Low energy spin polarized radioactive beams as a probe of thin films and interfaces


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Abstract

A spectrometer for β-detected nuclear magnetic resonance (β-NMR) has been commissioned at the ISAC facility at TRIUMF. A beam of low energy highly spin polarized 6Li+ can be decelerated and implanted into ultra-thin structures 6–400 nm thick. β-NMR provides local information on the electronic and magnetic properties of materials which is similar to conventional NMR but can be used as a sensitive probe of ultra-thin films, interfaces and other nano-structures. We report here on the status of the spectrometer and preliminary results on a simple metal film.

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1. Introduction

Nuclear magnetic resonance (NMR) and related nuclear methods are widely used in condensed matter physics. The magnetic moment of a nucleus acts as a sensitive probe of the local magnetic and electronic environment. All forms of magnetic resonance require generation of nuclear spin polarization out of equilibrium followed by a detection of how that polarization evolves in time. The spin precession rate or Larmor frequency is a measure of the local magnetic field at the nucleus, whereas the spin relaxation rate is determined by spin dynamics near the Larmor frequency. However, there are also significant differences which influence the specific applications. For example, in conventional magnetic resonance a relatively small
nuclear polarization is generated by applying a large magnetic field after which it is tilted with a small RF magnetic field. An inductive pickup coil is used to detect the resulting precession of the nuclear magnetization. Typically one needs about $10^{18}$ nuclear spins to generate a good NMR signal with stable nuclei. Consequently conventional NMR is mostly a bulk probe of matter. On the other hand, in related nuclear methods such as muon spin rotation (μSR) [1] or β-detected NMR (β-NMR) [2,3] a beam of highly polarized radioactive nuclei (or muons) is generated and then implanted into the material. The polarization tends to be much higher – between 10% and 100%. Most importantly, the time evolution of the spin polarization is monitored through the anisotropic decay properties of the nucleus or muon which requires about 10 orders of magnitude fewer spins. For this reason nuclear methods are well suited to studies of dilute impurities, small structures or interfaces where there are few nuclear spins.

The principles of β-NMR are almost identical to μSR. As in μSR the nuclear detection method allows experiments to be performed in any magnetic field including zero field. Condensed matter applications generally require a high signal to noise which means high polarization and high rate. So far this has been much easier to achieve in the case of muons compared to radioactive nuclei. However, at radioactive ion beam facilities such as ISOLDE and ISAC it is possible to generate intense ($>10^9$/s) highly polarized (80%) beams of low energy radioactive nuclei [4]. Under these circumstances one can realize a significant enhancement in the signal to noise in β-NMR. Furthermore one has the added possibility to control the depth of implantation on an interesting length scale (6–400 nm).

Although in principle any beta emitting isotope can be studied with β-NMR the number of isotopes suitable for use as a probe in condensed matter is much smaller. The most essential requirements are: (1) a high production efficiency, (2) a method to efficiently polarize the nuclear spins and (3) a high β decay asymmetry. Other desirable features are: (4) small Z to reduce radiation damage on implantation, (5) a small value of spin so that the β-NMR spectra are relatively simple and (6) a radioactive lifetime that is not much longer than a few seconds. Table 1 gives a short list of the isotopes we have identified as suitable for development at ISAC. Production rates of $10^9$/s are easily obtainable at ISAC. $^8$Li is the easiest to polarize and therefore was selected as the first one to develop as a probe.

We have recently commissioned a low energy highly polarized beam of radioactive $^8$Li and the details on the polarizer are given in a separate article [5]. Here we concentrate on the high field spectrometer for β-NMR and give some preliminary results which demonstrate the unique capabilities of the method.

## 2. Experimental

A layout of polarized beamline and β-NMR spectrometers is given in Fig. 1. High nuclear spin polarization in the radioactive beam is achieved using a collinear optical pumping method in which polarized light from a laser is directed along the beam axis [4]. The method is well established for the case of alkalis such as $^7$Li where the neutral atom can be excited with visible laser light [4]. The first step in the procedure is to neutralize the ion beam by passing it through a Na vapor cell.

![Diagram](image-url)

### Table 1

Examples of isotopes suitable for β-NMR

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Spin</th>
<th>$T_{1/2}$ (s)</th>
<th>$\gamma$ (MHz/T)</th>
<th>β-Decay asymmetry (A)</th>
<th>Production rate (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^8$Li</td>
<td>2</td>
<td>0.8</td>
<td>6.26</td>
<td>0.33</td>
<td>$10^8$</td>
</tr>
<tr>
<td>$^{11}$Be</td>
<td>1/2</td>
<td>13.8</td>
<td>22</td>
<td>0.33</td>
<td>$10^7$</td>
</tr>
<tr>
<td>$^{15}$O</td>
<td>1/2</td>
<td>122</td>
<td>10.8</td>
<td>0.7</td>
<td>$10^8$</td>
</tr>
<tr>
<td>$^{17}$Ne</td>
<td>1/2</td>
<td>0.1</td>
<td>0.33</td>
<td></td>
<td>$10^6$</td>
</tr>
</tbody>
</table>

The production rates are projections except in the case of $^8$Li.
neutral beam then drifts 1.9 m in the optical pumping region in the presence of a small longitudinal magnetic holding field of 1 mT. The D1 atomic transition of neutral Li $2s^2S_{1/2} \rightarrow 2p^2P_{1/2}$ occurs at about 671 nm. There is time for about 10–20 cycles of absorption and spontaneous emission which lead to a high degree of electronic and nuclear spin polarization. The final step is to strip off the valence electron by passing it through a He gas cell. So far the highest nuclear polarization achieved is about 80% with an overall transmission efficiency of about 20%. Typically one operates with 60% polarization and 33% transmission.

The polarized $^8$Li ion beam is then passed through two 45° electrostatic bending elements which route the beam into one of three experimental stations. Since the beam optics are all electrostatic the polarization direction is unchanged by these bends. Consequently the beam entering the high field spectrometer is longitudinally polarized; whereas at the two other stations the beam is transversely polarized. In this paper we are concerned mainly with the high field spectrometer. The section just before the spectrometer has three electrostatic Einzel lenses and three adjustable collimators which control the beam spot on the sample.

A schematic of the spectrometer is shown in Fig. 2. The polarized beam enters from the left and passes through a hole in the back detector before entering the last Einzel lens at the entrance to a high homogeneity 9 T superconducting solenoid. The beam spot at the center of the magnet is a sensitive function of Einzel lens voltage, magnetic field and beam energy. Images of the $^8$Li beam at the sample position were obtained using a plastic scintillator and a CCD camera. These show that the beam spot is 3–4 mm in diameter.

One of the most important features of the spectrometer is that the ions can be implanted over a wide range of energies (1–90 keV) corresponding to an average implantation depth of between 6 and 400 nm, respectively. This is accomplished by placing the spectrometer on a high voltage platform which is electrically isolated from ground. The energy of implantation is controlled by adjusting the platform bias voltage. Note the grounded tube surrounding the electrode of the Einzel lens which extends into the bore of the magnet. The deceleration occurs as the beam exits this gold plated copper tube.

The high field spectrometer has longitudinal geometry such that the polarization and magnetic field are both along the beam axis. This is necessary for measurements in high magnetic fields where both the incoming ions and outgoing betas are strongly focussed by the magnet. The forward detector is on the beam/magnet axis and is located...
several cm downstream of the sample. In order to detect betas in the backward direction (opposite to the beam direction) it is necessary that the detector be outside the magnet since the betas are confined to the magnet axis while inside the magnet bore. Although the solid angles subtended by the two detectors in zero field are very different they have similar detection efficiencies in high magnetic fields due to the focussing effect of the solenoid.

Many experiments will be performed on materials at cryogenic temperatures and so an important design specification is the UHV vacuum requirement necessary to avoid a buildup of residual gases on the surface of the sample. Also since the low energy beam cannot pass through any windows the final leg in the beamline is also UHV compatible. Differential pumping with large cryopumps is used to reduce the pressure from $10^{-7}$ Torr upstream of the spectrometer to a design goal of $10^{-10}$ Torr in the main chamber. The sample cryostat is mounted on a large bellows so that it can be withdrawn from the magnet bore in order to change the sample though a load lock on top of the main vacuum chamber (see Fig. 2). Plastic scintillation detectors are used to detect the betas from $^{8}\text{Li} \rightarrow ^{8}\text{Be} + v_e + e^{-}$ for which the endpoint energy is 13 MeV. Since beta rates can reach $10^7/s$ the detectors are segmented to reduce rate dependent distortions in the spectra due to dead time. The plastic scintillators and light guides are held in reentrant stainless steel housings with thin stainless steel windows, isolating the detectors from the UHV vacuum chamber, but allowing transmission of the low energy betas.

3. Results

3.1. Gold foil

Fig. 3 shows a typical $\beta$-NMR resonance for $^{8}\text{Li}$ implanted in gold foil at 300 K. The spectrum is...
obtained by applying a large static magnetic field \((H_0 = 3 \text{T})\) along the initial polarization direction \((z)\) and a small perpendicular RF magnetic field \((H_1 \leq 0.1 \text{ mT})\). One then records the beta decay asymmetry as a function of RF frequency while a continuous beam of polarized \(^8\text{Li}\) is implanted into the sample. When the frequency of the RF matches the Larmor frequency of the \(^8\text{Li}\) nucleus \((\gamma H_0)\) the nuclear polarization precesses leading to a reduction in the time averaged asymmetry. The measured asymmetry has been normalized to the asymmetry off resonance \(A_0\) which is about 0.15.

The solid curve is a fit to two resonances corresponding to two crystallographic sites. The position of each resonance is a sensitive measure of the local magnetic field at the \(^8\text{Li}\) site. In a metal the dominant terms are the applied field and the hyperfine field due to polarization of the conduction electrons at the Fermi surface. The latter is referred to as a Knight shift [6] and can be estimated by comparing to the frequency in an insulator such as MgO. Both lines in Fig. 3 are within a few 100 ppm of the free Larmor frequency and thus imply the two sites have cubic symmetry. Otherwise the electric quadrupole moment \((Q = 22 \text{ mB})\) of \(^8\text{Li}\) would lead to quadrupolar splittings which are typically large on this frequency scale. There are only three cubic sites in an fcc lattice – the substitutional (S), the octahedral interstitial (O) and the tetrahedral interstitial (T). The T site is probably too small to accommodate Li. We expect the S site to have a smaller Knight shift than an interstitial since the coupling with the conduction electrons is expected to be less. Thus we tentatively assign the large amplitude line to the S site and the small amplitude line to the O site. This is consistent with a previous study of \(^8\text{Li}\) in Cu [7] which also has an fcc crystal structure.

The line width of 500 Hz is remarkably narrow and corresponds to a magnetic field resolution of 0.08 mT. This is about an order of magnitude better than in a μSR experiment but is still much greater than the intrinsic resolution of about 0.0001 mT determined by the lifetime of \(^8\text{Li}\). The observed linewidth may be due to a variety of effects including magnetic field inhomogeneity, nuclear magnetic dipoles, RF power broadening, residual crystalline imperfections and variations in the conduction electron density near the surface.

### 3.2. Nuclear quadrupole splitting in \(\text{SrTiO}_3\)

\(^8\text{Li} (I = 2)\) has a small quadrupole moment which couples to the electric field gradient (EFG) at non-cubic sites and leads to a splitting of the resonance. If the EFG tensor is axially symmetric then in the high field limit there will be four equally spaced resonances centered about the Larmor frequency. These correspond to the four allowed magnetic dipole transitions between the five magnetic sublevels \((m = -2, -1, 0, 1, 2)\) with the selection rule \((\Delta m = \pm 1)\). The four allowed transition frequencies are given by

\[
\nu(m \leftrightarrow m - 1) = \gamma H_0 + 3v_Q|m - 1/2|3 \cos^2 \theta - 1],
\]

where \(\gamma H_0\) is the Larmor frequency, \(v_Q = e^2 qQ/(4I(2I-1))\) is the nuclear quadrupolar frequency and \(\theta\) is the angle between the symmetry axis of the EFG tensor and the magnetic field. The resonance frequencies in high field correspond to transitions between adjacent magnetic sublevels. In the present experiment only one of the four possible resonances (either \(v(2 \leftrightarrow 1)\) or \(v(-2 \leftrightarrow -1)\) depending on the helicity) is clearly observed since only one magnetic sublevel \((m = 2\) or \(-2)\) is occupied appreciably when the nuclear polarization is large.

![Fig. 3. \(^8\text{Li}\) β-NMR resonance in gold foil at 300 K in a magnetic field of 3 T. The asymmetry is normalized to the asymmetry off resonance. Note the two resonances explained in the text.](image-url)
An example can be seen in Fig. 4, which shows the $\beta$-NMR spectrum in SrTiO$_3$ with the applied field along a [100] orientation. The plot shows the deviation in the normalized beta decay asymmetry plotted as a function of RF frequency for the two polarization directions. The main lines are all explained assuming the $^8$Li adopts a site with axial symmetry along a [100] direction.

An example can be seen in Fig. 4, which shows the $\beta$-NMR spectrum in SrTiO$_3$ with the applied field along a [100] orientation. The plot shows the change in the normalized beta decay asymmetry plotted as function of RF frequency for nuclear polarization parallel and antiparallel to the magnetic field direction. The main resonances in the spectrum are explained by assuming the local EFG tensor at the $^8$Li site has a [100] axis of symmetry which may occur even when the crystal structure is cubic. For each polarization there are two lines with an amplitude ratio of 2:1 and a frequency shift ratio of $-1:2$ relative to the Larmor frequency $\gamma H_0$. The larger amplitude line with the smaller shift is attributed to the $^8$Li with $\theta = 90^\circ$ whereas the smaller amplitude lines are attributed to a center $\theta = 0^\circ$. Note in a cubic crystal there are two sites with $\theta = 90^\circ$ for every site with $\theta = 0^\circ$. Reversing the polarization changes the magnetic substrate occupation from $m = -2$ to $+2$ which in turn changes the sign of the frequency shift.

3.3. Thin silver film on Al$_2$O$_3$

One application of the sharp resonance in Fig. 3 is to investigate the local magnetic properties of thin films and interfaces. For example there are several intriguing problems associated with the properties of a superconductor near its surface [8,9]. It has been demonstrated with low energy muons that the region just outside the material can be studied by depositing a thin film of simple metal on top of the superconductor [10]. Ag and Au are good metals to use as an overlayer since one expects narrow resonances which in turn imply high resolution in measurements of a field distribution near the surface.

As a control for this type of experiment we studied a 90 nm thick silver film evaporated on top of a smooth sapphire substrate. The sapphire is non-cubic and does not show any resonance close to the Larmor frequency. Spectra from the silver film at various temperatures are shown in Fig. 5. Note the single resonance at 270 K whose width is slightly broader than seen for the Au foil in Fig. 3. The increased width is attributed to the higher RF.
power used on the silver film. As the temperature is lowered to 110 K a second resonance appears which, like in the gold, is at a slightly higher frequency. Since the silver and gold have the same crystal structure the site considerations mentioned above are the same. Note as the temperature is lowered further to 110 K the occupation of the lower frequency line diminishes while that of the higher frequency line increases. Below 100 K most of the Li is at the high frequency site, suggesting there is a thermally induced transition between the two sites. For example this would be consistent with a transition from the O interstitial to a substitutional (S) site.

The main point to be drawn from this is that silver appears to be a good choice for an overlayer material for investigating magnetic fields near the surface of a material. The lines in Fig. 5 are resolved because the external field is relatively high. In much lower magnetic fields, where many experiments would be performed, we expect a single narrow line at all temperatures since the frequency shift scales with $H_0$. This in turn suggests that such a measurement of the magnetic field distribution near the surface of superconductor can be carried out with very high resolution. Further studies are in progress to confirm this.

4. Conclusion

In conclusion, we have commissioned a novel spectrometer for $\beta$-NMR at the new ISAC facility. Test experiments have been performed which demonstrate the very high frequency resolution one can obtain in simple metals such as gold and silver. We suggest this is a sensitive way to investigate magnetic field distribution near the surface of a material. In addition we observed the effect of a nuclear electric quadrupolar interaction on the resonance spectrum in SrTiO$_3$. Due to the high nuclear polarization only a single resonance is observed for each inequivalent site. Together with the polarized beam development at ISAC the new instrument should provide a novel opportunity to investigate the magnetic properties of thin films and interfaces.

References