2018

Comparison of 8Li and 9Li spin relaxation in SrTiO3 and Pt: A means to distinguish magnetic and electric quadrupolar sources of relaxation

Aris Chatzichristos
University of British Columbia

Ryan M. L McFadden
University of British Columbia

Victoria L. Karner
University of British Columbia

David L. Cortie
University of British Columbia, dcortie@uow.edu.au

C D. P Levy
TRIUMF

See next page for additional authors

Comparison of 8Li and 9Li spin relaxation in SrTiO3 and Pt: A means to distinguish magnetic and electric quadrupolar sources of relaxation

Abstract

We demonstrate that the ratio of 1/T1 spin-lattice relaxation rates (SLR) of two different isotopes (here 8Li and 9Li) can be used in order to identify the predominant relaxation mechanism within the β-NMR technique. We studied with both isotopes a Pt foil and two samples of single crystal SrTiO3. In Pt, the ratio of the SLR rates was 6.82(29), which is close to but less than the theoretical limit of ~7.68 for pure magnetic relaxation. In SrTiO3, the weighted averaged SLR ratio of the two samples was 2.7(3), which is close but larger than the theoretical limit of ~2.14 expected for pure electric quadrupolar relaxation. This indicates that the primary source of relaxation in SrTiO3 is electric quadrupolar in origin and that magnetic effects have a much smaller importance in this material. The low effective asymmetry of 9Li was the dominant cause of uncertainty of the measurements in this study. We propose a system of tagging the beta-decays in coincidence with the alpha decays that take place in two of the three primary decay channels of 9Li as a way of increasing the effective asymmetry and enhance the signal of 9Li β-NMR.

Authors

Aris Chatzichristos, Ryan M. L McFadden, Victoria L. Karner, David L. Cortie, C D. P Levy, W A. MacFarlane, Gerald D. Morris, Matthew R. Pearson, Zaher Salman, and Robert F. Kiefl

Comparison of ^{8}Li and ^{9}Li spin relaxation in SrTiO$_3$ and Pt: A means to distinguish magnetic and electric quadrupolar sources of relaxation

A. Chatzichristos[1,2], R.M.L. McFadden[2,3], V.L. Karner[2,3], D.L. Cortie[1,2,3], C.D.P. Levy[4], W.A. MacFarlane[2,3], G.D. Morris[4], M.R. Pearson[4], Z. Salman[5] and R.F. Kiefl[1,2,4]

[1]*Department of Physics and Astronomy, University of British Columbia, Vancouver, BC V6T 1Z1, Canada*
[2]*Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver, BC V6T 1Z4, Canada*
[3]*Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z4, Canada*
[4]*TRIUMF, 4004 Wesbrook Mall, Vancouver, BC V6T 2A3, Canada*
[5]*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*

E-mail: *aris.chatzichristos@alumni.ubc.ca*

We demonstrate that the ratio of $1/T_1$ spin-lattice relaxation rates (SLR) of two different isotopes (here ^{8}Li and ^{9}Li) can be used in order to identify the predominant relaxation mechanism within the β-NMR technique. We studied with both isotopes a Pt foil and two samples of single crystal SrTiO$_3$. In Pt, the ratio of the SLR rates was 6.82(29), which is close to but less than the theoretical limit of ~ 7.68 for pure magnetic relaxation. In SrTiO$_3$, the weighted averaged SLR ratio of the two samples was 2.7(3), which is close but larger than the theoretical limit of ~ 2.14 expected for pure electric quadrupolar relaxation. This indicates that the primary source of relaxation in SrTiO$_3$ is electric quadrupolar in origin and that magnetic effects have a much smaller importance in this material.
The low effective asymmetry of ^{9}Li was the dominant cause of uncertainty of the measurements in this study. We propose a system of tagging the beta-decays in coincidence with the alpha decays that take place in two of the three primary decay channels of ^{9}Li as a way of increasing the effective asymmetry and enhance the signal of ^{9}Li β-NMR.

KEYWORDS: Beta-detected nuclear magnetic resonance, Spin relaxation, Isotopic comparison

1. Introduction

Beta-detected NMR (β-NMR), much like μSR, uses the parity violation of beta decay to detect the NMR signal, either from a neutron-activated sample, or from a beam of highly polarized radionuclides implanted in a sample material [1]. The most common β-NMR isotope used at TRIUMF as an implanted probe is ^{8}Li, which, in contrast to the spin-1/2 muon, is a spin-2 nucleus and has a non-zero electric quadrupole moment and thus it is sensitive to electric field gradients, not only to magnetic fields. The very different lifetimes of the ^{8}Li and muon (1.21 s versus 2.2 μs) make the two techniques complementary, since they can detect dynamics on very different time scales. A challenge with ^{8}Li β-NMR is identifying the dominant mechanism of spin-lattice relaxation (SLR), namely whether the origin of relaxation is electric quadrupolar or magnetic. It is possible to distinguish between SLR mechanisms by comparing the SLR rate of two different isotopes, in this case ^{8}Li and ^{9}Li [2].

Isotopic comparison has been used in classical NMR [3] and in this study we applied this tech-

nique to β-NMR. We measured the SLR rates for ^{8}Li and ^{9}Li in the same samples of Pt foil and SrTiO$_3$. Pt was selected as a test case for pure magnetic relaxation, while SrTiO$_3$ is a non-magnetic insulator, but the source of its relaxation is not well understood. With this work we demonstrate that its relaxation is mainly electric quadrupolar in origin.

The major challenge with this technique is that ^{9}Li has a much smaller effective asymmetry than ^{8}Li, due to its more complicated beta-decay scheme. In particular, ^{9}Li decays to ^{9}Be by three main decay channels, two of which have opposite asymmetries that nearly cancel after weighting by the branching ratios. Based on Table I, the theoretical asymmetry a for ^{9}Li is

$$a = 0.505 \times (-2/5) + 0.34 \times (3/5) + 0.1 \times (-1) \approx 0.1, \tag{1}$$

Table I. The branching probability, asymmetry (a) and decay products of each decay mode of ^{9}Li.

^{9}Be state	Probability	a	Decay mode
ground state	50.5%	-2/5	stable
2429.4 MeV	34%	3/5	n+2α
2780 MeV	10%	-1	n+2α

It should in principle be possible to enhance the β-NMR signal from ^{9}Li by tagging events according to whether an alpha is emitted or not, which would allow us to distinguish between the different decay channels and isolate their contributions. To that end, we are planning on using Ag-doped ZnS as an alpha detector, because of its very high efficiency for alphas, which can subsequently be detected by a photomultiplier tube (PMT). We acquired a ^{8}Li β-NMR resonance spectrum in ZnS, so we can later measure the asymmetry enhancement with the alpha detection system under ideal circumstances, where the ^{8}Li stops in the ZnS itself.

2. Isotopic Comparison Method

By implanting the β-NMR radioactive beam in a pulsed mode and in the absence of a RF field, one can study the spin-lattice relaxation (SLR) in a sample by monitoring the decay of beta asymmetry versus time. SLR can provide information on the fluctuations of the internal fields in the vicinity of the stopping sites of the probe nuclei. The total SLR rate $1/T_1$ is generally caused by various processes, some of them magnetic (e.g. ferro-magnetism, conduction electron scattering) and some electric quadrupolar (such as diffusion and a non-zero electric field gradient (EFG) at the probe's stopping site) which can be grouped into a magnetic and an electric quadrupolar rate $1/T_1^{\mathrm{M}}$ and $1/T_1^{\mathrm{Q}}$. It is common (but not universal) for a single mechanism to dominate the relaxation in a given material, with other mechanisms being either suppressed or completely absent.

In order to distinguish the source of relaxation in a sample, it is crucial to note that the magnitude of the relaxation rate of each contribution for a given probe nucleus scales according to its spin, I, magnetic moment, μ, and electric quadrupole moment, Q. By measuring the SLR rates for two different isotopes under identical experimental conditions one can calculate the SLR rate ratio, R:

$$R(I, I') \equiv \frac{1/T_1(I)}{1/T_1(I')} = \frac{1/T_1^{\mathrm{M}}(I) + 1/T_1^{\mathrm{Q}}(I)}{1/T_1^{\mathrm{M}}(I') + 1/T_1^{\mathrm{Q}}(I')}, \tag{2}$$

In the case that the relaxation is caused solely by magnetic effects, Eq. (2) reduces to the ratio of pure magnetic relaxation, R_{M} [4]:

2

$$R_{\mathrm{M}}(I, I') = \left(\frac{\mu/I}{\mu'/I'}\right)^2 = \left(\frac{\gamma}{\gamma'}\right)^2, \tag{3}$$

with μ and γ denoting the magnetic moment and gyromagnetic ratio of each isotope. The above equation is valid in the limit of fast fluctuations (i.e., $\tau_c^{-1} \gg \omega_0$, where τ_c is the NMR correlation time and ω_0 is the Larmor resonance frequency), so that $1/T_1$ is independent of ω_0.

In the case of pure electric quadrupolar relaxation, Eq. (2) reduces to the limit, R_{Q} [4]:

$$R_{\mathrm{Q}}(I, I') = \frac{f(I)}{f(I')}\left(\frac{Q}{Q'}\right)^2, f(I) = \frac{2I + 3}{I^2(2I - 1)}. \tag{4}$$

where Q are the nuclear quadrupole moments.

Eqs. (3) and (4) reveal that by using the known nuclear moments of the isotopic probes [5] one can impose boundaries on the ratio of the relevant relaxation rates. For ^{8}Li and ^{9}Li, the ratio $T_1^{-1}(^9\mathrm{Li})/T_1^{-1}(^8\mathrm{Li})$ should be smaller – or equal in the case of pure magnetic relaxation – than $R_{\mathrm{M}} = 7.680$ and larger – or equal in the case of pure electric quadrupolar relaxation – than $R_{\mathrm{Q}} = 2.136$.

3.   Experimental Configuration

This experiment was performed at TRIUMF's Isotope Separator and Accelerator Facility (ISAC) in Vancouver, Canada. ISAC can generate and deliver to the dedicated β-NMR and β-NQR spectrometers an intense beam of many isotopes of various elements, among which are ^{8}Li and ^{9}Li. The details on the characteristics and geometry of these spectrometers can be found elsewhere [6].

Prior to implantation in the sample, the Li$^+$ ion beam gets spin polarized in flight by circularly polarized laser light that pumps the Li $^2S_{1/2} -^2 P_{1/2}$ optical D_1 transition. The degree of nuclear polarization of the beam after stopping in the sample has been found by previous work to be $\sim$ 70% [7].

4.   Results

To show that the method of isotopic comparison is applicable to β-NMR, we studied two materials with very different properties. The first one was Pt, a d-band metal, in which the stopping site of lithium exhibits a small or negligible quadrupolar interaction [8]. Thus, in this material the relaxation rate should be primarily magnetic, originating from the scattering of conduction electrons to the lithium ions (i.e., Korringa relaxation [9]). The second material studied was SrTiO$_3$, which is a non-magnetic insulator. It has been shown by previous work with β-NMR [10], that ^{8}Li feels a large quasi-static quadrupolar interaction. This is not to say a priori, however, that magnetic interactions are absent in this material. For example, any O^{2-} vacancies, either intrinsic to the sample or created by the implantation of lithium, would create two paramagnetic Ti^{3+} ions. Such paramagnetic defects could have magnetic fluctuations of low frequency, which would contribute to the SLR of lithium.

4.1   β-NMR in Platinum

The resonance spectra at 1.90 T and 300 K for both ^{8}Li and ^{9}Li can be seen in Fig. 1. For ^{8}Li, the intrinsic Gaussian FWHM was found to be 0.85(10) kHz. This value is somewhat smaller than those reported previously in Pt [8, 11], where power broadening was not taken into account. For ^{9}Li, a single resonance at 33.18685(28) MHz with FWHM of 6.8(6) kHz is observed. Note that the width of the resonance is considerably broader than for ^{8}Li, reflecting the influence of power broadening by the RF field ($B_1 \sim 35\mu$T). The large RF field is necessary to maximize the signal, due to the smaller asymmetry of ^{9}Li.
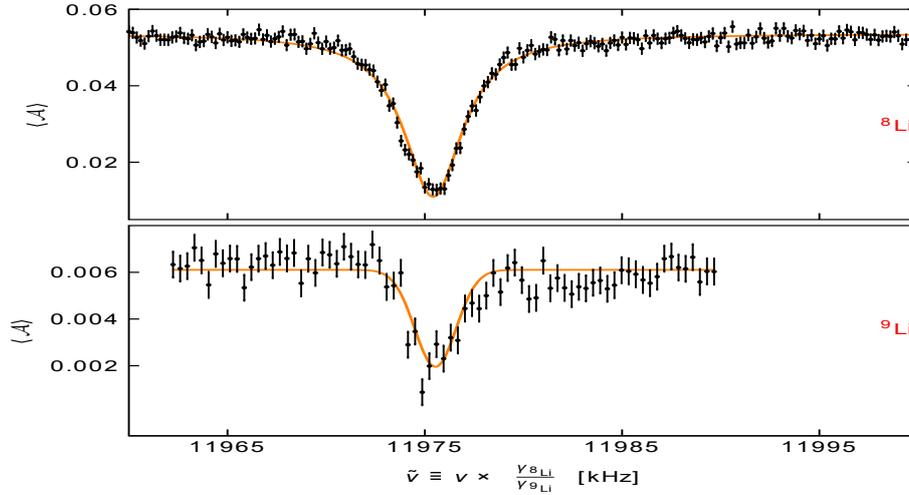
Fig. 1.   Resonance spectra in Pt foil at 300 K and 1.90 T with ^{8}Li (*top*) and ^{9}Li (*bottom*). The frequency has been normalized to the gyromagnetic ratio of each isotope.

The fact that the resonance measurements in Pt show a single narrow line, indicates that the implanted lithium ion occupies a site with a vanishing (static) EFG. Therefore, a single exponential function of the following form is sufficient to fit the SLR spectra:

$$A(t - t') = \exp\left[-\lambda\left(t - t'\right)/T_1\right], \tag{5}$$

The SLR rates for both isotopes were measured in magnetic fields of 1.90 T (see Fig. 2) and 6.55 T at a temperature of 300 K for both ^{8}Li (Fig. 2(a)) and ^{9}Li (Fig. 2(b)).
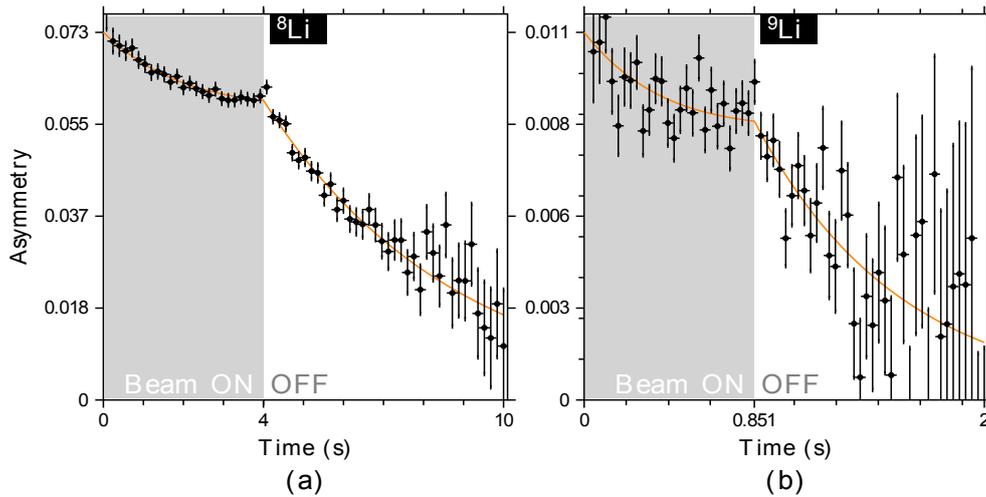

Fig. 2.   SLR spectra of ^{8}Li (*left*) and ^{9}Li (*right*) in Pt foil at 1.9 T and 300 K.

The ratios of $T_1^{-1}(^9\text{Li})/T_1^{-1}(^8\text{Li})$ at 6.55 T and 1.90 T are in good agreement with each other and we find a relaxation rate ratio, R_{Pt}, of 6.8(4) and 5.9(9) at 6.55 T and 1.90 T, respectively.

4.2   β-NMR in SrTiO₃

For the second part of this work, we studied the non-magnetic insulator $SrTiO_3$. This is a material in which the relaxation is expected to stem primarily from electric quadrupolar fluctuations. Previous work with ^8Li β-NMR [12, 13] shows that the implanted lithium probes occupy a single non-cubic site.

We studied two $SrTiO_3$ samples with dimensions 10x8x0.5 mm³. The first one (S1) was single crystal $SrTiO_3$, while the second sample (S2) had in addition a 30 nm $LaTiO_3$ capping layer. Given that all measurements were made with an implantation energy of 18 keV, only a negligible fraction of the probing ions stopped in the $LaTiO_3$ film, or near the interface and thus the measurement on the S2 film probed only the $SrTiO_3$ substrate.
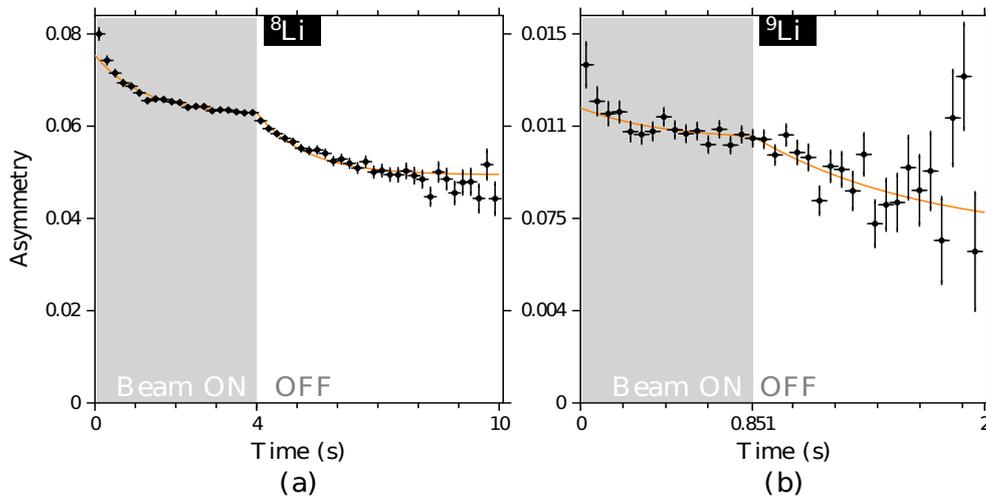

Fig. 3.   SLR spectra of ^8Li (*left*) and ^9Li (*right*) in $SrTiO_3$ (S2) at 10 mT and 300 K.

Figure 3 shows the SLR spectra for ^8Li and ^9Li at 10 mT and 300 K taken at the substrate of sample S2. One can clearly see that the relaxation does not decay to zero in the timescale of our measurements, which means that a single exponential is not sufficient to fit these spectra. All SLR spectra in both $SrTiO_3$ samples were fitted by a biexponential function, having one fast relaxing and one slow relaxing component. The slow relaxation rate was systematically consistent with zero, thus a fitting function with a non-relaxing component was used [14]:

$$A(t - t') = f \exp\left[-\lambda\left(t - t'\right)\right] + (1 - f),\qquad(6)$$

where f is the fraction of the relaxing asymmetry ($0 \leq f \leq 1$) and $\lambda \equiv 1/T_1$.

The fitting procedure revealed that the fraction f of the relaxing asymmetry was unchanged in all measurements on the S1 sample, so it was set to 0.347(3) and was shared by all fitted spectra. In the S2 sample, the relaxing fraction was found independently to be 0.341(2), very similar to S1.

The fit acquired using Eq. 6 does not include a small but very fast relaxing component that can be identified at the early part of Figure 3. Given the large statistical uncertainties of the ^9Li spectrum, it would be overfitting to add an extra fast relaxing component, in addition to the two terms of Eq. 6. Moreover, this very fast relaxing component is not present in other studies on $SrTiO_3$ (including our current measurements at sample S1), which means that this extra fast relaxation is most probably related to lithium stopping outside the sample (e.g. due to beam instabilities or backscattering off the target material). In low magnetic field, having a percentage of the incoming lithium stopping outside

the sample often manifests as a small but very fast relaxing component, irrelevant to the material under study.

The ratio of ^{9}Li/^{8}Li relaxation rates in SrTiO$_3$, R_{STO}, was calculated from our measurements at 300 K in both SrTiO$_3$ samples: In sample S1, R_{STO} was found to be 2.9(4) and 2.4(5) in sample S2.

4.3   β-NMR in ZnS:Ag

Fig. 2 and 3 reveal that the uncertainty associated with the ^{9}Li measurements was much larger than ^{8}Li, even though we typically spent ∼ 10 times more time for the acquisition of the ^{9}Li spectra. The figure of merit for a β-NMR measurement is A^2N, where A is the observable asymmetry and N is the total number of decay events. Thus, to further develop the capabilities of the isotopic comparison method in β-NMR, we designed a system that should be able to enhance the effective initial asymmetry of ^{9}Li by a factor of 6. That system, coupled with the development of certain aspects of TRIUMF's ISAC facility that would allow for an increase of the intensity of ^{9}Li$^+$ beams by a factor of ∼ 10, should suppress greatly the uncertainty of future ^{9}Li measurements, making the figure of merit for ^{9}Li comparable to ^{8}Li.

A key aspect of the new system, which will be tested in the following months, is the detection of the alpha particle coming from the decay of ^{9}Li.

An efficient α-detection system can enhance the initial asymmetry of the ^{9}Li spectra significantly, since it should be possible to register two spectra in parallel, one with the beta detected in coincidence with an alpha, and one without an alpha. The former would have an initial asymmetry of $a = 0.236$, twice as big as that obtained without α-detection. The latter spectrum will have an increased initial asymmetry of $a = 0.4$ if the alpha detection efficiency is close to 100%, making the effective asymmetry of the measurement 6 times larger than that without alpha detection.

Also, note that when the ^{9}Li decays into an excited state of ^{9}Be, it subsequently emits *two* alpha particles, at an angle of 180°. This means that an efficient alpha detector can register all decays that emit an alpha, by just covering half the solid angle, namely 2π, instead of the nominal 4π. Thus, our proposed detection system consists of a hat-like detector over the sample with a hole for the beam to enter, as well as a system of lenses to guide the produced photons from the scintillator to a photomultiplier tube (PMT) outside the ultra high vacuum (UHV). Most of the alphas will only have to cross a few nanometers of material (depending on the implantation depth) to reach the scintillator, so they will escape the sample without much attenuation. This has been confirmed with a Geant4 simulation.

We intend to use ZnS:Ag as an alpha scintillator and to that end, we studied its β-NMR signal for the purpose of measuring the enhancement factor under ideal circumstances, namely when the alpha detection efficiency is close to 100%. ZnS is a cubic material in the sphalerite form. When doped with Ag, the resulting compound is known to be an extremely bright scintillator [15] (∼ 95,000 ph/MeV). Commonly it is used in a polycrystalline form, sprayed as a powder on a surface. The incoming alphas produce a high number of photons, with an intensity peak at a wavelength of 460 nm [16], caused by the recombination between shallow donors and simple silver substitutional acceptors [Ag$_{Zn}$] [17]. The small thickness of the powder suppresses significantly the scintillation due to incoming betas, which attenuate in a much longer range, making this material ideal for the alpha-detection system of this study.

In this experiment, we studied with the ^{8}Li β-NMR technique a polycrystalline powder of ZnS doped with 6% Ag, deposited on a Al$_2$O$_3$ substrate. We acquired a resonance spectrum at 10 K (Fig. 4) and in addition verified that the scintillating properties of this material are unchanged in a wide range of temperatures (5-310 K), by imaging the scintillation produced by the implanted beam with a CCD camera.

The resonance spectrum was fitted best with two Lorentzian curves, both centered at the same frequency (129.197(4) kHz). The two curves had very different widths: The narrow one had a FWHM
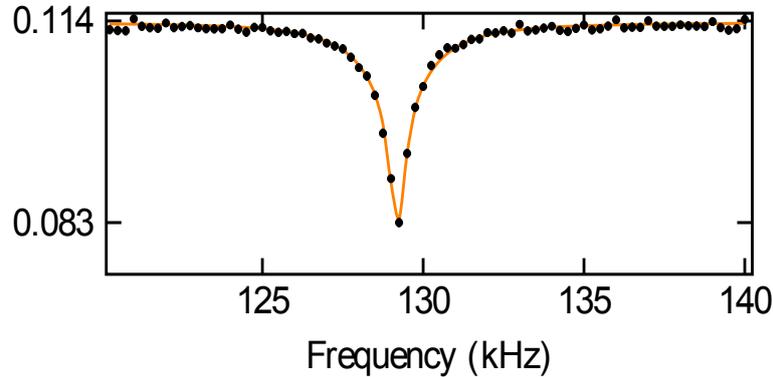
Fig. 4.   Resonance spectrum for ^{8}Li in ZnS:Ag at 10 K.

of 0.64(5) kHz, whereas the wide line had a FWHM of 2.61(25) kHz. The amplitude of the narrow line was twice as big as that of the wide line.

Based on the unit cell structure of ZnS, we expect ^{8}Li ions to inhabit the tetrahedral interstitial sites, with four sulfur nearest neighbors. The multicomponent nature of the resonance is most likely related to the disordered nature of the sample since it is $\sim$ 6% Ag doped with other defects present as well. We attribute the narrow resonance to lithium ions being in a slowly relaxing environment, whereas the wide resonance should be due to ^{8}Li being at positions that lead to fast but inhomogeneous relaxation. Such centers of relaxation could be complexes of Ag$^+$ with other paramagnetic centers and other defects, which can produce a small EFG at the ^{8}Li site.

5.   Ratio of Relaxation Rates

In platinum, the weighted average ratio of the relaxation rates at 1.90 T and 6.55 T was found to be: R_{Pt} = 6.82(29). This value is close to the limit of pure magnetic relaxation, R_M, but more than one standard deviation away from it.

This discrepancy could be explained by the fact that the measurements were taken at 300 K. At this temperature, the lithium probes could feel a small fluctuating EFG due to phonon-lithium scattering or local lattice vibrations. These effects would give rise to electric quadrupolar relaxation, but the fact that the temperature dependence in this material is known to be linear [18] imposes a strict upper boundary to their relative strength.

In SrTiO$_3$, the weighted average value of R_{STO} at the first sample was found to be 2.9(4), close, but not inside experimental error from the limit of pure electric quadrupolar relaxation. When the measurement of R_{STO} in the second sample, which yielded 2.4(5), is taken into account, the final value of R_{STO} from all our measurements yields 2.7(3). This brings the ratio closer to the electric quadrupolar limit, but a small discrepancy persists.

This implies that there is a small magnetic component to the relaxation, which is probably due to the existence of O vacancies, which would create paramagnetic Ti^{3+} ions.

These vacancies were probably intrinsic defects in the SrTiO$_3$ samples, rather than extrinsic, caused by the implantation of lithium. Based on the number of implanted ions, the illuminated volume of the samples and the number of Frenkel pairs that a typical lithium ion of this energy would create, the concentration of implantation related Frenkel pairs was estimated to be in the order of 100 ppm in SrTiO$_3$ and $\sim$ 50 ppm in Pt. This concentration is orders of magnitude smaller than that of the intrinsic oxygen vacancies in the SrTiO$_3$ samples, which were in the order of $\sim$ 1%.

6. Conclusions

In this work we used the ratio R of $T_1^{-1}(^9\text{Li})/T_1^{-1}(^8\text{Li})$ in Pt and SrTiO$_3$, in order to distinguish the source of spin-lattice relaxation in each case.

In Pt, the ratio R_{Pt} was found to be very close to the limit of pure magnetic relaxation, but they were not in agreement inside experimental error. This was attributed to the non-zero temperature, which could lead to a fluctuating EFG. Measurements at lower temperature are needed, in order to verify this.

In SrTiO$_3$, the ratio R_{STO} was very close to the limit of pure quadrupolar relaxation. The measurement at one of the two samples agrees with that limit, but the measurement at the other, as well as their weighted average, is slightly larger than R_Q. This indicates that there might be a small magnetic contribution to the relaxation, which could be caused by the presence of O vacancies giving rise to paramagnetic Ti^{3+} ions.

The above results indicate that isotope comparison can distinguish the source of spin-lattice relaxation in β-NMR. This can be a vary valuable tool for the future development of β-NMR, since it can be used any time the source of relaxation cannot be determined by varying the temperature or the magnetic field.

The major limitation of this technique is the fact that the effective asymmetry of ^{9}Li is highly suppressed, because the three main decay channels of this isotope have opposite asymmetries, that nearly cancel. To surpass this limitation, we are going to tag the beta decays in coincidence with an alpha particle and thus distinguish between different decay channels.

References

[1] W. A. MacFarlane, Solid State Nucl. Magn. Reson. **6869**, 1(2015).

[2] A. Chatzichristos, R. M. L. McFadden, V. L. Karner, D. L. Cortie, C. D. P. Levy, W. A. MacFarlane, G. D. Morris, M. R. Pearson,Z. Salman, and R. F. Kiefl, Phys. Rev. B **96**, 014307 (2017).

[3] I. Tomeno and M. Oguchi, J. Phys. Soc. Jpn. **67**, 318 (1998).

[4] A. Abragam, Principles of Nuclear Magnetism (Oxford UniversityPress, 1983).

[5] R. B. Firestone and V. S. Shirley, Table of isotopes, 8th ed. (J.Wiley, New York, 1996).

[6] Morris, G. D. and MacFarlane, W. A. and Chow, K. H. and Salman, Z. and Arseneau, D. J. and Daviel, S. and Hatakeyama, A. and Kreitzman, S. R. and Levy, C. D. P. and Poutissou, R. and Heffner, R. H. and Elenewski, J. E. and Greene, L. H. and Kiefl, R. F., Phys. Rev. Lett. **93**, 157601 (2004).

[7] W. A. MacFarlane and T. J. Parolin and D. L. Cortie and K. H. Chow and M. D. Hossain and R. F. Kiefl and C. D. P. Levy and R. M. L. McFadden and G. D. Morris and M. R. Pearson and H. Saadaoui and Z. Salman and Q. Song and D. Wang, J. Phys.: Conf. Ser. **551**, 012059 (2014).

[8] I. Fan and K. H. Chow and T. J. Parolin and M. Egilmez and M. D. Hossain and J. Jung and T. A. Keeler and R. F. Kiefl and S. R. Kreitzman and C. D. P. Levy and R. Ma and G. D. Morris and M. R. Pearson and H. Saadaoui and Z. Salman and M. Smadella and Q. Song and D. Wang and M. Xu and W. A. MacFarlane, Physica B **404**, 906 (2009).

[9] J. Korringa, Physica **16**, 601 (1950).

[10] W. A. MacFarlane and G. D. Morris and T. R. Beals and K. H. Chow and R. A. Baartman and S. Daviel and S. R. Dunsiger and A. Hatakeyama and S. R. Kreitzman and C. D. P. Levy and R. I. Miller and K. M. Nichol and R. Poutissou and R. F. Kiefl, Physica B **326**, 209 (2003).

[11] O. Ofer and K. H. Chow and I. Fan and M. Egilmez and T. J. Parolin and M. D. Hossain and J. Jung and Z. Salman and R. F. Kiefl and C. D. P. Levy and G. D. Morris and M. R. Pearson and H. Saadaoui and Q. Song and D. Wang and W. A. MacFarlane, Phys. Proc. **30**, 156 (2012).

[12] Salman, Z. and Reynard, E. P. and MacFarlane, W. A. and Chow, K. H. and Chakhalian, J. and Kreitzman, S. R. and Daviel, S. and Levy, C. D. P. and Poutissou, R. and Kiefl, R. F., Phys. Rev. B **70**, 104404 (2004).

[13] Salman, Z. and Kiefl, R. F. and Chow, K. H. and Hossain, M. D. and Keeler, T. A. and Kreitzman, S. R. and Levy, C. D. P. and Miller, R. I. and Parolin, T. J. and Pearson, M. R. and Saadaoui, H. and Schultz, J. D. and Smadella, M. and Wang, D. and MacFarlane, W. A., Phys. Rev. Lett. **96**, 147601 (2006).

[14] M. Smadella and Z. Salman and K. H. Chow and M. Egilmez and I. Fan and M. D. Hossain and R. F. Kiefl and S.R. Kreitzman and C.D.P. Levy and W.A. MacFarlane and A. I. Mansour and G. D. Morris and T. J. Parolin and M. Pearson and H. Saadaoui and Q. Song and D. Wang, Physica B **404**, 924 (2009).

[15] J. S.McCloy, M. Bliss, B. Miller, Z. Wang, S. Stave,Journal of Luminescence **157** 416423 (2015)

[16] D. Qin, G. Yang, G. He, L. Zhang, Q. Zhang, L. Li, Chalcogenide Letters **9** 441 - 446 (2012)

[17] N R J Poolton, J. Phys. C: Solid State Phys. 20 5867 (1987)

[18] Ofer, O. and Chow, K. H. and Fan, I. and Egilmez, M. and Parolin, T. J. and Hossain, M. D. and Jung, J. and Salman, Z. and Kiefl, R. F. and Levy, C. D. P. and Morris, G. D. and Pearson, M. R. and Saadaoui, H. and Song, Q. and Wang, D. and MacFarlane, W. A., Phys. Rev. B **86**, 064419 (2012).