Nuclear Ordering in Lithium and an Upper Limit on its Ambient Pressure Superconducting Transition Temperature

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(Received 18 June 2004; published 4 October 2004)

We have discovered spontaneous ordering of nuclear spins in lithium metal by NMR measurements at very low temperatures. In low magnetic fields, $B < 0.2$ mT, the NMR spectra show a pronounced low-frequency anomaly. Also, nonadiabatic response to a slowly varying magnetic field was observed. A rich phase diagram with three different nonparamagnetic regions is proposed. We estimate a critical spin temperature $T_c \approx 350$ nK at $B = 0$. We also report the absence of superconductivity in lithium at normal pressure down to $T_e \approx 100$ μK ($B < 10$ nT).

DOI: 10.1103/PhysRevLett.93.157201 PACS numbers: 75.30.Kz, 74.10.+v, 75.30.Cr, 76.60.Jx

Lithium is often regarded as the prototype metal due to its apparent simplicity. However, to begin with, its low-temperature lattice assembly is not that trivial, as competing close-packed structures have been found to coexist [1]. The lattice incorporates two subsystems, the nuclear spins and conduction electrons, both of which possess entropy even at very low temperatures. This entropy is eventually expended by the formation of an ordered state—magnetic or superconductive—the exploration of which was the purpose of the present experiment.

The occurrence of superconductivity in lithium at reasonable temperatures has been predicted by many theoretical studies [2–6]. The estimates for T_c vary from over 1 K to a few microkelvins, most predictions suggesting a T_c at the millikelvin range. Prior experiments, however, did not indicate any transition down to 4 mK [7,8]. Another perspective to this issue has been brought by the recent experiments under extremely high compression. Fresh observations confirm the earlier cue of superconductivity in lithium under high pressure, where the critical temperature was found to become as high as 15 K [9–12]. We have now cooled uncompressed lithium down to 100 μK at a very low magnetic field, $B < 10$ nT, without observing superconductivity.

^{7}Li, 92.5% abundant with a spin 3/2, is an excellent target for NMR studies due to its reasonably large magnetic moment $\mu_7 = 3.26\mu_N$. The remaining 7.5% of ^{6}Li, with $I_6 = 1$ and $\mu_6 = 0.82\mu_N$, do not contribute much to the magnetic behavior, but can be used as a probe in analyzing the interactions between the nuclear spins [13].

Lithium is dominantly a dipolar-coupled nuclear magnet, more so than any other investigated metal [14]. For this reason, the nuclear-spin ensembles in insulators may be thought of bearing the closest resemblance to the present case [15]. In particular, we may mention the studies of the lithium compounds LiF and LiH (see [15] and references therein). Analogy to those experiments is not quite as straightforward as it would appear, though, as the methods of polarizing and demagnetizing the nuclear spins in insulators in the rotating frame of reference modifies the dipolar spin Hamiltonian [15].

Nuclear-spin order in insulators has been possible due to extremely weak coupling of the spins to the lattice. Even in metals, the nuclear-spin temperature can be reduced by several orders of magnitude below that of the lattice and electrons. While the intermediate microKelvin regime is the practical limit for refrigerating the body of well-prepared specimens, their nuclear spins may be polarized by a high magnetic field and by subsequent adiabatic demagnetization be cooled to the nanokelvin regime and even below [16]. The temperatures of these subsystems can be maintained apart for time scales set by the spin-lattice relaxation, which may be tens of hours in lithium metal under the circumstances discussed here.

By such procedures we were able to prepare a magnetically ordered state of nuclear spins in lithium. On the basis of measurements of the spectral resonance shapes, observation of nonadiabatic effects, and determination of the spin temperature, we propose a nontrivial phase diagram with several distinct regions of different characteristics. We obtained the critical temperature of 350 nK in zero magnetic field.

The sample material was purchased from Alfa Aesar [17], whose analysis indicated 99.97% purity. The content of magnetic impurities (iron) was at most 4 ppm, and we measured the residual resistivity ratio 900 ± 100. Lithium reacts eagerly with air, whereby the samples were protected by copper capsules [18].

The best conditions for observing the two phenomena under discussion are somewhat contradictory, so that we prepared two different samples to satisfy both. A low transition temperature of superconductivity is associated with a very low critical magnetic field and potential supercooling of the normal state in any finite field. Therefore, the superconductivity (SC) sample was placed inside an efficient magnetic shield with a cylindrical layered high-permeability–superconducting (Pb)–high-permeability structure. The NMR sample, on the other

hand, had to be polarized in a field of the order of 1 T, and only moderate magnetic shielding was needed to reduce the remnant field after the demagnetization to micro-Tesla level. Further, the NMR sample had to be thin to ensure penetration of the excitation field at frequencies of the order of 10 kHz. In contrast, the superconducting transition could be monitored at low frequencies, and so the sample was made bulkier in order to improve the signal-to-noise ratio.

The SC sample was composed of two lenticular disks of lithium with a diameter of $\sim$4 mm and a thickness of $\sim$1 mm. They were prepared by pressing lumps of lithium between a small cup and a flat cover formed of annealed 120 μm copper foil, which was extended stripewise to provide the thermal link. Two separate capsules were bound together by a common tightly wound single-turn copper-wire pickup coil with an opposing balance loop, and bolted on the cold surface of the refrigerator. The NMR sample consisted of a stack of 24 thin (50 μm) spots of lithium between 25 μm copper foils. Details of its preparation can be found in Refs. [19,20].

The samples were cooled in our two-stage nuclear-demagnetization cryostat [21]. SQUIDs coupled to wide-band pickup circuits were used to amplify the susceptibility signals driven by nano-Tesla level excitation.

In attempts to observe the Meissner effect, a temperature of (105 ± 10) μK was achieved. The ambient field inside the magnetic shield was estimated to be 20 nT but even lower values were aspired by sweeping slowly an axial magnetic field (± 1 μT) by a copper solenoid inside the shield. True minimum of a few nano-Tesla is plausible.

For the NMR measurements the thermal bath provided by the copper nuclear stage was set to around 300 μK and several cycles of sample polarization in 1–2 T (0.5–2 days), demagnetization ($<$1 h), and measurements (1–3 days) were repeated until the nuclear stage had warmed up to some 500 μK. A signal due to the copper nuclei of the capsule disfigured the lithium spectra recorded right after the demagnetization, but the decidedly faster relaxation of the copper signal (Korringa constants $\kappa_{\mathrm{Cu}} = 1$ sK and $\kappa_{\mathrm{Li}} = 44$ sK) cured such distortions soon without any further effort. After about 1 h of relaxation in zero field, the signal was clean from copper, with lithium still polarized at about 70%–80%.

The entropy of an ensemble of spins can be described by its polarization, even though, that is, strictly speaking, ill-defined at fields of the order of the internal local field B_{loc} and below. We determined the polarization p at a high-field ($B \gg B_{\mathrm{loc}}$) and returned adiabatically to the low measuring field. The purely dipolar coupling between lithium nuclei gives $B_{\mathrm{loc}} = 240$ μT.

Two methods for determining p were employed, each being more reliable at opposite ends of the p scale. The quasistatic susceptibility $\chi(13\ \mathrm{Hz}) \approx \chi'(0)$, which we chose to measure at 3 and 7 mT, holds a well-established relation to p, once a general scaling factor has been found [19]. The reproducibility was good throughout, but the measurement accuracy set the useful range to some $p >$ 1%. A larger signal is obtained in zero field, so that we determined an empirical relation between p and $\chi(13\ \mathrm{Hz}, 0\ \mathrm{mT})$, which reduces to a linear dependence at low enough p. Above $p \sim 50\%$, though, the result varied between different runs, which is in itself an indication for the existence of an ordered state, whose specific configuration depends on the way of preparation of that state.

Spin temperatures were determined at several fields below 2 mT by using the thermodynamic relation $T = \Delta S/\Delta Q$. The technique is described, e.g., in Ref. [16].

The NMR absorption curves measured in zero field and also in another representative value of the magnetic field comparable to B_{loc} are shown in Fig. 1. Spectra at other field values, as well as some further details of the measurement and of the data analysis can be found in Ref. [19]. The most remarkable feature of the data in Fig. 1 is the sharp peak at low frequencies in the zero-field spectra at high degrees of polarization. The peak frequency drops to as low as 0.2 kHz, whereas the paramagnetic spin system would respond at about $\mu_7 B_{\mathrm{loc}}/(hI) \approx 4$ kHz. That is, indeed, about where the maximum drifts to when the polarization decreases. In a finite field, the low-p NMR signal peaks at a frequency corresponding to $\sim\sqrt{B^2 + B_{\mathrm{loc}}^2}$, i.e., at about 6 kHz for the 0.25 mT data in Fig. 1. In applied field, the increasing polarization shifts the peak toward higher frequencies, which is an effect of the dipolar interaction [13]. The shoulder at the highest polarizations between 10–15 kHz is due to the double-spin mode [13].

We shall give evidence that the order in $B = 0$ changes character at about $p \approx 40\%$, i.e., around the fourth spectrum from the top in Fig. 1. This is also where the upturn curvature below 10 kHz disappears, but some remainder of the low-f anomaly persists to much lower polariza-

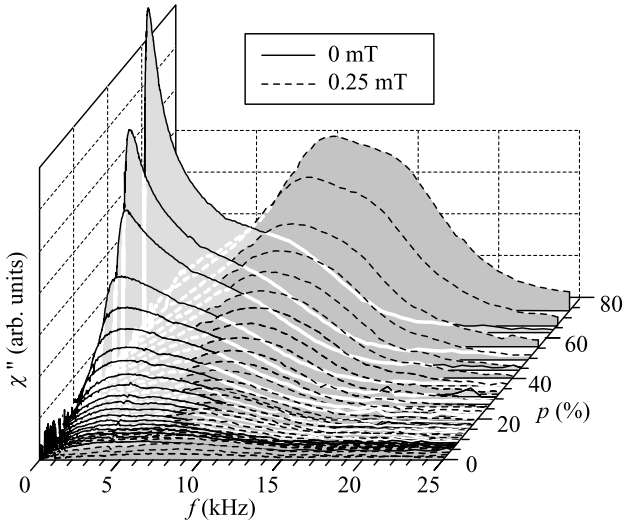

FIG. 1. NMR absorption (dynamic susceptibility χ'') of ^{7}Li at $B = 0$ and at 0.25 mT ($\sim B_{\mathrm{loc}}$) at polarizations $p = 0\%$–75%.

tions. To analyze these changes consistently over the whole polarization scale and as the function of a magnetic field, we computed the first moment of the spectra, but on the logarithmic frequency scale in order to emphasize the changes taking place at very low frequencies. These data are shown in Fig. 2 both as individual data points as a function of polarization at a selection of fields, and also concisely as a contour diagram.

A division at $B \sim 0.25$ mT into a low-field and a high-field region is evident. The shift of the weight of the spectra to low frequencies at low B/high p is seen as the turning of the contours to nearly vertical. However, this evolution takes place gradually without any clear discontinuities and at about $p \approx 3\%$ there is still some of this tendency left. We take that as an indication of a broad region of short-range order (SRO). This makes it very difficult to point any particular critical values from these data.

To better demarcate the ordered state and to systematically investigate the low-B/high-p signal irreproducibility mentioned already, we executed a set of measurements, where the spin system was disturbed by slowly varying the orientation of a magnetic field with approximately constant magnitude. We first recorded the susceptibility at 0.05 mT, then set the static field to a desired value below, at, or above the measuring field, shaked the field back and forth to an angle of about 45° at a frequency of 0.5 Hz for 6–450 periods, returned to the measuring field, and recorded $\chi(0.05\ \mathrm{mT})$ again. Any loss of the signal, $\Delta\chi$, was used as the measure of irreversibility associated with such treatment. Four examples of such data are shown in Fig. 3. The nonadiabatic behavior is clearly strongest at low B and high p but, interestingly, the trend is nonmonotonic at intermediate fields. Close to B_{loc}, the field shaking actually enhanced the signal at highest p (negative $\Delta\chi$), which indicates that some sort of degaussing may have taken place.

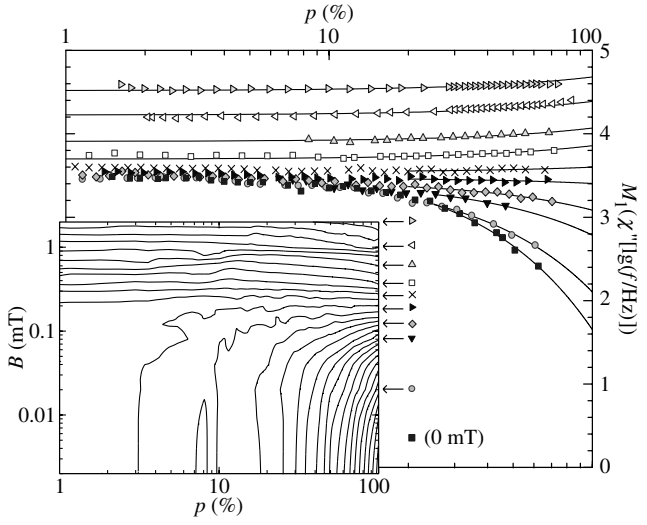

FIG. 2. First moment of the absorption spectra on a logarithmic frequency scale, $M_1(\chi''[\log(f/\mathrm{Hz})])$, is shown in the main frame at selected magnetic fields, which are indicated by the arrows and corresponding symbols at the side of the contour graph. When these data are plotted as contours (small frame), the nonparamagnetic behavior shows up as a deviation from nearly horizontal lineation. The curves in the main frame are linear fits to the data (on linear axes), used to aid the construction of the contour diagram.

All our shaking measurements at fields 0.01–0.25 mT are represented as a contour graph in Fig. 4. Now, we may sketch a boundary around the region of irreversible behavior (thick black dashed line; the square symbols are based on linear fits, such as in Fig. 3). The zero field is met at about $p \approx 40\%$ ($S \approx 0.9 S_{\mathrm{max}}$), where the spin temperature is estimated to be 350 nK.

Other measurements support the additional lines sketched on Fig. 4. At the lower SRO region many quantities—see, e.g., Fig. 2—depart from the paramagnetic behavior. The border points (crosses) and the lower dashed light-gray line have been placed following the deviation from a simple paramagnetic relation between $\chi(0)$, p, and B. We propose that substantial short-range order develops there.

In higher fields, another two distinct regions are marked on the basis of our temperature measurements [20]. At the high-B/low-p line (open circles, dashed light-gray line) the T-S curves depart from the high-temperature expansion $(S - S_{\mathrm{max}}) \propto 1/T^2$; the change of temperature slows down while the entropy drops rapidly, until some stagnation of S is approached at the high-B/high-p line (solid circles, dashed dark-gray line). This would indicate a maximum of the specific heat of the spin system, although the temperature data are not regular enough to allow any definite conclusions on that. Proper heat capacity measurements are thus needed to clarify the situation in this region of our tentative phase

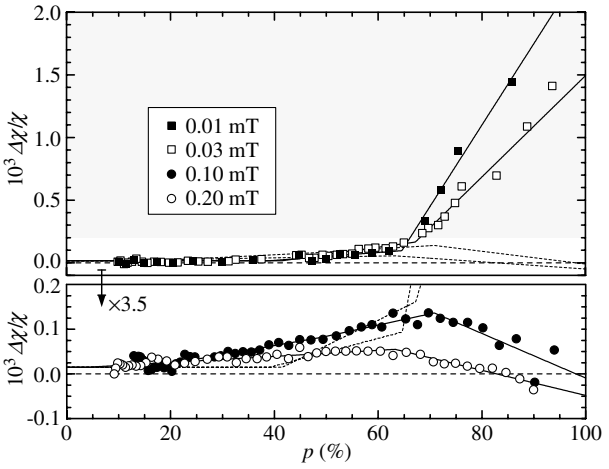

FIG. 3. Changes of susceptibility, $\Delta\chi/\chi$, at 0.05 mT due to shaking of the field at four different values. The changes are normalized per cycle around an angle ±45°. For clarity, the data are divided into two panels due to their different magnitudes. Solid lines are piecewise linear fits.

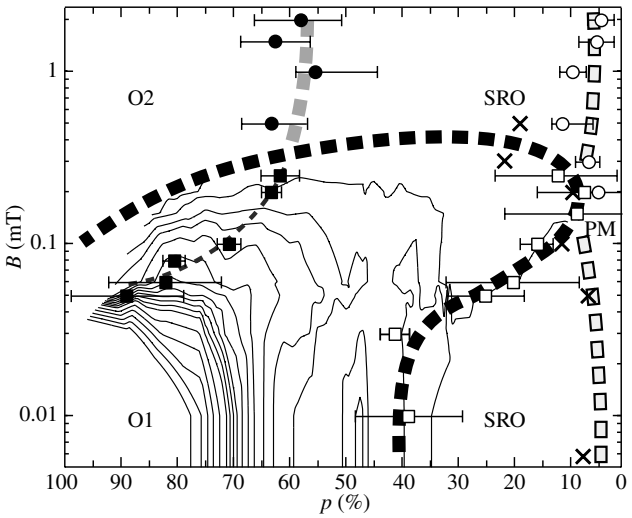

FIG. 4. Tentative phase diagram of the nuclear spins in lithium as functions of polarization and the magnetic field. The contours represent the irreversibility data like those in Fig. 3. The broad dashed lines separate the two ordered regions (O1 and O2), short-range ordered (SRO), and a paramagnetic (PM) region.

diagram. Apparently, though, the spin system has developed, through short-range order again, into a uniformly polarized state, which can adapt to the changes of the direction of the external field, viz., no losses occurred in the shaking experiments. It may be accidental, but the maximum of the irreversibility (thin dashed line and solid squares in Fig. 4) in low B seems to extend the routing of the suggested line of high-B ordering. Also, the figure indicates coalescence of the boundaries at about 10% and 0.2 mT, but it is not possible to be quite definite upon the exact path of the boundaries there.

In conclusion, we have provided evidence for a surprisingly complex ordered phase diagram of the nuclear spins in lithium. Many observations fit a picture of a ferromagnetic state, which is uniformly polarized at high fields, but splits into a domain state at low fields, then irreversible with respect to changes of the direction of almost arbitrarily small magnetic field. Interestingly, the lossy state extends to very low polarizations at fields comparable to the internal local field. Large regions with precursory nonparamagnetic effects, obviously due to short-range order, were observed below and above the local magnetic field.

The largest observed value (SI units) of the static volume susceptibility in $B = 0$ was $\chi \approx 12$, exceptionally large for a nuclear magnet. No reliable value for the Weiss parameter was obtained, as its estimate varied from positive to negative depending on the range of data under inspection.

We did not observe superconductivity of lithium at normal pressures down to 100 μK. Accepting some suppression due to impurities, a true T_c for pure Li larger than 0.2 mK is considered unlikely. Further, the existing high-pressure data are not complete enough to judge if a structural phase transition is needed to trigger the superconductivity, or if it would still occur at finite temperatures at moderate pressures. Studies of mutual influence of nuclear magnetism and superconductivity [22] would be of great interest if the T_c of lithium could be tuned to the milli-Kelvin regime.

We acknowledge financial support by the Academy of Finland (Finnish Centre of Excellence Program 2000–2005) and by the European Union (large scale facility program ULTI-III). K. J. appreciates the support by Finnish National Graduate School in Materials Physics.

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