Nuclear Spin Relaxation of $^8$Li in a Thin Film of La$_{0.67}$Ca$_{0.33}$MnO$_3$

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Abstract

We report $\beta$-NMR measurements of the nuclear spin relaxation rate ($1/T_1$) in a thin film of La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) using a low energy beam of spin polarized $^8$Li. In a small magnetic field of 150 G there is broad peak in $1/T_1$ near the Curie temperature ($T_c = 259$ K) and a dramatic decrease in $1/T_1$ at lower temperatures. This is attributed to a critical slowing down of the spin fluctuations near $T_c$ and freezing of the magnetic excitations at low temperatures, respectively. In addition there is a small amplitude, slow relaxing component at high temperatures which we attribute to $^8$Li in the STO substrate. There is indication that the spin relaxation rate in the substrate is also peaked at $T_c$ due to close proximity to the magnetic film. These results establish that low energy $\beta$-NMR can be used as a probe of magnetic fluctuations in magnetic thin films over a wide range of temperatures.

Key words: $\beta$-NMR, LCMO, manganites, ferromagnetism

1. Introduction

The manganites are a well-studied class of materials for their rich phase diagram, responses to external stimuli such as magnetic fields and sharp insulator-metal (IM) and magnetic transitions[1]. Numerous probes have shown that the magnetic transitions are unconventional, that phase separation likely plays a key role, and that the phases compete near these transitions. In La$_{1-x}$Ca$_x$MnO$_3$ ($x > 0.2$), a coupling of the charge and spin degrees of freedom of the Mn ions is thought to involve double exchange and strong Hund coupling between the spins of the itinerant Mn charge carriers and the core spins. In materials with fewer charge carriers ($x < 0.2$), Jahn-Teller effects and polarons dominate the behaviour. In many of these materials, charge order, orbital order, ferromagnetic, antiferromagnetic and paramagnetic phases...
can be accessed by changing temperature, applying an external magnetic field, varying concentrations of constituent ions such as Ca or exposing the material to light.

Manganites have also been shown to be very sensitive to various external stimuli such as visible light[2–4], x-rays[5], and magnetic fields. For instance, ultra-short pulses of light perturb the magnetic state on short timescales[3,4] while exposure to CW laser light can alter the magnetic state on minute and hour timescales[2]. The charge state is also perturbed by exposure to ultrafast pulses[6] and x-rays[5], where it is thought that a charge ordered state is destroyed upon illumination. Phase separation is believed to play a key role in many of these phenomena[7]. Evidence for phase separation comes from numerous measurements such as μSR[8], surface techniques[9], neutron scattering[10], and NMR[11]. In particular, the NMR results yield coexisting antiferromagnetic and ferromagnetic phases whose volume fractions can be tracked with temperature and field.

In this paper, we report low energy β-NMR measurements of nuclear spin relaxation of ⁶Li in a thin film of La₀.₆₇Ca₀.₃₃MnO₃ with a ferromagnetic transition at \( T_c = 259 \) K. The nuclear spin relaxation rate in the film and in the substrate are sensitive to the spin fluctuations over a wide range of temperatures above and below the ferromagnetic transition. These results show that low energy β-NMR can be used to probe spin dynamics in thin films and near the surface region.

2. Experimental results

Experiments were performed at the ISAC radioactive ion beam facility at TRIUMF using ⁶Li and the low-field β-NMR spectrometer. The ⁶Li (\( \gamma_{Li} = 6.3 \) MHz/T) decays with a mean lifetime of \( \tau = 1.21 \) s, and the high energy β electron is emitted preferentially opposite to the nuclear spin direction, allowing a measurement of the Li nuclear polarization \( (P(t)) \). Spin lattice \( (T_1) \) relaxation is measured using a novel long pulse method in which a pulse of ⁶Li considerably longer than the mean lifetime is implanted in the sample. The polarization function \( P(t) \) is then monitored during the pulse. Although the form \( P(t) \) is slightly more complicated than the conventional short pulse method the sensitivity to both fast and slow relaxation is much higher. More details on low energy β-NMR are given in Refs.[12–14].

The LCMO films were synthesised by pulsed laser deposition at the University of Toronto on epitaxially polished SrTiO₃ substrate and have a thickness of approximately 2,500Å. In fig. 1 the simulated implantation profile of a beam of ⁶Li ions with the nominal energy 28 keV in LCMO is shown. The peak occurs near the middle of the film (1,500Å) and 95.7% of the implanted ⁶Li stop in the LCMO film. The measurements presented in this paper were performed at 28 keV implantation energy and therefore mostly probe the bulk of the thin film.

The insulator-metal transition is shown in fig. 2a. The material is semiconducting at room temperature and metallic at low temperatures with the transition at \( T = 259 \) K. In fig. 2b, the magnetization in an applied field of 100 G is shown. The magnetic transition also occurs at \( T_c = 259 \) K, at the same temperature as the insulator-metal transition.

![Fig. 1. Simulated implantation profile of ⁶Li ions at 28 keV implantation energy in 2,500Å thick LCMO film on SrTiO₃ substrate. The implantation profile is calculated with TRIM Monte Carlo simulation.](image-url)
Fig. 2. a) Resistance across LCMO film in zero magnetic field. b) Magnetization in an applied field of 100 G. The insulator-metal and magnetic transitions both occur at $T_c = 259$ K.

Figure 3 shows spin relaxation measurements in a small magnetic field ($B = 150$ G) in a few different temperatures. $^8$Li is implanted during the time shown ($0 \leq t \leq 4$ s). The number of Li in the sample is highest at $t = 4$ s and the polarization has reached a steady-state value. The measured polarization is determined by both $\tau = T_1$ and $\tau$. In general, for any spin-lattice relaxation function $f(t, t_p : \lambda)$ where the polarization of a short pulse occurring at $t_p$ is measured at a later time $t$, the polarization follows:

$$P_{\text{ave}}(t) = \frac{\int_0^t e^{-t/(\tau \lambda)} f(t, t_p : \lambda) dt_p}{\int_0^t e^{-t/\tau} dt}$$  \hspace{1cm} (1)

For $f(t, t_p : \lambda) = e^{-\lambda(t-t_p)}$, e.g. single exponential relaxation,

$$P_{\text{ave}}(t) = \frac{\tau' (1 - e^{-t/\tau'})}{\tau (1 - e^{-t/\tau})} \quad (t \leq \Delta) \hspace{1cm} (2)$$

where $\tau' = \tau/(\tau+1/\lambda)$. The data in fig. 3 are fit to the sum of Eq. 1 with $f(t, t_p : \lambda) = e^{-(\lambda_{\text{fast}}(t-t_p))^{\beta}} \quad (\beta = 0.5)$ and Eq. 2 ($\lambda_{\text{slow}}$) over the entire time range.

At low temperature, the initial asymmetry is close to the full asymmetry expected (0.19) and most of the relaxation is visible in the $^8$Li time window. A fast component relaxes on a timescale of 100ms while most of the signal relaxes on the timescale of seconds. As the temperature increases the relaxation rates increase sharply. At and above $T_c$, the fast relaxation is barely visible in the $^8$Li time window (fig. 3c,d). On a long time scale there is still a small amplitude (5% of full asymmetry 0.19) signal from a slowly relaxing component. We attribute this to small fraction of the $^8$Li reaching the STO substrate as indicated from the TRIM simulations (see fig. 1).

Below $T_c$ the relaxation rate of the signal attributed to STO is about an order of magnitude larger than in a blank STO substrate[15] and about a factor of two larger above $T_c$. This difference can be attributed to the spin fluctuations in the LCMO film near $T_c$. The implanted $^8$Li in the STO substrate lies mostly within a few hundred Angstroms of the LCMO interface (see fig. 1) and therefore will experience large long-range magnetic fields that increase the relaxation rate ($\lambda \propto B^2_{\text{loc}}$). This is confirmed by the fact that at $T = 260$ K, the relaxation rate in the STO increases sharply (visible in fig. 3c). This is expected since the fluctuations in the LCMO are slowest at $T_c$. This suggests it is possible to use the signal in the substrate to monitor fluctuations in the film. This could be particularly useful in situations where the relaxation in the film itself is too fast to observed directly e.g. near the transition.

In fitting the low temperature data we fixed the polarization and relaxation rates for the small amplitude STO component from the measurements near $T_c$. At the lowest temperature ($T = 10$ K), the relaxation from the LCMO ($\lambda_{\text{fast}}$) is slowest (fig. 3 a). Here we fit the data to the two components and determine the total asymmetry of the signal (0.126), which is fixed for all fits at higher temperatures. The fast relaxation rate is shown in fig. 4. Near $T_c$ the relaxation rate is outside the $^8$Li time
window in agreement with reported values of $\lambda$ from $\mu$SR data\cite{8}. Therefore we plot a lower bound for the relaxation rate. However above $T_c$, $\lambda_{fast}$ falls back into our time window. This behaviour is expected for a ferromagnet since the spin relaxation rate should peak near $T_c$. Above $T_c$ there is a critical slowing down of fluctuation as one approaches the transition from above whereas, well below $T_c$, $\lambda_{fast}$ drops due to the freezing out of the magnetic excitations.

In conclusion, we present the first $^8$Li $\beta$-NMR measurements in La$_{0.67}$Ca$_{0.33}$MnO$_3$ using a novel long pulse method for measuring spin relaxation. The $^8$Li nuclear spin relaxation rate increases sharply near the ferromagnetic transition. These results demonstrate that low energy $\beta$-NMR can be used to probe magnetic spin fluctuations in thin magnetic films.

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References


