Nuclear ordering and superconductivity in lithium

Juha Tuoriniemi
Low Temperature Laboratory, Helsinki University of Technology, PO Box 5100, FI-02015 TKK, Finland
E-mail: jtuorini@cc.hut.fi

Abstract.
Lithium metal constitutes a unique system of nuclear spins and conduction electrons, where the energy scales of the collective behavior among the two distinct, though interpenetrating, subsystems are of the same order of magnitude. We have demonstrated experimentally the onset of magnetic ordering of the nuclear spins in lithium below 0.3 µK in zero magnetic field as well as the transition to the superconducting state of electrons below 0.4 mK. So far, these two ordering phenomena have been observed only in different samples in different experimental arrangements due to the conflicting requirements of large polarizing magnetic field for one and careful magnetic shielding for the other. In this paper we consider the possibility to perform an experiment combining both aspects and discuss upon plausible outcome of such experiments.

1. Introduction
The concept of investigating the competition of mutually adverse ordered states of the nuclear spins and conduction electrons in metals has been outlined many times in the past [1, 2, 3, 4, 5, 6] but practically no experimental realizations exist. Magnetic order of the nuclear spin system is associated with emergence of an internal magnetic field in the substance matter, which has an evident influence on the tendency for the conduction electrons to form the coherent superconducting state as means to lower the total energy of the system. On the other hand, the nuclear spin system may behave differently in normal or superconducting host, as the conduction electrons play a role in mediating the interactions between the nuclei in the short range and because the screening of the long range couplings becomes different upon such a change of state of the conduction electrons. The scarcity of experimental studies on this subject is primarily due to the lack of suitable materials for such research and secondarily due to the demanding conditions for such experiments.

In order to obtain a fertile conflict between the two described states of order in a metal, one needs to have a ferromagnetically ordered nuclear spin system in a very weak superconductor. A nuclear antiferromagnet, such as copper or silver [7, 8], would barely disturb or be disturbed by the superconductivity. The internal field due to the nuclear spins averages out in an antiferromagnet over long distances and the conduction electrons, even in the superconducting state, behave essentially as individual normal electrons over short distances much less than the coherence length. This is crucial from perspective of the nuclear spins, as the indirect couplings through the conduction electrons operate over distances just a couple lattice periods. Therefore, an antiferromagnetically ordered nuclear spin system can well reside in a superconducting metal unchanged even if it would primarily be the interactions through normal conduction electrons
that were decisive in forming the particular ordering pattern of the spins via the indirect exchange
couplings. These arguments are, however, still basically hypothetical, since there are no real
examples of antiferromagnetically ordered nuclear spins within a superconductor, let alone
the fact that the experimental means to study such systems would be much limited by the deficiency
of the most common susceptibility methods in the case of a superconductor.

More common way of removing the fine balance between nuclear magnetism and
superconductivity would rather be the overwhelming strength of the superconductivity. This
means, on one hand, that there is no control over the magnetic field sensed by the nuclei across
the region of interest for their spontaneous ordering, since the onset of superconductivity would
simply quench any net internal magnetic field. Further, the nuclear spins would just marginally
contribute to the total field, even if fully polarized, being far insufficient to alter the state of the
conduction electrons in any appreciable manner. Most remarkable example in this category is
probably AuIn$_2$ [9], where there is indeed a distinct drop in the critical field of superconductivity
at the onset of magnetic ordering of the nuclear spins, but not much finer nuances beyond that
have been observed. There are other well demonstrated examples, such as Al [10], Sn [11]
and In [12], where finite nuclear magnetization at very low temperatures makes a noticeable
contribution to the total magnetic field cutting down the range of superconductivity, but this is
still merely a minor perturbation. Rhodium is exceptionally weak superconductor [13], but the
nuclear spin system in that metal behaves antiferromagnetically [14], so that this combination,
after all, also falls into the category of weak mutual influence [15].

In the following we give arguments showing that lithium metal may be the best candidate
ever for more complicated interplay between nuclear magnetic ordering and superconductivity
and provide practical guidelines, which are considered essential in order to successfully perform
the proposed experiment.

2. Nuclear magnetic order in lithium
We have shown that the nuclear spin system in natural lithium develops spontaneous magnetic
order below about 0.3 $\mu$K at zero magnetic field, that the system exhibits anomalies attributable
to ferromagnetic order when the nuclear entropy is less than about 80% from its maximum value,
and that the order changes character at a field of about 0.3 mT [16]. The last feature is probably
due to a change in the domain structure assisted by the magnetic field.

In order to prepare the nuclear spin system deep into the ordered state, one needs to subject
the sample to a magnetic field of order 3 T for about one day at a temperature of order 0.1 mK.
This is sufficient to nearly fully polarize the nuclear spins. The subsequent demagnetization cools
the nuclei to temperatures several orders of magnitude below that of the lattice and electrons
and allows the appearance of spontaneous nuclear order, which can be maintained for several
hours to perform the desired palette of investigations.

3. Superconductivity in lithium
Natural uncompressed lithium was observed to transform into the superconducting state below
about 0.4 mK at extremely low magnetic field of order 10 nT [17]. All samples under similar
conditions were superconducting below 0.2 mK, but one of the samples became just partly
superconducting at 0.4 mK. These are the lowest critical temperatures observed for any metal,
and they are, of course, associated with very low critical magnetic field as well. A field of about
0.1 $\mu$T was sufficient to prevent the superconducting transition from being triggered at any
temperature and the normal state was restored from the superconducting state at about 0.9 $\mu$T
at the lowest temperatures achieved. Fields of this order are easily generated by the nuclear
spin system in lithium metal, once macroscopically polarized.

One key element in the superconductivity experiment was very careful magnetic shielding,
so that the samples were never exposed to fields larger than just a few $\mu$T. This means that
the nuclear spins in this case were not polarized at all, and therefore had no influence on the observed superconducting properties. In order to have observed any such effect, the nuclear spin temperature should have been at least two orders of magnitude lower.

4. Practical considerations for an interplay experiment

To bring about conditions for strong interplay effects between the nuclear spin system and the superconductivity in lithium, one should first polarize the spins in fields of order teslas, and then, after the demagnetization, to protect the sample to a fraction of microtesla in order to give opportunity for the superconducting state to appear. Although these requirements are strongly conflicting, such a scheme is technically feasible as judged on the basis of our experience with corresponding manipulation on rhodium metal [18].

First, the sample environment must be protected from the remanence field of the polarizing superconducting magnet by means of a high-permeability shield with sufficient capacity. Such a shield is saturated in high magnetic fields, thus becoming neutral during the period of polarizing the nuclei. Once the external field drops below a certain value, typically of order ten millitesla, the shield becomes effective and reduces the interior field by preferably more than a factor of 1000 in the lowest fields.

The demagnetization should be terminated by a suitable degaussing sequence, which may reduce the remanence field of the big superconducting solenoid itself and, more importantly, this will improve the shielding properties of the high-permeability material around the sample. The proper sequence must probably be found by trial and error, starting with virgin conditions, where the superconducting state of the sample has first been confirmed before ever energizing the big magnet for the first time. Then the field is brought to successively higher values, while frequently verifying the possibility to observe the superconducting transition in between, until the desired strength of the main field has been achieved. Such a procedure was found successful in our experiments on rhodium, where finally a field of 3 T could be used [18].

It is also important to exclude any auxiliary superconducting materials from within the magnetic shield, as they are prone to collect pinned flux once exposed to high magnetic fields. In particular, the measurement coils for signal detection and small magnetic field manipulation should be made of normal metal, most conveniently from copper or silver. This means that there is small resistive heating, when the currents are applied, but this may be designed to be negligible, except perhaps for the static experimental field coil, if nuclear order at millitesla fields is to be investigated. The static field coils and the signal excitation coil is best anchored to the thermal radiation shield at the dilution fridge base temperature, while the signal pick-up coil probably may sit right on the sample in order to achieve the optimal filling ratio. This coil must then be thermalized to the first nuclear refrigerating stage, which sustains the thermal bath for the lattice and the conduction electrons of the sample.

The lithium sample must be protected from chemical reactions with anything in the environment. This is best accomplished by using preshaped thin copper foils, which offer both the chemical protection and provide good thermal contact to the sample [19]. The cross sectional area of the sample may need be a couple of square millimeters to ensure good signal levels, and it should be made flat in one dimension (< 1 mm) in order to reduce eddy current heating during the sample demagnetization. The best choice for coupling the signal to be measured is a SQUID, which makes it possible to use extremely gentle excitation and still observe signals with reasonable quality. Care must be exercised to provide sufficient bandwidth for the measurements, as the regime of interest extends down to a couple Hertz.

5. Plausible observations

The temperature of the nuclear spins and the conduction electrons in lithium can be manipulated almost independently from each other, as the spin lattice relaxation time is very long at the
relevant range of temperatures. This is a consequence of the reasonably large magnitude of the Korringa constant: \( \kappa = 44 \text{ sK} \). By making very small changes to the magnetic field, by changing the nuclear polarization either by letting it relax on its own or by applying additional heating by virtue of NMR absorption, or by changing the electronic temperature determined by the external thermal bath, one can favor the presence of either nuclear order or superconductivity. When this preference is turning from one state to the other, it is expected that unusual compromising configurations may appear. In the simplest case the emerging nuclear magnetization would just destroy the superconducting state, although it would be energetically favorable in terms of the temperature and external magnetic field. In somewhat more complicated scenario the nuclear spin system would adjust the range of homogeneous order either by forming a new kind of domain structure or by a continuous modulation of magnetization. This way the internal magnetic field would cancel out in the length scale relevant for the superconductivity so as to allow its presence together with nuclear spin order satisfying the spin-spin couplings to good proportion in the shorter range.

Lithium offers potential to even more exotic experiments, where the isotope content of the sample could be varied between the two stable isotopes \(^7\text{Li}\) and \(^6\text{Li}\). Their nuclear properties differ exceptionally much, still being just two different isotopes of the same element. As the mass difference is also not negligible, this should have an observable influence on the superconductivity alone.

In conclusion, we anticipate that nuclear order and superconductivity cannot reside in lithium metal simultaneously independent from each other, which is a condition very difficult to bring about in an experiment. This requires a rare set of material properties for the sample and, from the technical point of view, an extraordinary control of magnetic field over ranges from several teslas to nanoteslas. Practical guidelines to achieving this were given in this report.

References

[1] Pobell F, Herrmannsdörfer T, Rehmann S and Wendler W 1996 *Czech. J. Phys.* **46** 3279–85
[2] Kulic M L, Buzdin A I and Bulaevskii L N 1997 *Phys. Rev. B* **56** 11415–8
[3] Dyugaev A M, Vagner I D and Wyder P 1997 *JETP Lett.* **65** 810–3
[4] Sonin E B 1998 *J. Low Temp. Phys.* **110** 411–6
[5] Tuoriniemi J T and Knuttila T A 2000 *Physica* B **280** 474–8
[6] Dyugaev A M, Vagner I D and Wyder P 2001 *JETP Lett.* **73** 411–4
[7] Jyrkkö T A, Huikko M T, Louasnmaa O V, Siemansmeyer K, Kakurai K, Steiner M, Clausen K N and Kjems J K 1988 *Phys. Rev. Lett.* **60** 2418–21
[8] Sonin E B 1998 *J. Low Temp. Phys.* **110** 411–6
[9] Knuttila T, Laurila K, Lindgärd P A, Louasnmaa O V, Oja A S, Siemansmeyer K, Steiner M, Tuoriniemi J T, Weinfurter H 1990 *Phys. Rev. Lett.* **64** 1421–4
[10] Tuoriniemi J T, Numnila K K, Vuorinen R T, Louasnmaa O V, Metz A, Siemansmeyer K, Steiner M, Leffmann K, Clausen K N, Rasmussen F B 1995 *Phys. Rev. Lett.* **75** 3744–7
[11] Herrmannsdörfer T, Rehmann S, Seibold M and Pobell F 1998 *J. Low Temp. Phys.* **110** 405–10
[12] Rehmann S, Herrmannsdörfer T and Pobell F 1997 *Phys. Rev. Lett.* **78** 1122–5
[13] Herrmannsdörfer T, Rehmann S, Seibold M and Pobell F 1998 *J. Low Temp. Phys.* **110** 363–8
[14] Herrmannsdörfer T 2000 *Physica* B **280** 368–9
[15] Herrmannsdörfer T and Tayurskii D 2001 *J. Low Temp. Phys.* **124** 257–69
[16] Buchal Ch, Pobell F, Mueller R M, Kubota M and Owens-Bradley J R 1983 *Phys. Rev. Lett.* **50** 64–7
[17] Hakonen P J, Vuorinen R T and Martikainen J E 1993 *Phys. Rev. Lett.* **70** 2818–21
[18] Knuttila T A, Tuoriniemi J T and Leffmann K 2000 *Phys. Rev. Lett.* **85** 2573–6
[19] Juntunen K and Tuoriniemi J T 2004 *Phys. Rev. Lett.* **93** 157201
[20] Juntunen K I and Tuoriniemi J T 2005 *J. Low Temp. Phys.* **141** 235–93
[21] Tuoriniemi J, Juntunen-Nurmiluukas K, Uusvuori J, Pentti E, Salmela A and Sebedash A 2007 *Nature* **447** 187–9
[22] Knuttila T A, Tuoriniemi J T, Leffmann K, Juntunen K I, Rasmussen F B and Numnila K K 2001 *J. Low Temp. Phys.* **123** 65–102
[23] Tuoriniemi J, Juntunen K and Uusvuori J 2003 *Physica* B **329** 1294–5