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 β-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 β-NMR can be used as a probe of magnetic fluctuations in magnetic thin films over a wide range of temperatures.

Key words: β-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 $La_{1-x}Ca_xMnO_3$ ($x > 0.2$), 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

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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 ^{8}Li in a thin film of $La_{0.67}Ca_{0.33}MnO_3$ 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 ^{8}Li and the low-field β-NMR spectrometer. The ^{8}Li ($\gamma_{Li} = 6.3$ 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 ^{8}Li 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 $SrTiO_3$ substrate and have a thickness of approximately 2,500Å. In fig. 1 the simulated implantation profile of a beam of ^{8}Li 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 ^{8}Li 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.

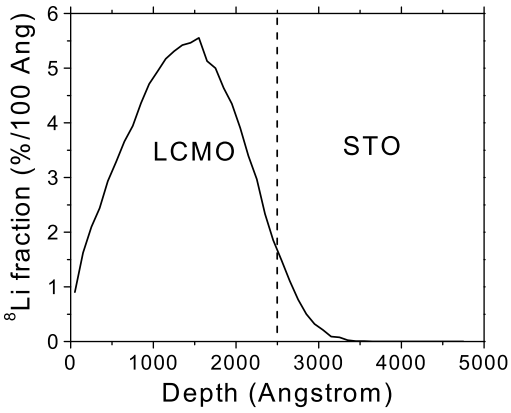

Fig. 1. Simulated implantation profile of ^{8}Li ions at 28 keV implantation energy in 2,500Å thick LCMO film on $SrTiO_3$ substrate. The implantation profile is calculated with TRIM Monte Carlo simulation.

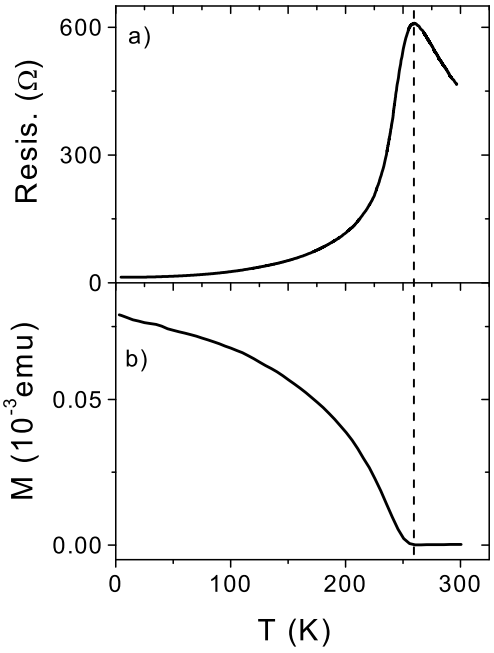

Fig. 2. a) Resistance across LCMO film in zero magnetic field. b) Magnetization in an applied field of 100 G. The insulator-metal and magnetic transitions both occur at $T_c = 259$ K.

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 $\lambda = 1/T_1$ and τ. 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:

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

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

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

where $\tau' = \tau/\lambda(\tau + 1/\lambda)$. The data in fig. 3 are fit to the sum of Eq. 1 with $f(t, t_p : \lambda) = e^{-(\lambda_{fast}(t-t_p))^\beta}$ ($\beta = 0.5$) and Eq. 2 (λ_{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 ($\lambda \propto B_{loc}^2$). 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 (λ_{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 λ from μSR data[8]. Therefore we plot a lower bound for the relaxation rate. However above T_c λ_{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 λ_{fast} drops due to the freezing out of the magnetic excitations.

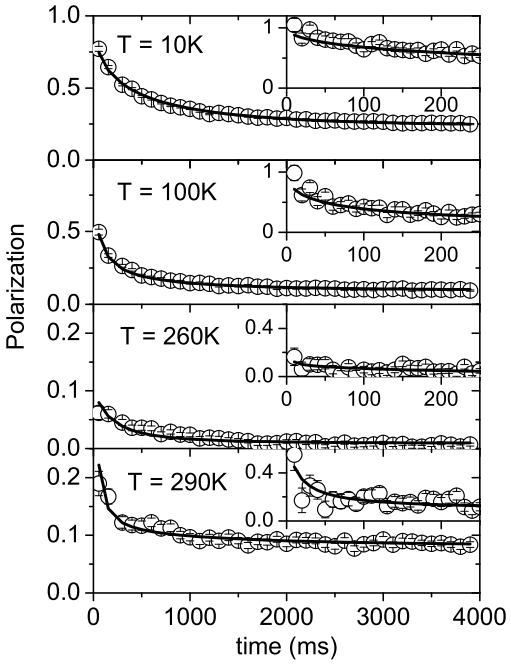

Fig. 3. Relaxation of the polarization of ^{8}Li decay in the LCMO Ca=0.33 film measured with ^{8}Li β-NMR at various temperatures. A 4 s pulse of Li beam is delivered onto the film starting at $t = 0$. The curves are fits to the sum of a stretched exponential ($\beta = 0.5$) and an exponential function. Note that the y-axis for panels c and d are expanded compared to panels a and b. Insets: Polarization on an expanded time scale. The time axis is the same for each inset.

In conclusion, we present the first ^{8}Li β-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 β-NMR can be used to probe magnetic spin fluctuations in thin magnetic films.

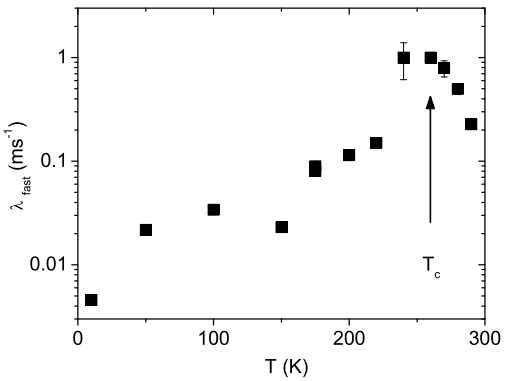

Fig. 4. Relaxation rate of the fast component from fits in fig. 3. This relaxation is attributed to the LCMO layer.

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