Nuclear Spin Relaxation/Resonance of $^8$Li in Al


Abstract

A low energy beam of spin polarized $^8$Li has been used to study the behaviour of isolated $^8$Li implanted into a 150 nm thick film of Al on an MgO substrate. The spin relaxation rate $1/T_1$ and $\beta$-NMR lineshape were measured as a function of temperature in a large magnetic field of 4.1 T. The resonances from different sites are unresolved due to the large nuclear dipolar interaction with the host $^{27}$Al magnetic dipole moments. Nevertheless the temperature variation of the site averaged $1/T_1$ and Knight shift show evidence for a transition between the octahedral $O$ and substitutional $S$ sites at about 150 K, as observed in other fcc metals.

Key words: $\beta$-NMR, $^8$Li, metals, spin relaxation

1. Introduction

Nuclear magnetic resonance (NMR) is used extensively to study the electronic and magnetic behaviour of quantum materials e.g. superconductors. However, conventional NMR is of limited use in studies of thin films and interfaces of quantum materials due to the lack of sensitivity. Recently, we have developed a novel technique of depth-controlled beta-detected nuclear magnetic resonance ($\beta$-NMR), in which a low energy beam of highly polarized radioactive ions is used as a microprobe of local properties. So far our studies have focussed on $^8$Li which has spin $I = 2$, lifetime $\tau = 1.21s$, nuclear gyromagnetic ratio $^8\gamma = 6.3015$MHz/T, and a small quadrupole moment $Q/e = +32$ mb. Since the information on nuclear polarization is obtained through the emission of a high energy electron from a radioactive decay, $\beta$-NMR has roughly 10 orders of magnitude higher sensitivity compared to conventional NMR and is thus well suited to ultra-thin structures and heterostructures [1]. Since simple metals are often components of more complicated heterostructures it is important to characterize the implanted probe in pure metals.

In this paper, we report $\beta$-NMR spectra and relaxation measurements in Al. This follows previous work on $^8$Li in other simple fcc metals, e.g. Ag[1], Cu[2] and Au[3,4]. In Ag and Au the resonances from different sites are narrow and well-resolved due to the Knight shift and the fact that the nuclear dipolar broadening from the host nuclear moments is small. There are no quadrupolar splittings, implying that $^8$Li occupies two different sites with cubic symmetry. Based on the temperature dependence of the signals and previous $\beta$-NMR work we propose the $^8$Li resides primarily in the octahedral interstitial site ($O$) at low temperatures and makes a transition to the substitutional ($S$) site at higher temperatures. As in the case of Cu, the resonances from different sites are unresolved in Al. Nevertheless, the temperature dependence of the average Knight shift and spin relaxation rate are consistent with a model in which $^8$Li occupies mainly an interstitial site at low temperatures, and moves to the substitutional ($S$) site at higher temperatures. Unlike other fcc metals, in Al there is a small peak in $1/T_1$ at about 25 K.
2. Experiment

The sample studied here is a 150 nm thick Al film on an 8 x 10 mm² (100) MgO substrate. It was grown by thermal evaporation of a high purity (99.999%) Al source with a growth rate of about 20Å/s under a background pressure of 10⁻⁶ Torr. The polycrystalline film showed a weak preferred orientation along a (111) direction as characterized by x-ray diffraction. The sample was mounted on a coldfinger He flow cryostat in ultrahigh vacuum (UHV) at the center of a 9T superconducting solenoid. For this experiment, all measurements are done at an external magnetic field $H_0 = 4.1$T where the beam spot is 3-4 mm in diameter.

The beam of spin-polarized $^8\text{Li}^+$ is produced at ISAC by bombarding a Ta target with the primary 500 MeV proton beam from the TRIUMF cyclotron. The radioactive ion beam is extracted at a nominal energy of 28 keV and purified using a high resolution magnetic isotope separator. A high degree of nuclear spin polarization is generated in-flight by co-linear laser pumping. In this method the $^8\text{Li}^+$ ion beam is first neutralized, then optically pumped and finally re-ionized so that it can be guided electrostatically to the sample chamber [1,5,6]. By choosing the helicity of the laser light, the orientation of the nuclear spin of the $^8\text{Li}^+$ beam can be made either parallel or antiparallel to the beam direction.

The beam energy (and corresponding mean implantation depth) are controlled by applying a bias to a high voltage platform on which sits the sample chamber, cryostat, $\beta$-NMR spectrometer, and associated electronics. After implantation the $^8\text{Li}$ beta decays, emitting a high energy electron in a direction preferentially opposite to the nuclear spin direction at the time of decay. In this way, the average nuclear polarization can be monitored as a function of time or RF frequency. Fast plastic scintillation counters positioned in the forward (F) and backward (B) directions, with respect to the sample, are used to detect the high energy electron. Measurements of the spin-lattice relaxation rate $1/T_1$ use a fast electrostatic kicker to make a pulse cycle consisting of 0.5 s of beam followed by 10 s of beam-off. Time-differential histograms $N_F(t)$ and $N_B(t)$ are accumulated for many cycles in each helicity. The quantity of interest is the $\beta$-decay asymmetry $A(t) = [N_F(t) - N_B(t)]/[N_F(t) + N_B(t)]$, which is proportional to the spin polarization. The time dependence of the polarization after the beam goes off is a direct measure of the spin-lattice relaxation rate $1/T_1$. Typically we fit the difference in asymmetry obtained for the two helicities $A^+(t) - A^-(t)$ since this removes any correction due to the different solid angles for the $F$ and $B$ detectors.

3. Results & Discussion

Examples of the time dependent polarization of $^8\text{Li}$ after the beam is turned off are shown in Fig. 1(a). The spin relaxation fits well to a single exponential decay function $A(t) = A_0 \exp(-t/T_1)$, where $A_0$ is the initial asymmetry and $1/T_1$ is the spin-lattice relaxation rate. The temperature dependence of $1/T_1$ is shown in Fig. 1(b). In high magnetic fields, we expect the dominant source of spin relaxation to originate from Körtinga scattering with the conduction electrons. For a single site this should give rise to a simple linear variation in $1/T_1$ versus $T$. However, if the $^8\text{Li}$ site, and resulting Fermi contact interaction, change as a function of temperature a more complicated behaviour will be observed[7]. Based on results in other fcc metals it is reasonable to assume that the $^8\text{Li}$ occupies mostly the substitutional $S$ site at room temperature. The lower dashed curve in Fig. 1(b) corresponds to the expected $1/T_1$ below 30K if the $S$ site were 100% occupied at all temperatures. Between about 125K and 50K, there is indication of a change in slope and therefore a different site, which we tentatively assign to the interstitial $O$ site. This is consistent with other $\beta$-NMR measurements for $^8\text{Li}$ in Al[8], Cu[9] and Ag[7]. The corresponding slopes are calculated to be $1/(T_1T)_O = 0.08(4) \times 10^{-9}$s⁻¹K⁻¹ and $1/(T_1T)_S = 0.80(3) \times 10^{-9}$s⁻¹K⁻¹. Note however there is also a small peak at about 25K which is not seen in other fcc metals. This is evidence for a third site. Since there is no loss in the resonance amplitude [see Fig. 3(a)] the $^8\text{Li}$ must remain in a site with cubic symmetry or be moving rapidly between sites of lower symmetry. One possibility is the tetrahedral interstitial site [10].

Complementary resonance measurements were also made. In this case the time averaged $\beta$-decay asymmetry $A$ is measured with a continuous beam while slowly sweeping the frequency $\nu$ of a small RF magnetic field $H_1$ applied perpendicular to $H_0$ and the $^8\text{Li}$ spin polarization. The loss of forward-backward asymmetry is proportional to the number of $^8\text{Li}$ on resonance at a given frequency. Typical spectra are shown in Fig. 2. In simple metals, the largest contribution to the frequency shift $\delta = (\nu - \nu_0)/\nu_0$ is from the Fermi contact interaction with the conduction electrons. The resulting Knight shift is expected to be almost independent of temperature [12]. A good estimate of the Knight shift is obtained using a reference signal from a diamagnetic insulator, which in the present case is the MgO substrate. This was easily done by increasing the beam energy to 28 keV so that a small fraction of the beam penetrates the Al film and stops in the MgO. Note the sharp peak in the bottom panel of Fig. 2, which corresponds to a frequency in the MgO equal to $\nu_0 = 25842.65(5)$ kHz. All the other results were obtained with an implantation energy of 10 keV corresponding to a mean implantation depth in the middle of the Al film as calculated using SRIM2006 [13]. As may be seen from Fig. 2, the resonances from the different sites are unresolved. There is, however, a frequency shift between 300 K and 10K which is attributed to the site change. The central frequency at high and low temperatures (corresponding to the $S$ and $O$ sites) are indicated by vertical dashed lines in Fig. 2.
Fig. 1. (a) Spin relaxation of $^8$Li in 150 nm Al/MgO at various temperatures at an implantation energy of 10 keV. (b) Spin relaxation rate of $^8$Li in Al versus temperature. The dotted lines are the linear fits for the $S$ and $O$ sites respectively. The solid curve is a guide for eye. A more detailed calculation is given in ref. [7].

\[ A_0 - A \exp[-(\nu - \nu_r)^2/2\sigma^2], \]

where $A_0$ is the baseline of the asymmetry, $A$ is the amplitude, $\nu_r$ is the average resonance frequency, and $\sigma$ is the linewidth. The temperature dependence of amplitude, average frequency and linewidth are shown in Fig. 3. Note the amplitude is almost constant as a function of temperature, implying that all the $^8$Li remains in cubic sites independent of temperature. Fig. 3(b) shows that the average resonance frequency $\nu_r$ increases by $\sim 1$ kHz below 150 K. Assuming the $^8$Li is mostly in the substitutional site at 300K, we find $\nu_S = 25844.76(4)$ kHz. One must correct this for demagnetization effects. In our geometry an amount $\delta K = 8\pi/3\chi_p$ should be added to correct the Knight shift[14] where $\chi_p = 3 \times 10^{-6}$ emu/cm$^3$ is the Pauli susceptibility of Al [15]. This leads to a correction of $\delta K = 25$ ppm and a corrected Knight shift $K_S = +107(3)$ ppm. One can then calculate the Korringa ratio, $T_1TK_S^2/\chi$, where $\chi = (h/4\pi k_B)(\gamma_e/\gamma_n)^2$, where $\gamma_e$ is the electron gyromagnetic ratio and $\gamma_n$ is the nuclear gyromagnetic ratio. For $^8$Li , $\chi = 1.2002 \times 10^{-5}$ s-K, and the Korringa ratio $T_1TK_S^2/\chi = 1.19(5)$. This is similar to other fcc metals and is consistent with the nearly free electron model, as expected for Al. This confirms that the Li is sensing the Fermi surface of Al much like a host nuclear spin.

The linewidth in Fig. 3(c) shows the same trend as the frequency shift, with the value of $\sigma$ rising from about 1.6 kHz to about 2.0 kHz. Power broadening in this measurement can be neglected so that the dominate contribution to the linewidth is from the magnetic dipolar interaction with host nuclear spins [16]. For comparison the theoretical Van Vleck values for the undistorted substitutional, octahedral interstitial and tetrahedral interstitial sites in polycrystalline Al are $\sigma_{th}^S = 1.14$ kHz, $\sigma_{th}^O = 2.18$, and $\sigma_{th}^T = 2.75 kHz$ respectively[8]. These are roughly consistent with our site assignment at high and low temperatures respectively. The differences are attributed to the simple nature of the calculation, which does not take into account the slight (111) preferred orientation of the film or the lattice distortion around the $^8$Li[17].

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References

Fig. 3. Parameters fitted with a simple Gaussian function for the resonance data are shown by circles. The solid lines are guide for the eye. (a) The amplitude (A) versus the temperature. (b) The average resonance frequency (νr) versus the temperature. (c) The gaussian linewidth σ of the resonance versus the temperature.