Quadrupolar split ^{8}Li β-NMR in $SrTiO_3$

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Abstract

We have measured the temperature dependence of the β-NMR resonances of ^{8}Li$^+$ implanted in the top few thousand Å of a crystal of $SrTiO_3$ in a magnetic field of 3 T $\parallel$ $\langle 100 \rangle$. A well–resolved quadrupolar splitting of the resonance is observed indicating a noncubic Li site with $\langle 100 \rangle$ symmetry and a quadrupolar frequency ν_Q(211K) = 153.2(4) kHz. The cubic–to–tetragonal phase transition is reflected in the linewidths demonstrating that β-NMR is a sensitive probe of the structure near a surface.

Key words: β-NMR, $SrTiO_3$, Quadrupolar splitting

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Strontium titanate ($SrTiO_3$) is probably the best–studied perovskite transition metal oxide. It is interesting for its prototypical soft mode stuctural phase transition ($\sim$ 105 K)[1], its ferroelectric properties[2], and as a high dielectric constant layer in heterostructures based on Si[3]. It has also emerged as an important substrate material for thin films of high T_c superconducting cuprates and related materials[4]. Characterization of the substrate signal in such epitaxial thin films and heterostructures was the initial motivation for this work.

In this experiment, a beam of highly longitudinally spin polarized $^8Li^+$ with kinetic energies up to 30.5 keV is directed onto the sample in an ultrahigh vacuum coldfinger cryostat in a longitudinal magnetic field of 3 T. At this energy the $^8Li^+$ stops within $\sim$4000 Å of the surface. Linearly polarized RF magnetic field (perpendicular to the nuclear polarization) is stepped through a range of frequencies, yielding a resonant loss of polarization (as reflected in the forward–backward decay asymmetry) when the RF frequency matches the resonance frequency for the ^8Li nuclei. In the absence of quadrupolar splitting the resonance condition is simply $\nu = \nu_0 = \gamma H$, the Larmor frequency. The data are taken in a fast cw mode where the RF frequency is stepped fast relative to the ^8Li lifetime ($\tau_{1/2} = 842$ ms) with a continuous beam. In this situation the observed resonances are asymmetric due to the relatively slow recovery of the polarization after a resonance is traversed. In fact, it can be shown to be of the form,

$$f^{\mathrm{obs}}(\nu) = A \int_{-\infty}^{+\infty} f(\kappa)\theta(\nu-\kappa)e^{-(\nu-\kappa)/\dot{\nu}\tau} d\kappa, \quad (1)$$

where $f(\kappa)$ is the lineshape, θ the unit step function, and $\dot{\nu}$ is the RF sweep rate. While $f^{\mathrm{obs}}(\nu)$ is less straightforward to analyze, fast sweeping has the advantage that it is less sensitive to the longterm stability of the beam and its polarization.

The single crystal ⟨100⟩ $SrTiO_3$ wafer (10 x 8 x 0.5 mm) from Applied Technology Enterprises exhibits an RMS surface roughness of 1.5 Å as determined by atomic force microscopy.

Fig. 1 shows an example of the spectra at 211 K. The two spectra correspond to forward and backward polarized ^{8}Li which are selected by the helicity of the laser light in the on-line polarizer. The baseline asymmetries are subtracted and the result scaled by the full asymmetry (half the baseline difference $\sim$ 12%). The spectrum is clearly split into four major lines, two in each helicity channel, due to the quadrupolar interaction of the spin 2 nucleus. Since a cubic site has electric field gradient (EFG) zero by symmetry, virtually all the corresponding Li occupies a noncubic site in the $SrTiO_3$ lattice, i.e. not a substitutional site of either cation. In contrast to the μ^+, the quadrupolar splitting provides another means to determine the ^{8}Li site. Above the transition, the resonances are very narrow, indicating that the crystal is well–ordered in the vicinity of the Li.

The quadrupolar interaction couples the nuclear spin to the local EFG (q). When the scale of the coupling $\nu_Q \ll \nu_0$, the transitions between the magnetic sublevels (m) are split to first order as

$$\nu_{m\leftrightarrow m-1}|_{m=-1\cdots 2} = \nu_0 - \frac{\nu_Q}{2}(m - \frac{1}{2})[3\cos^2(\theta) - 1], \quad (2)$$

where $\nu_Q = e^2qQ/4h$, Q ($\approx +32$ mb) is the nuclear electric quadrupole moment, e the electronic charge and θ the angle between the applied magnetic field and the symmetry axis of the EFG tensor, assuming the EFG is cylindrically symmetric[5].

Due to the high nuclear polarization, only the $m = \pm 2$ sublevels are significantly populated initially[1]; thus only the $\pm 2 \leftrightarrow \pm 1$ transitions (the outer transitions) will have significant intensity. We attribute the observation of four lines, with splittings in the ratio 2:-1 and intensities 2:1, to a single site with the EFG symmetry axis parallel to a cubic axis of the crystal, e.g. the face–centre site coordinated by four oxygen ions. The magnetic field renders the cubic axis parallel to it ($\theta = 0^o$) inequivalent to the two (90^o) axes which then account for the two inner lines. The small signal at ν_0 accounts for a small fraction (5%) of the implanted Li and may be a background signal from Li stopped outside the sample. The resonances appear to account for quite small fraction of the total asymmetry[2]; however, the main reason for this is simply that the quadrupolar splitting has lifted the degeneracy of the magnetic transitions, and only a single transition is irradiated at a time (with our single frequency RF). A much less significant effect is that the RF field ($B_1 \sim 50\ \mu$T) may not have fully saturated each transition. Considering these factors, we conclude that the site we observe accounts for most of the implanted Li. The quadrupole frequency ν_Q we find is quite large in $SrTiO_3$ compared to other oxides[7] including the high T_c superconductor YBCO[8], which may allow an improved measurement of the ^{8}Li quadrupole moment provided the NMR of stable Li on this site can be detected[7].

The temperature (T) dependence of the two 90^o lines was measured down to 10 K. Detailed analysis of the lineshape was not warranted with the relatively low signal-to-noise, but the leading edges of the resonances were fit to $a + b[1 + \exp((\nu - \nu_r)/\delta\nu)]^{-1}$, which gives a reasonable measure of the position ν_r and

[1] The nuclear spins are polarized by optically pumping an atomic transition with circularly polarized light (see §1.C.f of Ref.[5]). The direction of nuclear polarization is selected by the polarization direction of the light. Recently, a related technique has been used to enhance the conventional NMR in semiconductor heterostructures[6].

[2] Spin lattice relaxation is not important in this regard. We measured T_1 using a 0.5 s pulsed beam in a time differential mode and estimate $T_1 \approx 60\text{s} \gg \tau$ at 10 K and even longer at room temperature.

halfwidth $\delta\nu$, for data of the form of Eq. (1).

The splitting of the lines ($= \frac{3}{2}\nu_Q$) is shown as a function of T in Fig. 2a. The T dependence of ν_Q is thus weak (as is typical) with a relative change of about 2% up to 300 K. The splitting does not change dramatically at the structural phase transition, but the tetragonal distortion in this phase is less than 0.1% of the cubic lattice constant[9]. In contrast, note the lines broaden significantly below the transition (Fig. 2b), likely due to the formation of twin domains in the tetragonal phase[10]. This demonstrates that ^{8}Li β-NMR may be a sensitive local structural probe near the surface, which in $SrTiO_3$ exhibits distinct critical phenomena compared to the bulk[9]. Note the beam energy can be adjusted to probe much closer to the surface of the sample (~60 Å).

In conclusion, we observe a quadrupolar split β-NMR spectrum of ^{8}Li implanted in crystalline $SrTiO_3$. We attribute the spectrum to a site with axial symmetry along a cubic crystal direction. These results are important as a characterization of the substrate signal for ^{8}Li β-NMR in high T_c films[8]. As a consequence of these results, it will be possible to observe the associated nuclear *quadrupolar* resonance in zero applied field in $SrTiO_3$. Such a resonance will likely find significant application as a sensitive *zero-field* probe of local magnetic fields in heterostructures such as high T_c thin films.

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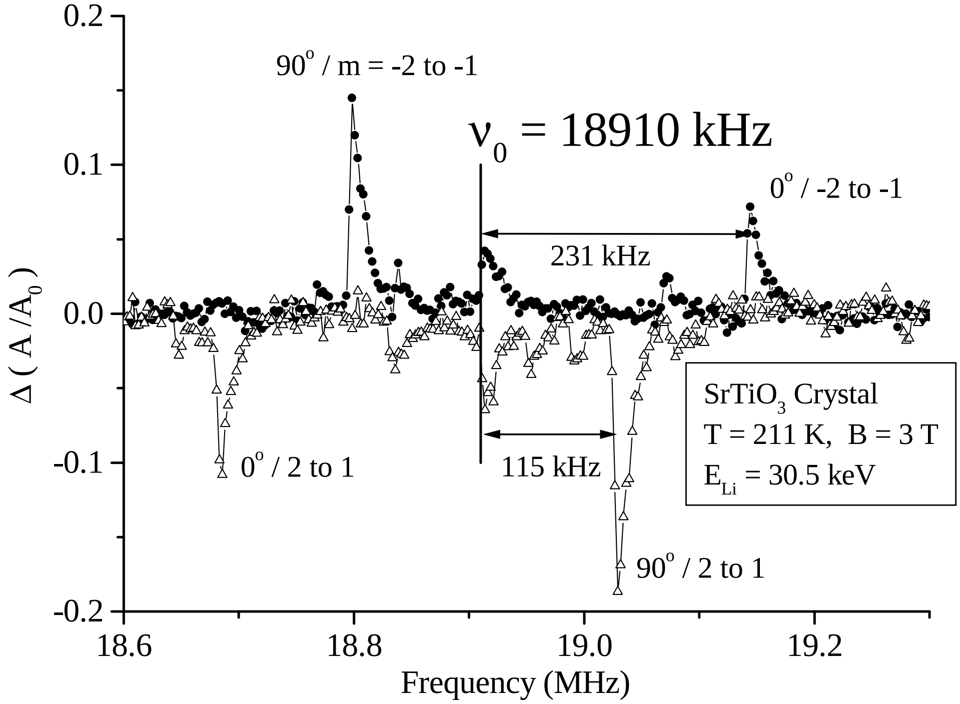
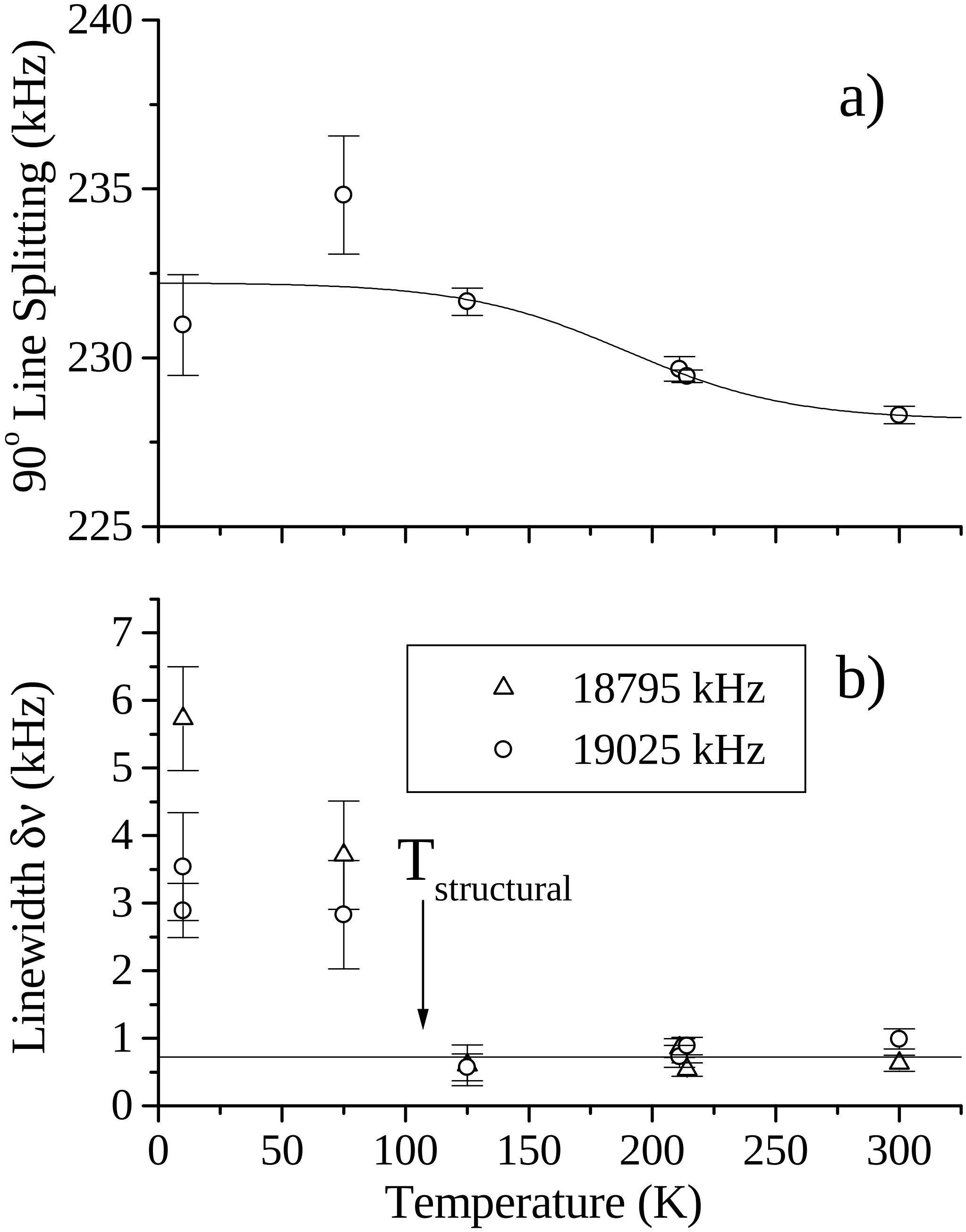
Figure Captions

Fig. 1: The spectrum at 211 K. The circles and triangles correspond to opposite polarization (laser helicity). The smaller features near the Larmor frequency ν_0 may be the inner transitions $m = \pm 1 \leftrightarrow 0$. The asymmetry of the lines is due to the fast RF sweeping from low frequency.

Fig. 2: Temperature dependence of the 90^o transitions: a) The splitting ($= \frac{3}{2}\nu_Q$); the curve is a guide to the eye. b) The resonance width; The line indicates the average width (730 Hz) above the transition at $\sim$ 105 K.



0.2
0.1
0.0
-0.1
-0.2
Δ (A /A0)
90o / m = -2 to -1
ν0 = 18910 kHz
0o / -2 to -1
231 kHz
115 kHz
0o / 2 to 1
90o / 2 to 1
SrTiO3 Crystal
T = 211 K, B = 3 T
ELi = 30.5 keV
18.6
18.8
19.0
19.2
Frequency (MHz)



240
235
230
225
90° Line Splitting (kHz)
a)
7
6
5
4
3
2
1
0
Linewidth δν (kHz)
b)
18795 kHz
19025 kHz
T structural
0
50
100
150
200
250
300
Temperature (K)