconductor from more exotic pairings [5].

Another common occurrence for $^8$Li$^+$ implanted in metals is a temperature dependent site change. At low temperature, the $^8$Li$^+$ is trapped at a metastable interstitial site, but at higher temperatures, it makes a thermally activated transition, into a nearby vacancy and becomes substitutional [2,11,3,9]. In fact interstitial Li diffuses appreciably in Ag only at much higher temperatures than the observed transition (450 K [6]), and the transition may instead be due to the onset of vacancy mobility in Ag (Stage III annealing [7]). The main objective of this work is to elucidate the modification to the simple Korringa temperature dependence caused by such a site change.

2. Experimental

The data described here were taken on two samples of Ag, a 500 nm film evaporated on an SrTiO$_3$ substrate and a 25 micron foil. The $\beta$-NMR experiment was carried out at the ISAC facility at TRIUMF using a beam of highly polarized radioactive $^8$Li$^+$ with a typical rate $R_0 \approx 10^7$/s.
Fig. 1. The temperature dependence of the $^8\text{Li}$ spin lattice relaxation in a silver foil at $H_0 = 150$ G. The beam pulse length is $\Delta = 4$ s.

into a beam spot about 3 mm in diameter. The $^8\text{Li}$ nucleus has a spin $I = 2$, $\gamma = 630.15$ Hz/G, and an electric quadrupole moment $Q = +31.4$ mB. Details on the polarizer and spectrometer can be found in Refs. [8,9]. Resonance measurements were carried out with a continuous beam and a continuous wave radio-frequency (RF) magnetic field applied transverse to the spin polarization. Spin-lattice relaxation measurements were carried out with a pulsed beam of length $\Delta$ with the RF field off. Data was collected over a range of applied field $H_0$. Examples of the spin lattice relaxation data in the Ag foil are shown in Fig. 1, and their analysis is discussed in the next section. An example of resonance data is shown in Fig. 2, where we show the resonances with the beam polarized in both directions (parallel and anti-parallel to $H_0$) in order to clearly define the off-resonance baseline asymmetry $b$ (see also Ref. [9]).

3. Theory & Discussion

When a continuous beam of spin-polarized probes of lifetime $\tau$ is implanted at a constant rate, and if the implanted probes relax as $p(t) = \exp(-\lambda t)$, a dynamic equilibrium polarization is established at a value

$$\bar{p} = \frac{1}{\tau} \int_0^\infty p(t)e^{-t/\tau}dt = \frac{1}{\lambda\tau + 1}.$$ 

In a $\beta$-NMR resonance measurement, using a continuous beam, when the RF magnetic field is off resonance (and has therefore no effect on the polarization), we obtain the experimental “baseline” asymmetry, $b = a\bar{p}$ (see Fig. 2), where $a$ is the experimental factor that accounts for the asymmetry of the beta decay, the geometry of the detectors, etc. Therefore, the baseline is determined by $\lambda$, with $\lambda = 0$ yielding the maximal $b(= a)$. One can easily invert the above to find

$$\lambda = \frac{a - b}{\tau b},$$

which has the single unknown parameter $a$.

The spin lattice relaxation rate in the silver film was measured in $H_0 = 3$ Tesla in time differential mode using short ($\Delta = 0.5$ s) beam pulses [9]. The resulting spectra

Fig. 2. The definition of the off resonance baseline asymmetry $b$ in a continuous wave resonance measurement. The asymmetry is integrated for 1 second with the RF field applied at the frequency given by the ordinate. The data shows the two resonances from the two sites in Ag. The two curves correspond to the two helicities of the polarizing light.

Fig. 3. The temperature dependence of the $^8\text{Li}$ spin lattice relaxation rate in two samples of Ag. The open circles are from values of the average off resonance baseline asymmetry scaled as described in the text. The fit curve is the activated site change model described in the text.

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were fit to a single exponential to yield the Korringa rate (stars in Fig. 3). The initial asymmetry using such short pulses is high, but the statistics is rather low, as a limited number of probes are implanted. More recently, we measured $\lambda$ in a 25$\mu$m Ag foil using much longer beam pulses (Fig.1), and fit the time dependent asymmetry during and after the pulse to yield a more complete data set through the site change at about 170 K (filled squares in Fig. 3). The slopes of these two measurements are similar, but slightly smaller for the foil. The foil data, however, clearly reveal the effect of the site change between about 110 and 170 K, $\lambda$ executes a crossover from a steep low temperature line to a shallower high T slope. We also include $\lambda$ values from the resonance baseline of Morris et al.,[9] using Eq.(1) at 3 T (open circles), with the constant $a = 0.195$ chosen to match the foil at 100 K.

We now develop a simple theoretical model of this crossover. Let us define the beam polarization from the optical polarizer as $p_{01}$. In terms of the populations $p_{m}$ of the $2I + 1$ magnetic sub-levels of the probe nucleus $p_{0} = (\Sigma p_{m})/I$. We account for two inequivalent sites (1 and 2), each with characteristic single exponential relaxation rate $\lambda_1, \lambda_2$, and include a thermally activated transition $1 \rightarrow 2$. We assume implantation results in initial probe fractions at each site $f_1$ and $f_2 = 1 - f_1$ that are independent of temperature, and that the rate of site change is $v = v_0 \exp(-E_b/T)$, where $v_0$ is the attempt frequency for the energy barrier of height $E_b$ (in K). We consider the polarization of a probe nucleus implanted at time $s'$ and decaying later at time $s$,

$$p(s,s') = p(t = s - s') = p_1(t) + p_2(t). \tag{2}$$

The polarization for the two sites follow the rate equations:

$$\dot{p}_1 = -\lambda_1 p_1 - v p_1 \tag{3}$$

$$\dot{p}_2 = -\lambda_2 p_2 + v p_2. \tag{4}$$

subject to the initial conditions $p_1(0) = f_1 p_0$ and $p_2(0) = f_2 p_0$, which has solution:

$$p(t) = p_1(t) + p_2(t)$$

$$= [Me^{-(\lambda_1 + v)t} + (1 - M)e^{-\lambda_2 t}], \tag{5}$$

where

$$M = \frac{p_0 f_1 (\lambda_2 - \lambda_1)}{(\lambda_2 - \lambda_1) - \nu}. \tag{6}$$

Experimentally, to measure $1/T_1$, we observe the time-resolved experimental asymmetry $A(t)$, during and after a pulse of beam, represented by $R(t''') = R_0(\theta(t''') - \theta(t''' - \Delta))$, where $\theta$ is the unit step function, and $R_0$ is the constant instantaneous rate. For a generic polarization function $p(t)$, the observed asymmetry (averaged over the incident pulse and probe lifetime) is

$$A(t) = \frac{A}{N(t)} \int_{-\infty}^{t} R(t'')e^{-t''/\tau} p(t'')dt', \tag{7}$$

i.e. the Laplace transform of the product of the square beam pulse with the polarization function. The number of probes in the sample at time $t$ is

$$N(t) = \int_{-\infty}^{t} R(t'')e^{-t''/\tau} dt', \tag{8}$$

which normalizes the previous expression, and $A$ is the proportionality constant between the observed asymmetry in the detector count rates and the instantaneous average polarization of all the probes in the sample. Substituting the biexponential two site relaxation function from Eq. (5) into Eq. (7), we find that during the pulse ($0 \leq t \leq \Delta$)

$$A_d(t) = \frac{M}{\lambda_1 \tau} \left( \frac{1 - e^{-\lambda_1 t}}{1 - e^{-\lambda_1 t / \tau}} \right) +$$

$$\frac{1 - M}{\lambda_2 \tau} \left( \frac{1 - e^{-\lambda_2 t}}{1 - e^{-\lambda_2 t / \tau}} \right), \tag{9}$$

where $\lambda_1 = \lambda_1 + \nu + \tau^{-1}$ and $\lambda_2 = \lambda_2 + \tau^{-1}$. After the pulse ($t > \Delta$) the asymmetry follows a simple biexponential:

$$A_a(t) = \frac{M}{\lambda_1 \tau} \left( \frac{1 - e^{-\lambda_1 \Delta}}{1 - e^{-\lambda_1 \Delta / \tau}} \right) e^{-(\lambda_1 + \nu)(t-\Delta)} +$$

$$\frac{1 - M}{\lambda_2 \tau} \left( \frac{1 - e^{-\lambda_2 \Delta}}{1 - e^{-\lambda_2 / \tau \Delta}} \right) e^{-\lambda_2(t-\Delta)}. \tag{10}$$

Notice that the amplitudes of the two components after the pulse depend upon the relaxation rates and $\Delta$ such that if one component has a relaxation rate much faster than $\Delta^{-1}$, then its contribution to the signal after the pulse is highly suppressed.

Though the solution above is biexponential, the data appears single exponential after the pulse, probably because the two relaxation rates are similar. Thus we assume the measured single exponential relaxation rate represents the weighted average of the two components with weighting factors given by the relative amplitudes in Eq. (10). The resulting expression is algebraically cumbersome, but not difficult to evaluate, so it was used in a least squares fit to the data (black squares only) in Fig. 3. The data fit reasonably well, except near the site transition, where the model is much sharper in temperature than the data. It is possible to obtain a better fit by allowing the attempt frequency $v_0$ to be very low (on the order of kHz), which is unphysical for an ion in most crystal potentials. More likely, the site change is characterized by a distribution of energy barriers and attempt frequencies corresponding to a variety of configurations for the interstitial Li and nearby vacancies. This would yield a smeared-out transition as observed.

However, the fit shown corresponds to $v = [10^{12} \text{ s}^{-1}] \exp(-[4040 \text{ K}])$ with Korringa slopes (in $10^{-3} \text{ s}^{-1} \text{ K}^{-1}$) $\lambda_1/T = 3.55 \pm 0.32$ and $\lambda_2/T = 1.22 \pm 0.10$, and the initial fraction $f_1 = 0.6 \pm 0.1$. This value for $\lambda_2/T$ should be taken as an improvement on the value (0.95) found in Ref.[9]. Using
this value we find an improved estimate of the Korringa constant for \(^8\)Li in Ag,[3]

\[
\mathcal{K} = \frac{(K c)^2 T_1 T}{1.20 \times 10^{-5} \text{ s K}},
\]

(11)

For the high temperature site 2, using the demagnetization corrected Knight shift from Ref.[9][10], we get \(\mathcal{K} = 1.1 \pm 0.3\).

4. Conclusions

We have shown how the Korringa linear temperature dependence of the spin lattice relaxation rate is modified by a site change transition of the implanted \(^8\)Li\(^+\), and developed a simple model of this phenomenon that represents some of the behavior. However, the assumption of a single activation law for the site change is too simple to model the detailed temperature dependence. Similar behavior has been observed in other simple metals, such as Au [3], Nb [4] and Cu [11]. We also showed how the baseline from resonance experiments can be used as a measure of \(1/T_1\).

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References