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NMR spectra of highly polarized lithium

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We have studied the magnetic resonance of the nuclear spin system in lithium down to spin temperatures well below 1 μK. The observed emergence of a distinguished low frequency maximum at low fields indicates clear disparity from the paramagnetic behavior.

1. INTRODUCTION

Nuclear magnetic resonance measurements have often given the first evidence for the magnetically ordered state of various nuclear spin systems.[1] Only a few pure metals – copper, silver, and rhodium – have been systematically studied in the regime of high nuclear polarization and low magnetic fields, where spontaneous nuclear ordering should emerge. Although magnetically ordered states have been clearly demonstrated in copper and silver – even at negative nuclear temperatures in silver – deformations of the spectral shape of the NMR response are not very pronounced in these cases.[2–4] In contrast to these, we present here NMR spectra of lithium metal, where an extremely strong low-frequency anomaly develops upon presumed nuclear magnetic ordering in low fields.

Natural lithium consists of two isotopes: ^{6}Li (8%, spin 1) and ^{7}Li (92%, spin 3/2), whose magnetic moments differ considerably, $\mu_6 = 0.82\ \mu_N$ and $\mu_7 = 3.26\ \mu_N$. Thus, the contribution of ^{6}Li to the NMR spectra is very small compared to that of ^{7}Li.

Lithium is the lightest metal with a presumably simple conduction-band structure. However, the lattice structure of this metal is not at all trivial at low temperatures, and the sample may, in fact, have a slightly different composition in each cool-down due to the martensitic phase transition at 70–80 K. There the body-centered cubic phase changes to a mixture of different structures: a Sm-type 9R rhombohedral state is blended with face-centered

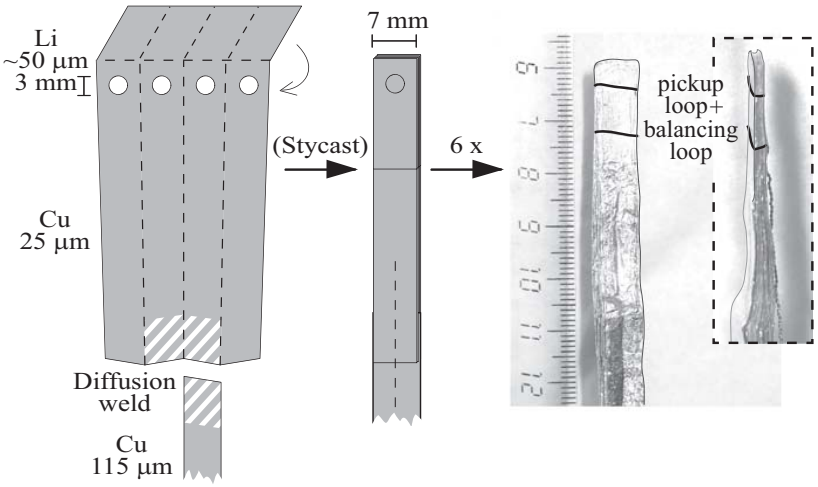

Fig. 1. Encapsulation of the lithium sample. Six copper foils, each embodying four pressed lithium spots, were folded to a stack 7 mm wide and about 2 mm thick. The pickup pair was wound directly on this stack. The photographs show the sample from the front and the side.

cubic and a polytype structure consisting of short-range cubic and hexagonal sequences.[5] This may give rise to quadrupole interactions, but since the quadrupole moments of the nuclei are small (-0.8 mBarn for ^{6}Li and -41 mBarn for ^{7}Li), their effects are supposed to be insignificant.

The interactions between lithium nuclei are dominated by the simple dipolar coupling. The indirect exchange is fairly weak, which is evinced by the large Korringa constant (44 sK). The free-electron model suggests a minute ferromagnetic Ruderman-Kittel coupling.[7] Due to their lightness the Li-nuclei have a moderate zero-point amplitude, which permits speculation upon the existence of a direct exchange contribution. The purely dipolar local field is 240 μT.

2. SAMPLE AND TECHNIQUES

The sample material was purchased from Alfa Aesar.[6] Their impurity analysis indicated a nominal lithium content of 99.97%, while the amount of magnetic impurities (Iron) was less than 4 ppm. We measured residual resistivity ratios as high as 900±100. Being very reactive, the lithium samples had to be capsuled tightly to prevent deterioration during the preparations. Careful tests indicated that copper is suitable as the cover material.[8] Our sample consisted of 24 thin ($\sim$ 50 μm) spots of lithium pressed in between

thin (25 μm) copper foils, which had been diffusion welded to thicker copper stripes providing the thermal link. The seams were secured by small amount of Stycast epoxy. The preparation of the sample is illustrated in Fig. 1.

The sample was cooled in a two-stage nuclear demagnetization cryostat.[9] The lattice temperature was usually adjusted to around 350 μK for a sequence of measurements. It could be maintained practically constant due to the vast heat capacity of our massive copper nuclear stage. The sample was polarized to some 85% in a magnetic field of 1.5 T in 16–24 h. By subsequent demagnetization the nuclear spin temperature could be reduced by several orders of magnitude below the lattice temperature. The NMR measurements were performed during the slow equilibration of those temperatures.

By use of a SQUID we achieved a good signal-to-noise ratio over the measuring band from 2 Hz up to 100 kHz by a modest excitation level, typically around 30 nT. The pickup coil consisted of two loops: a measuring loop and an oppositely oriented balancing loop, separated by a distance of 10 mm but both enclosing the same amount of copper, see Fig. 1. Nevertheless, some copper signal, overlapping with that of lithium at low fields, contaminated the first few spectra measured after the demagnetization. This was not a serious issue, though, as the copper signal decayed relatively fast due to the smaller Korringa constant of Cu ($\sim$ 1 sK). The data collected during such transient behavior is excluded from the graphs shown below. By this time the polarization of lithium nuclei had reduced to 70% or below.

The nuclear polarization was determined by measuring the quasi-static susceptibility ($\chi(13\text{ Hz}) \sim \chi'(0)$) at 3 and 7 mT. We use the relation

$$\chi'(0) = \mu_0 p M_{\rm sat}/[B + \mu_0(D_x - D_z)pM_{\rm sat}], \qquad (1)$$

where D_x and D_z stand for the demagnetization factors in the directions of the excitation field and the static field, respectively, while the saturation magnetization of Li gives $\mu_0 M_{\rm sat} = 0.93$ mT. Both fields were oriented symmetrically relative to the specimen, so that $D_x \approx D_z$. The scaling factor for Eq. (1) (the absolute scale of susceptibility) was obtained by measurements at higher temperature with reliably estimated values of nuclear polarization.

3. DATA ANALYSIS

The copper capsule with high electrical conductivity was reasonably transparent to the excitation field only at frequencies below 10 kHz, at which the skin depth roughly equals the thickness of the capsule. As the frequency band of the measurements extends far beyond this, nontrivial corrections for the frequency response were necessary. Two factors have to be considered:

the excitation field agitating the lithium nuclei depends on the frequency and the signal echoed back by the nuclei is attenuated in the copper jacket. The geometry of the sample was not regular enough to permit a reliable calculatory solution, so that some known characteristics of nuclear-resonance signals were used to facilitate the analysis.

The frequency response of the pickup circuit (including the effectively varying area of the pickup coil due to the finite skin depth) and of the amplifier chain was dealt with by simple background measurements at zero nuclear polarization. The differences to these, the lithium signals, were still obscured by complicated amplitude and phase relationships. However, we know that at high magnetic fields, where the resonance maximum falls far above the measuring band, the signal is purely dispersive, independent of frequency, and inversely proportional to the magnetic field. Measurements under such circumstances can be used for finding the appropriate corrections to de-convolute the genuine resonance shapes. We took such data at 7 mT, chosen as a compromise for obtaining a flat dispersive spectrum on one hand and maintaining a reasonable signal level on the other. The ^{7}Li resonance is then at about 120 kHz, more than ten half widths above the measuring band. In order to eliminate excess noise, smooth functions were fitted to the amplitude and phase of the difference data (the simple background subtracted) and these functions were then used to scale the amplitude and turn the phase of all other data. Such fitting was too unreliable at the lowest frequencies, where the raw-signal was very small, and so the simple background correction with an assumption of full penetration of the excitation field was employed below 100 Hz.

The consistency of the resonance shapes so obtained was checked by using the Kramers-Krönig relations. Once the frequency dependence of one of the components is known, the other one can be computed. The discrepancies remained small throughout but, nevertheless, a self-consistent pair of absorption and dispersion signals were constructed by superpositions of the data obtained by just using the background correction and by the subsequent cross-computation through the Kramers-Krönig relations.

4. RESULTS AND DISCUSSION

We measured the NMR frequency response of lithium at fields 0–2.5 mT and polarizations up to 70%. Four field values were applied cyclically after a demagnetization and polarization readings were recorded after each cycle. The due value for each individual spectrum was obtained by interpolation.

Figure 2 shows some absorption spectra measured at fields 0, 0.02, 0.04,

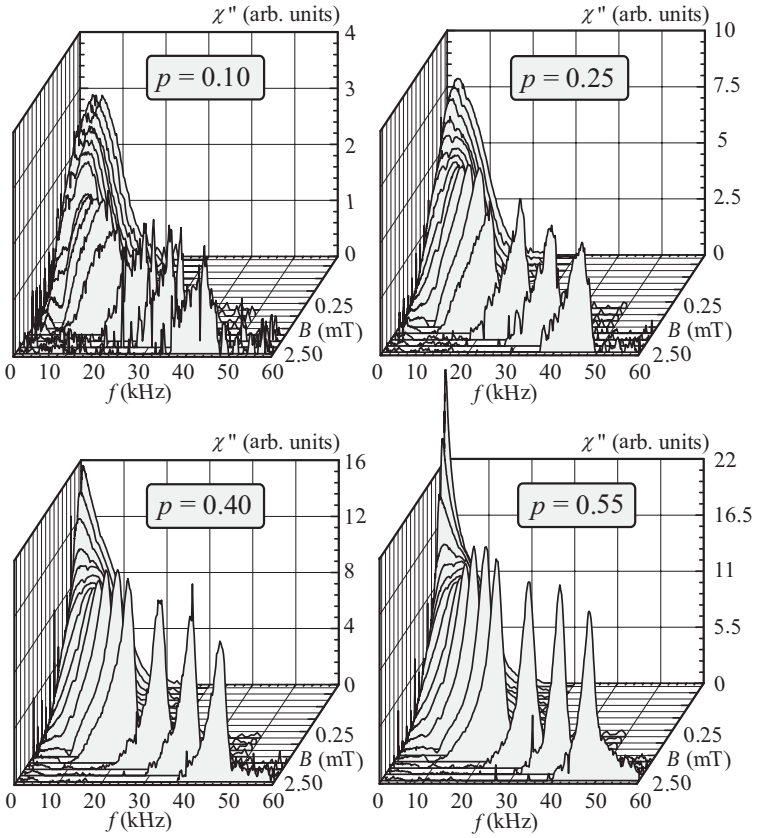

Fig. 2. Absorption spectra of polarized lithium nuclei. The sharp peak at low f, low B, and high p obviously indicates spin order.

and 0.08 mT, at 0.12, 0.15, 0.18, and 0.25 mT, at 0.35, 0.45, 0.60, and 0.80 mT, and at 1.0, 1.5, 2.0, and 2.5 mT. To obtain commensurable spectra at the selected values of nuclear polarization (10%, 25%, 40%, and 55%), consecutive measured spectra at a given field were superposed in correct proportions.

The data show many standard features of low field NMR, and also many expected spectral changes due to the increasing nuclear polarization are clearly visible. Already at low nuclear polarization the magnitude of the local field divides the measurements to two regimes: at high fields ($B \gg B_{\mathrm{loc}}$) the resonance frequency is directly proportional to the external magnetic field, whereas at low fields ($B \ll B_{\mathrm{loc}}$) f_0 is set by the local field, independent

of the external contribution. When the nuclei become polarized, the high-field spectra are shifted slightly toward higher frequencies due to the dipolar interactions. The peaks also become sharper as the random components due to the neighboring spins diminish. The area of the high-field peaks should be proportional to the nuclear polarization. The vertical scales of the four panels in Fig. 2 are chosen so that if this assumption holds, the area of the high-field peaks should appear the same in each panel.

In addition to such anticipated changes, an unexpectedly sharp low-frequency anomaly appears at high nuclear polarization at low magnetic fields (peaking out of the frame in Fig. 2). The absorption maximum was found to move to as low as 0.2 kHz at zero field, more than an order of magnitude below the ordinary paramagnetic resonance (~ 5 kHz). Remains of this structure are still visible at $p = 0.25$ and, in fact, they still exist at $p = 0.10$. Such pronounced feature can be taken as evidence for the existence of an ordered spin state of lithium nuclei. However, it is not possible to point out any specific value for the critical polarization (or more specifically for critical entropy) as the low-frequency peak grows up quite gradually without any notable discontinuities. Apparently the ordered state, whatever its exact character is, evolves through a broad short-range ordered region.

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