8 August 2002

# $^{8}$Li $\beta$-NMR in thin metal films

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## Abstract

We have measured the temperature dependence of the $\beta$-NMR resonances of $^{8}$Li implanted in thin films of Au and Ag. At room temperature single narrow resonances are observed. The absence of appreciable quadrupolar splitting or broadening indicates that the Li is isolated and at a site of cubic symmetry. As the temperature is lowered, a second resonance appears which is shifted higher in frequency by $\sim 100$ ppm. We attribute the two lines to two distinct cubic sites with slightly different Knight shifts and discuss the application of this result to study fundamental phenomena exhibited by nano-confined metallic electrons.

*Key words:* $\beta$-NMR, Thin Metallic Films, Knight Shift

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We present data on $\beta$-NMR of low energy $^8$Li implanted in thin films of silver and gold. The original purpose of this study was to establish the ranging of the $\beta$-NMR probe $^8$Li$^+$ at low energies ($E = 0.1 - 30$keV)[1]. As in the case of slow muons we expected the resonance in the metallic layer would be distinct from that of the substrate and relatively simple. However, it became clear that a detailed understanding of the spectra in these simple materials would have an important application in developing the technique as a near surface magnetic resonance probe of condensed matter. In particular, it is evident that the spectrum of $^8$Li in the high temperature superconductor YBCO[2] is quite complicated, consisting of signals from several different sites with distinct quadrupolar splittings. One application of the current results (which has already been demonstrated with slow muons[3]) is to study the vortex lattice field distribution *just outside* a type-II superconductor by stopping the probe in a thin simple metallic overlayer. It has also become clear that there are unexplained finite size phenomena in conventional NMR experiments on small metallic particles (e.g. [4]) which may be more clearly addressed using $\beta$-NMR in the simple well–defined geometry of a thin film.

In this paper we present results on two films: a 900 Å Ag film and a 500 Å Au film. The Ag film was deposited at UBC on an epitaxially polished sapphire $\langle 0001 \rangle$ substrate (Honeywell) in a conventional evapourator ($4 \cdot 10^{-6}$ torr) from 99.995% pure Ag (Goodfellow) at a rate of $\sim$ 12Å/s. Atomic force microscopy (AFM) indicates a typical 10 Å RMS surface roughness for these growth conditions. The Au film was deposited using an electron beam evapourator at Los Alamos ($10^{-8}$ torr) on a $\langle 100 \rangle$ $SrTiO_3$ substrate (equivalent to [5]) at $\sim$ 2Å/s, resulting in an RMS surface roughness of $\sim$ 4.5Å. The thicknesses were measured with a calibrated piezoelectric thickness rate monitor, reliable to a few

%. The samples were clamped to an Al sample holder bolted into the copper coldfinger of a UHV Helium cryostat in the high–field $\beta$–NMR spectrometer in the ISAC facility at TRIUMF.

A beam of highly polarized $^8$Li$^+$ with 10 keV kinetic energy was directed onto the samples in a longitudinal magnetic field of 3 T. Range studies indicated that at these energies, virtually all of the Li is stopped in the films[1]. Linearly polarized RF magnetic field ($B_1 \sim 100$ $\mu$T) was applied transverse to the polarization varying the frequency slowly relative to the $^8$Li lifetime. Resonances were then observed in the loss of forward–backward asymmetry as a function of frequency. The relatively intense $B_1$ results in power broadened lines of an approximately Lorentzian shape[6]. We can thus easily find the resonance position, but it is difficult to extract the intrinsic linewidths. The advantage of large $B_1$ is the large amplitude, confirming that the signal corresponds to almost all of the implanted $^8$Li.

The temperature dependences of the spectra in Ag and Au are shown in Figs. 1 and 2. The fits in the figures are to two Lorentzians with frequencies fixed from temperatures where each line is well resolved. Near room temperature, there is a single narrow line shifted positively by a few kHz with respect to a resonance in insulating MgO. For the Au film the resonance is somewhat broader than that observed in Au foil[2], but the Ag film resonance was narrower than that in a corresponding Ag foil. As the temperature is decreased a second line appears at higher frequency, gaining amplitude at the expense of the high temperature line as $T$ is lowered. The absence of quadrupolar splitting of the lines indicates that they both correspond to sites of cubic symmetry. Moreover, the narrow intrinsic linewidth indicates that the stopping sites are isolated from crystal defects.

We attribute the positive shift of the resonance frequency to a Knight shift $K$, i.e. a coupling to the temperature independent Pauli spin susceptibility ($\chi_s$)

of the conduction electrons (see the review [7]). Assuming a simple isotropic hyperfine coupling $A$, we have $K = A\chi_s$. It should be possible in the future to confirm that the observed shifts are magnetic in origin by measuring their scaling with field. In this scenario, the difference in the shifts of the two lines is due to different hyperfine coupling for the two sites. Ag and Au have FCC crystal structures (Fig. 3) with cubic lattice constant $a = 4.09$ and 4.08 Å respectively. In this structure there are three sites of cubic symmetry, the substitutional site (S), the octahedral (O) and tetrahedral (T) interstitial sites. The distances from these sites to the near neighbour lattice sites are $d = a/\sqrt{2}$, $a/2$ and $a/4$ (2.9,2.0,1.0 Å) with coordinations $Z = 12$, 6, and 4 respectively. The T site is likely too small to accomodate Li, and the two observed lines then correspond to S and O. This agrees with the sites deduced for another FCC metal, Cu[10].

The shifts of a few kHz appear to be quite independent of $T$ as expected (vertical lines in the figures) for Knight shifts. Interestingly, these Knight shifts are in the same range ($\sim 100-200$ ppm) as those of the $\mu^+$ in simple metals[11], but they are easier to measure due to the much longer $^8$Li lifetime ($\tau_{1/2} = 842$ ms). In contrast, they are much smaller than the intrinsic $K$ of the $^{109}$Ag NMR which is +5250 ppm[12] for example. This difference is due to a much larger hyperfine coupling to the Ag nucleus.

Assuming the filled core $1s$ orbital of $^8\text{Li}^+$ is inert, the hyperfine coupling of Li to the metallic bands of the host will be due to the partial occupation of the $2s$ orbital which is hybridized with the metallic band states. An idea of the size of this orbital is given by the Li *atomic* radius 1.23 Å. The host atom size can be defined by assuming a close–packed structure, i.e. $r = a/2\sqrt{2} \sim 1.45$ Å. A very simple model of the hyperfine coupling has $A \propto ZS$, where $S(d)$ is an overlap integral, which is a decreasing function of $d$ for large $d$. The differences in $Z$ and $d$ for the O and S sites compensate each other, and it is not clear which corresponds to the larger $A$. Moreover, the local electronic distribution is not simply that of the host since a charged impurity like $Li^+$ will be screened, being surrounded by long–range Friedel oscillations whose integral exactly compensates the impurity charge. Detailed calculations (such as discussed in [8]) will be necessary to determine $A$ or perhaps more reliably the ratio $A_S/A_O$. However, on thermodynamic grounds, one might expect that at high $T$, Li would be more able to diffuse to a vacant S site, suggesting $A_S < A_O$ in agreement with preliminary calculations[9].

The spectrum in the Ag film is quite independent of temperature below 100 K. In contrast, there is additional broadening in the Au film that develops at low temperature. It is unlikely that the structural phase transition of the substrate[5] is the origin of this broadening since the lattice distortion is less than 0.1 %. With the “transmission line” RF coil we use, $B_1$ (and thus the power broadening) will also be independent of temperature. It seems possible that the broadening could be due to a temperature dependent finite size effect such as has been found in very fine powders of Ag[4], but as a relative fraction of $K$ our broadening is much larger. A systematic study is now underway to try to relate the observed linewidths to properties of the film such as crystallinity, granularity and thickness, and to clarify the origin of the broadening along with its $T$ and $B$ dependence.

The application of a thin metal overlayer as a stopping layer for the $\beta$–NMR probe to study magnetic effects near a surface (such as the field of the vortex lattice just outside a superconductor) will be complicated by the intrinsic spectra. In this context, due to its $T$ independence at low $T$, Ag is the better choice of the two metals considered here. We have already accomplished a preliminary measurement of this sort[2].

We thank L.H. Greene and E. Dumont for providing the $SrTiO_3$ substrate and R. Abasalti, M. Good and D.J. Arsenau for technical assistance.

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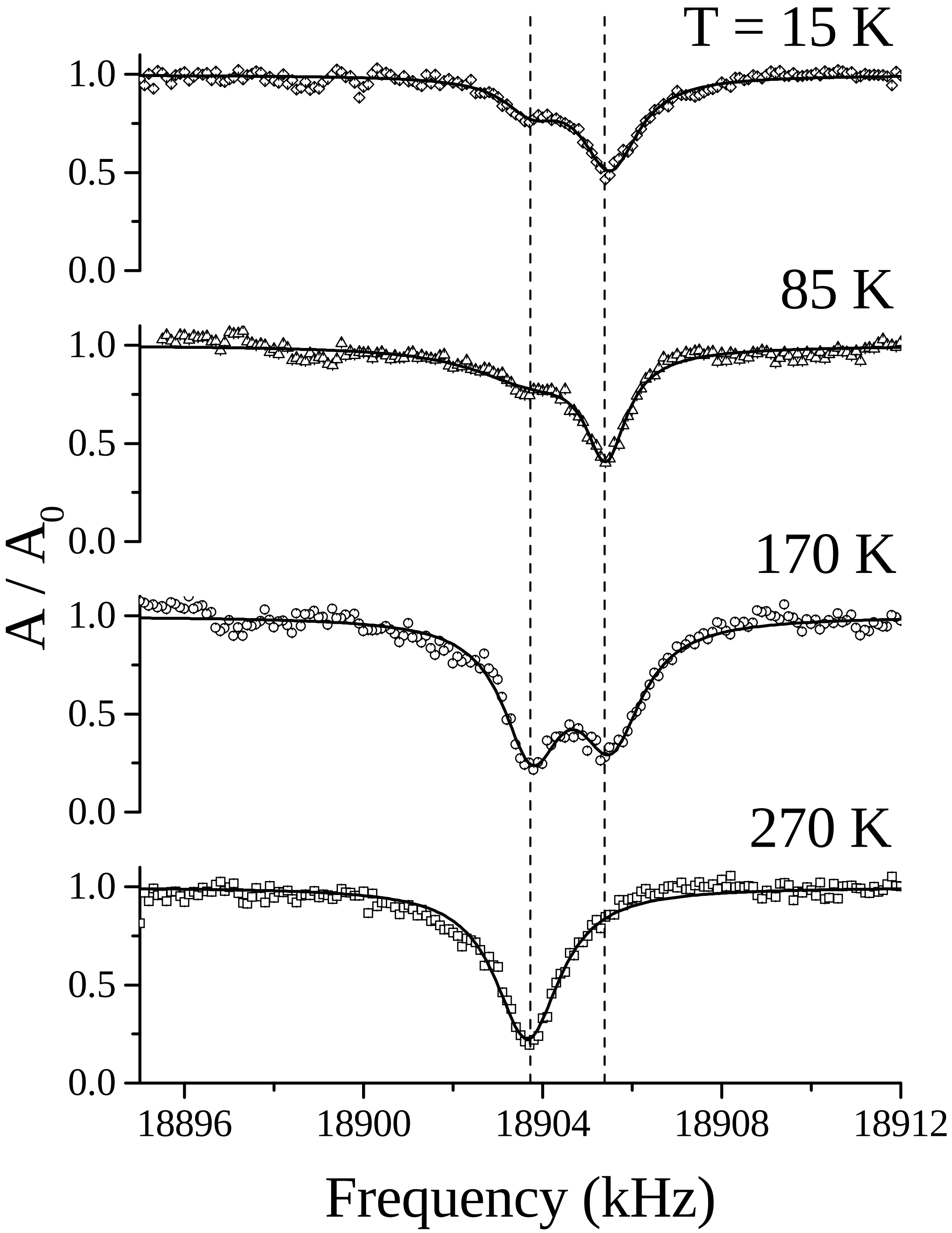
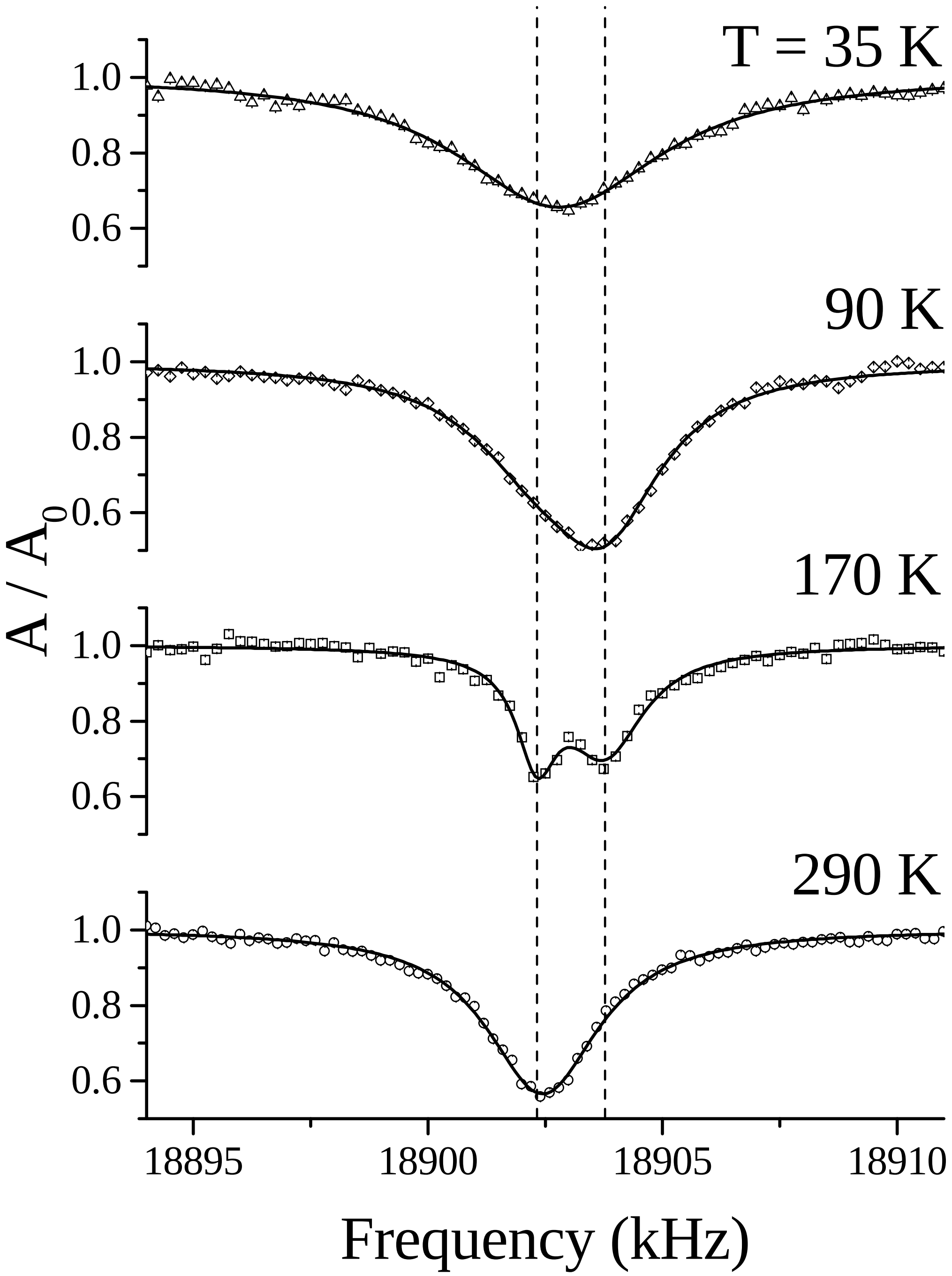
## Figure Captions

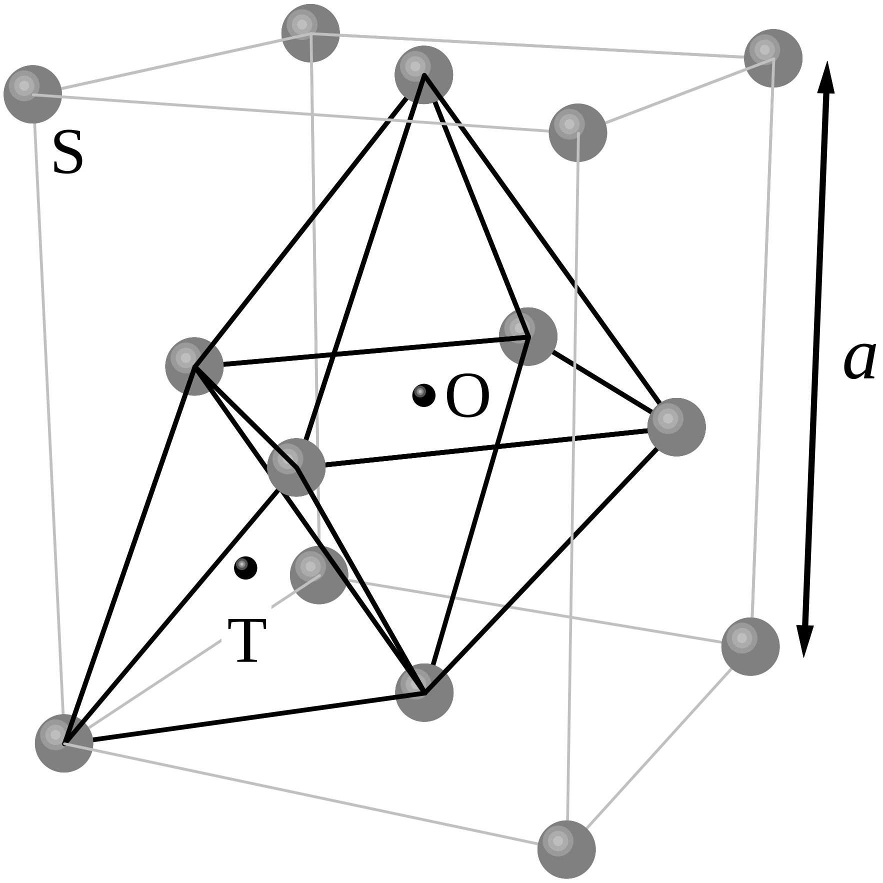
Fig. 1: The temperature dependence of the $^8$Li $\beta$–NMR resonance in a 900 Å film of Ag on an $Al_2O_3$ substrate.

Fig. 2: The temperature dependence of the $^8$Li $\beta$–NMR resonance in a 500 Å film of Au on a $SrTiO_3$ substrate.

Fig. 3: The FCC unit cell of Ag and Au, showing the high symmetry interstitial sites O and T as well as the substitutional site S.


T = 15 K
85 K
170 K
270 K
1.0
0.5
0.0
A / $A_0$
18896
18900
18904
18908
18912
Frequency (kHz)


T = 35 K
90 K
170 K
290 K
1.0
0.8
0.6
A / A0
18895
18900
18905
18910
Frequency (kHz)


S
O
T
a