2018

Beta Detected NMR of LaAlO3

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Publication Details

Karner, V. L., McFadden, R. M. L., Chatzichristos, A., Morris, G. D., Pearson, M. R., Levy, C., Salman, Z., Cortie, D. L., Kiefl, R. F. & MacFarlane, W. (2018). Beta Detected NMR of LaAlO3. Proceedings of the 14th International Conference on Muon Spin Rotation, Relaxation and Resonance (μSR2017) (pp. 011023-1-011023-6). Tokyo, Japan: The Physical Society of Japan.

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Abstract
Using 8Li β-NMR we studied the temperature dependence of the spin-lattice relaxation in LaAlO3 in high magnetic field. The relaxation in LAO is composed of two components: a fast-relaxing signal with a small amplitude, and a large amplitude, slow relaxing component. The data was fit using a highly-constrained model which assumes that the temperature dependence of the slow and fast component is the same at all temperatures. The 8Li relaxation suggests a T2 temperature dependence, indicating that the relaxation mechanism could be due to a coupling between the quadrupole moment of 8Li and the soft-mode, low energy phonons in LAO.

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Proc. 14th Int. Conf. on Muon Spin Rotation, Relaxation and Resonance (μSR2017)
JPS Conf. Proc. **21**, 011023 (2018)
https://doi.org/10.7566/JPSCP.21.011023

Beta Detected NMR of $LaAlO_3$

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(Received June 21st, 2017)

Using ^{8}Li β-NMR we studied the temperature dependence of the spin-lattice relaxation in $LaAlO_3$ in high magnetic field. The relaxation in LAO is composed of two components: a fast-relaxing signal with a small amplitude, and a large amplitude, slow relaxing component. The data was fit using a highly-constrained model which assumes that the temperature dependence of the slow and fast component is the same at all temperatures. The ^{8}Li relaxation suggests a T^2 temperature dependence, indicating that the relaxation mechanism could be due to a coupling between the quadrupole moment of ^{8}Li and the soft-mode, low energy phonons in LAO.

KEYWORDS: $LaAlO_3$, Soft-mode phonons, β-NMR

1. Introduction

$LaAlO_3$ (LAO) is an insulating, non-magnetic, Perovskite oxide. It is commonly used as a substrate and as a vacuum-like layer in heterostructures. However, LAO is interesting in its own right because the structural phase transition from cubic ($Pm\bar{3}m$) to rhombohedral ($R\bar{3}c$) Perovskite at 800 K involves a soft-mode optical phonon [1-6]. A soft mode is a phonon whose frequency goes to zero at the phase transition becoming the static lattice distortion. At low temperature (below $T_C \approx 800\ K$), lower symmetry state of LAO; there are two low energy phonons that arise from the new structure and that are the soft-modes in the low temperature phase. These optical phonons have remarkably low energy even far from the transition; one of the optical phonons has an energy of only 5 meV [4-6].

At the structural transition, the AlO_6 octahedra begin to rotate around a trigonal axis (the [111] cubic axis). Because in the Perovskite structure adjacent oxygen octahedra have common oxygen corners; half of them rotate by an angle in one direction, while the other half rotates by the same angle but in the opposite direction. As the cubic

symmetry breaks, these octahedra become distorted, either elongating or compressing along the rotation axis. The phase transition in LAO can be characterized as second order with the order parameter given by the rotation angle of the AlO_6 octahedra (ϕ) [1,7,8].

^{27}Al and ^{139}La NMR has been performed on $LaAlO_3$ above and below the phase transition. The quadrupolar coupling constants were found to vary as the square of the rotation angle (ϕ). In addition, ^{27}Al $1/T_1$ measurements were performed as a function of temperature. The resulting temperature dependence was interpreted to be an interplay between a contribution due to the soft-mode phonons, which varied as T^2; a critical term, which varied as $(T - T_C)^{-0.5}$, and from paramagnetic impurities [9].

LAO is also well known from the $LaAlO_3/SrTiO_3$ heterostructures in which the two insulating oxides have a two-dimensional electron gas at their interface which exhibits interesting electronic and magnetic properties [10,11]. It is also known for its role as an insulating layer in rare earth nickelate ($RENiO_3$) heterostructures [12]. As a substrate, it is commonly used to epitaxially grow transition metal oxide thin films because it is well matched in terms of the lattice constant.

In this paper, we report on investigations of the ^{8}Li spin lattice relaxation (SLR) in a $LaAlO_3$ crystal in high magnetic field. The relaxation, while extremely slow, shows a systematic temperature dependence consistent with a phonon relaxation mechanism, probably facilitated by quadrupolar relaxation. Remarkably, the spin lattice relaxation rate exhibits a power law dependence down to low temperatures without evidence for phonon freeze-out.

2. Experimental

Beta detected nuclear magnetic resonance (β-NMR) measurements were performed on a $LaAlO_3$ crystal at the ISAC facility at TRIUMF. β-NMR is a magnetic resonance technique in which a laser polarized radioactive ion beam is implanted into the sample of interest. The most common isotope used, and the one used in this experiment, is ^{8}Li which undergoes a beta decay. The ^{8}Li nucleus has spin $I = 2$, gyromagnetic ratio $\gamma = 6.3015\ \mathrm{MHz/T}$, and electric quadrupole moment $Q = +31.4\ \mathrm{mb}$. The polarization of the $^8Li^+$ is monitored by measuring the asymmetry of the beta decay along the initial polarization direction using suitably placed detectors. The high-field spectrometer has longitudinal geometry such that the applied magnetic field and the initial polarization have the same orientation. By changing the energy of the incident ion beam, between 0.1 and 30 keV, it is possible to perform a depth-resolved analysis of thin films, interfaces, and surfaces.

For this experiment, SLR measurements were performed with a pulsed beam of ^{8}Li, and no applied RF. Here, a pulse of $^8Li^+$ is implanted into the sample, and then the asymmetry is measured as a function of time. This provides information on the different relaxation mechanisms in the system. The pulse length was 4 s, and the total measured time was 16 s.

3. Results and Discussion

The relaxation in $LaAlO_3$ is very slow, which is not uncommon for an oxide insulator in a high magnetic field [13]. Figure 1 shows three raw SLR spectra; measured at room temperature, 100 K, and 4 K. From the raw data, it appears that the relaxation has two components: a very slow relaxing component of large amplitude and a small, fast relaxing component. Since the fast component is such a small fraction of the total amplitude it was considered of greater importance to fit the slow component correctly.

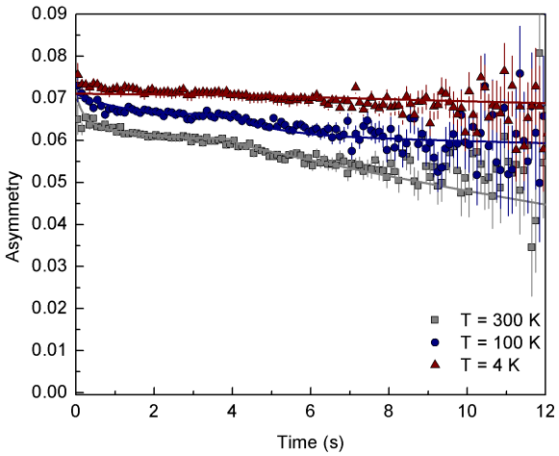

Figure 1. Comparison of the raw spin lattice relaxation spectra of $LaAlO_3$ at three temperatures; at 6.55 T, and 4.9 keV. In addition, the solid lines represent the fits obtained from the global fit for the temperatures displayed.

The asymmetry as a function of time ($p_z(t)$) is determined by the radioactive lifetime of ^{8}Li, $\tau = 1.21\ s$, and the spin lattice relaxation rate. Assuming a beam pulse duration of t_p and a general spin lattice relaxation function $f(t,t')$ for ^{8}Li implanted at t', the asymmetry as a function of time follows [10]:

$$p_z(t) = \begin{cases} \dfrac{\int_0^t e^{-(t-t')/\tau} f(t,t')\,dt'}{\int_0^t e^{-t/\tau}\,dt}; t \le t_p \\ \dfrac{\int_0^{t_p} e^{-(t_p-t')/\tau} f(t,t')\,dt'}{\int_0^{t_p} e^{-t/\tau}\,dt}; t > t_p \end{cases} \quad (1)$$

In order to model the spectra, it was assumed that the data was biexponential across the entire measured temperature range. In addition, the following constraints were made: (1) the fraction of the slow, and the fast component are temperature independent, and (2) the ratio between the fast and slow relaxation rates is temperature independent. The resulting spin lattice relaxation function used has the form:

$$f(t,t') = A_o[f_s e^{-\lambda(t-t')} + (1-f_s)e^{-k\lambda(t-t')}], \quad (2)$$

where A_o is the initial asymmetry, f_s is the fraction of the slow relaxing component, and k is the ratio of the relaxation rates between the fast and slow components. During the fitting only λ (or $1/T_1$) was varied; all the other parameters were shared between the different spectra. The values obtained for the shared parameters from the global fit are shown in Table I, along with the Minos errors. The assumption that $\lambda_f = k\lambda_s$ is perhaps too strong a constraint, but allowing λ_f to vary freely does not significantly change the values of the slow relaxation rate. In fact, the fast component can be modelled with a stretched exponential or a non-constrained exponential and the result for the slow component is the same. From this analysis, we cannot conclude whether the fast component is intrinsic to LAO or whether it is a background signal which slows as a function of temperature in roughly the same way as the slow component.

Table I. Values for the shared parameters obtained from the global fit of the LAO data using the constraints mentioned above, and the function shown in Eq. (2) ($\chi^2/DOF = 3482/3972 = 0.877$).

Shared Parameter	Fitted Value	Lower Minos Error	Upper Minos Error
A_o	0.08755(2)	-7.344E-05	7.412E-05
f_s	0.866(2)	-0.00134	0.00132
k	225	-7.76	8.18

The resulting $1/T_1$ as a function of temperature, obtained from this fitting, is plotted in Fig. 2. The horizontal error bars in Fig. 2 do not represent a temperature uncertainty, but rather reflect that the data were acquired while cooling and are a measure of the standard deviation from the average temperature of the sample during the data acquisition. In a nonmagnetic electronic insulator like LAO we expect the relaxation to be slow. The main low energy excitations of the ideal crystal are the lattice vibrations. These can couple to the ^{8}Li by the quadrupole interaction, and can cause relaxation by a Raman-like process. At high temperatures, this is expected to yield a slow T^2 temperature dependence; while below the Debye temperature, when optical modes freeze out, it should cross over to an exponential dependence [14-15]. The curve overlaid on the data in Fig. 2 represents a quadratic fit of the temperature dependence of the ^{8}Li $1/T_1$. The fact that reasonable agreement is achieved with a second-order polynomial indicates that the relaxation could be due to a spin-phonon relaxation mechanism. As previously mentioned, in the ^{27}Al data on $LaAlO_3$ a contribution to the $1/T_1$ data was observed due to the coupling between the Al nuclear spins and the soft-mode phonons. Even though the temperature range under investigation in this paper is far below the critical region for the LAO phase transition, the low energy of the soft-mode optical phonons makes it feasible that such a relaxation mechanism could persist to lower temperature.

Another possible source of relaxation is hopping motion of the implanted $^8Li^+$ that modulated the quadrupolar interaction. While Li^+ diffusion is possible in Perovskites, significant crystalline disorder is required for fast mobility at room temperature [16]. In other materials where $^8Li^+$ is known to be moving, e.g. rutile TiO_2 [17,18] the relaxation rates are much faster and more strongly temperature dependent. It may be possible that the increase in relaxation with temperature is due to the onset of motion with a T_1 minimum at higher temperatures above 300 K, but it is weaker than the expected activated dependence.

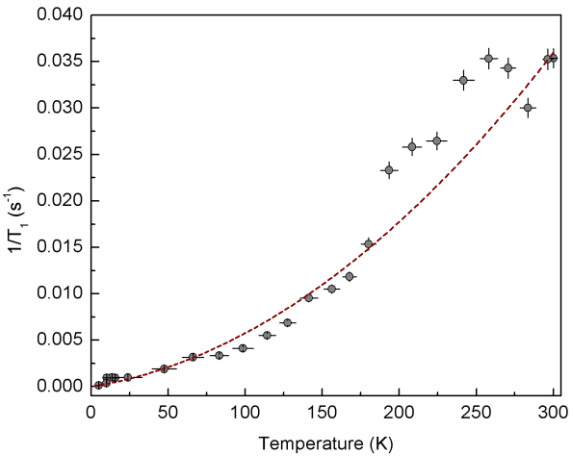

Figure 2. Slow component of the ^{8}Li spin lattice relaxation as a function of temperature for a $LaAlO_3$ crystal at 6.55 T. The dotted curve is a second-order polynomial.

This demonstrates that unlike the complimentary technique low energy muon spin rotation spectroscopy (μSR), ^{8}Li β-NMR is sensitive to properties of the host lattice due to its quadrupole moment. One major limitation for using β-NMR for measuring materials with such slow relaxation is that we are limited by the lifetime of our radioactive probe. Using the methodology outlined in the experimental section allows us to easily measure relaxation rates between 100 s^{-1} and 0.01 s^{-1}. As can be observed in Fig. 2, the low temperature points all have fitted values below the quoted minimum measurable values.

4. Summary

In this paper, we have studied the ^{8}Li spin relaxation in an insulating Perovskite oxide crystal $LaAlO_3$. LAO undergoes a soft-mode structural phase transition at 800 K. Below the transition, the soft-mode phonons have extremely low energy even far outside of the critical region for the phase transition. The ^{8}Li relaxation rate as a function of temperature shows a power law dependence indicating that the origin of the relaxation could be due to a coupling between the ^{8}Li nuclear spins and the soft-mode, low energy phonons. The measurements performed in this experiment are part of a set of control experiments related to understanding the relaxation rate in heterostructures which contain LAO.

Acknowledgment

We thank the CMMS at TRIUMF for their excellent technical support. This work was supported by NSERC Discovery Grants to RFK and WAM. RMLM and AC acknowledge additional support from their NSERC CREATE IsoSIM fellowships.

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