

# **NUCLEAR MAGNETISM AND SUPERCONDUCTIVITY: INVESTIGATIONS ON LITHIUM AND RHODIUM**

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Abstract <p>This thesis describes low temperature experiments on lithium. The experiments concentrate on investigating low temperature phase transitions of two subsystems in this metal: its nuclear spin and electronic systems. These phenomena were investigated in two separate sets of samples, each designed to meet the experimental requirements for the phenomena under investigation.</p> <p>The electronic ground state of lithium at ambient pressures is expected to be superconducting, but earlier experiments show that the metal remains normal at least down to 4 mK. In this thesis research, a lithium sample was cooled down to 0.1 mK, <math>B &lt; 10</math> nT, but no superconductivity was observed. A new upper limit for the superconducting transition temperature was established, over an order of magnitude lower than the earlier upper limit. Many theoretical estimates predict superconductivity already at higher temperatures, and its absence remains a puzzle. The superconductivity in lithium has been under considerable interest recently, since the superconducting phase was observed in the highly compressed state.</p> <p>The nuclear spin system of lithium was investigated as well. The large magnetic moment of the lithium-7 nuclei made lithium an interesting target for studies of nuclear magnetism. The spin system was cooled down by a two stage adiabatic nuclear demagnetization cryostat. The nuclear magnetic resonance (NMR) spectra, the spin temperature, and the static susceptibility were measured. The NMR spectra revealed the appearance of an anomalous peak at low frequencies. Also, the spin system was found to behave in an irreversible manner at low fields and high nuclear polarizations. These effects give evidence for the existence of a magnetically ordered state of the lithium nuclei. The type of the order was not resolved unambiguously, but some facts point to a ferromagnetic ordering. A tentative phase diagram was constructed for the system.</p> <p>Previously, nuclear magnetism and superconductivity in rhodium metal have been investigated. This thesis also includes some numerical and analytical modeling on the nuclear spin system of rhodium, aimed at the interpretation of the experimental data.</p>			
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# List of publications

This thesis is based on the following original publications.

- [P1] T. A. Knuuttila, J. T. Tuoriniemi, K. Lefmann, K. I. Juntunen, F. B. Rasmussen, and K. K. Nummila, *Polarized nuclei in normal and superconducting rhodium*, J. Low Temp. Phys. **123**, 65 – 102 (2001). © 2001 by Plenum Publishing Corporation.

The paper describes in detail the experiments on superconductivity and nuclear magnetism in rhodium.

- [P2] K. I. Juntunen, K. Lefmann, J. T. Tuoriniemi, and T. A. Knuuttila, *High Temperature Expansion and Exact Diagonalization of the Rhodium Nuclear Spin System Compared to Experimental Results*, J. Low Temp. Phys. **124**, 271 – 289 (2001). © 2001 by Plenum Publishing Corporation.

Here we calculate the complete high temperature expansions for a system with both dipolar and exchange interactions up to the third order, and the field dependent terms up to the 4th order. We calculate the energy states for a cluster of 16 spins of rhodium using exact diagonalization, and compare the results with high temperature expansions, their Padé approximants, and experimental data on rhodium.

- [P3] J. T. Tuoriniemi, K. I. Juntunen, and J. M. Uusvuori, *Thermal contact to lithium metal*, Physica B **329-333**, 1294 – 1295 (2003). © 2003 by Elsevier Science B. V.

Here we investigate the suitability of silver, copper and gold to be used as an encapsulation material for lithium. We measure contact

resistances for samples with pressed joints of lithium and the three metals. Copper is found to give good contact to lithium and small contact resistance, while silver and gold form an alloy with lithium and are thus not suitable for the encapsulation of lithium.

- [P4] J. T. Tuoriniemi and K. I. Juntunen, *Nuclei in cooperation*, J. Low Temp. Phys. **135**, 513 – 543 (2004). © 2004 by Plenum Publishing Corporation.

Two NMR phenomena, the double spin resonance and the suppression-enhancement effect of the isotopic lines, are analyzed, and the effect of the exchange parameter  $R$  on these phenomena is discussed. We review earlier results on this topic, present new, improved, data on copper, and re-examine some previous results.

- [P5] K. I. Juntunen and J. T. Tuoriniemi, *NMR Spectra of Highly Polarized Lithium*, Accepted for publication in J. Low Temp. Phys. (2005). © 2005 by Springer.

Here we show some of the measured NMR spectra of lithium and describe the data analysis in detail. The preparation of the NMR sample is also described.

- [P6] K. I. Juntunen and J. T. Tuoriniemi, *Nuclear Ordering in Lithium and an Upper Limit on its Ambient Pressure Superconducting Transition Temperature*, Phys. Rev. Lett. **93**, 157201 (1 – 4) (2004). © 2004 by the American Physical Society.

Here we present evidence for nuclear magnetic ordering in lithium. The low frequency anomaly in the NMR lineshapes at high polarizations is discussed. Irreversible effects are presented and discussed. Based on these characteristics, and also on the temperature measurements, we suggest a phase diagram with two regions of different long range order and also regions with precursory short range order. We also report on the absence of superconductivity in lithium down to 100  $\mu$ K,  $B < 10$  nT.

- [P7] K. I. Juntunen and J. T. Tuoriniemi, *Experiment on Nuclear Ordering*



*and Superconductivity in Lithium*, Report TKK-KYL-012 (2004). 52 pages.

Here we give a detailed description of the measurements on lithium. The experimental setups and measurements for the different samples on superconductivity and nuclear magnetism are described. Estimates of the local field and the interaction parameter  $R$  are presented. Spin lattice relaxation times are investigated. The entropy versus temperature curves, the quasi static susceptibility, and the heat capacities at different fields are presented. The NMR spectra of both the frequency- and field sweep methods are shown. The possible detection of a triple spin resonance is discussed. The construction of the phase diagram is described in detail.

## **Author's contribution**

All the publications listed here are results of team work. The lithium experiments were carried out by two persons, J. Tuoriniemi and the author. The author prepared the lithium samples, was responsible for the daily operation of the refrigeration system during the lithium measurements between summer 2002 and end of 2003, and carried out most of the data analysis. The author was mainly responsible for writing the text for publication [P7]. She wrote the first versions of the publications [P5] and [P6]. For publication [P1], her part was to analyze the changes in the NMR lineshapes due to eddy currents. The author was responsible for the high temperature expansion and Padé approximant calculations for publication [P2], she wrote some parts of the text and plotted the figures for this publication. For publication [P4], the author participated in the measurement of the new copper data and did most of the data manipulation for this new data. She prepared and measured the copper and gold samples for [P3]; most of the silver samples were prepared and measured in cooperation with J. Uusvuori.

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Otaniemi, November 2004

Kirsi Juntunen

# Chapter 1

## INTRODUCTION

This thesis describes experiments on lithium at ultralow temperatures. The experiments had two goals: to investigate the ground states of both the electronic and the nuclear spin systems of lithium.

The electronic system of lithium is expected to form a superconducting ground state at low enough temperatures and small enough magnetic fields. In a superconductor, many of the properties of a normal metal are radically altered. For example, magnetic fields are expelled from a superconductor, and electric currents flow without resistance. The first goal of the present experiment was to cool a sample of lithium at ambient pressure down to a much lower temperature than this metal has ever been cooled before, and to determine whether the metal can be brought into the superconducting state.

Also the nuclear spin system of lithium is expected to undergo a phase transition at very low temperatures. According to the third law of thermodynamics, the entropy of a system must vanish at zero temperature. A nuclear spin system has substantial entropy left down to very low temperatures, but eventually, at low enough temperatures, this entropy must be consumed by the formation of a magnetically ordered state. Spontaneous nuclear magnetic ordering can occur when the thermal energy of the spins becomes smaller than the energy of the magnetic interactions between the spins.

Lithium was an interesting candidate for studies of nuclear magnetism because of the large magnetic moment of the  ${}^7\text{Li}$  nuclei. Such studies in

this material have not, however, been performed before, partly because of the practical difficulties in working with it. In this thesis, investigations on nuclear magnetic ordering of the lithium nuclei in a natural isotopic mixture will be described. These phenomena were investigated by measuring the nuclear magnetic resonance (NMR) spectra, the temperature of the spin system, and the static susceptibility up to very high nuclear polarizations at ultralow temperatures.

In general, the two phenomena investigated in this thesis, nuclear magnetism and superconductivity, exist independently of each other because of the isolated nature of the nuclear spin and electronic systems. These phenomena may, however, have some mutual interactions; investigations of such interplay effects have been performed for some materials [1–5], but yet the understanding of these effects remains incomplete. The fact that observing these two phenomena, nuclear magnetism and superconductivity, simultaneously would allow studies of their interplay phenomena, was one of the motivations for the present experiments.

Another force driving these experiments was the ever surprising absence of superconductivity in lithium at ambient pressure. The present theoretical knowledge on this system strongly predicts superconductivity around, or even above the milli-Kelvin temperature regime [6–12]. Previous experiments at temperatures down to 4 mK have, however, revealed no signs of it [13, 14]. Since the cryostat equipment operated by the YKI group at the Low Temperature Laboratory is capable of reaching temperatures down to about 100  $\mu$ K, there was a good chance of being able to observe the expected superconductivity by cooling a sample down with this equipment.

The experiments described in this thesis do indeed provide evidence for the existence of nuclear magnetic ordering in lithium. The other goal of the experiment, observing superconductivity at ambient pressure, was not achieved, but a new upper limit of 0.1 mK for the transition temperature was established. The new upper limit is more than an order of magnitude lower than the earlier upper limit of 4 mK.

The first chapter of this thesis describes the physical phenomena involved with the investigated systems. In the next part, the experimental methods and procedures will be described. Then, the results will be presented.

## 1.1 Magnetism and Nuclear Magnetism

One can think of a magnet as a group of small magnetic dipoles located on crystal lattice sites. These objects can exchange energy with each other, or with the other degrees of freedom of the crystal. In Nuclear magnetism, the magnetic dipole moments arise from intrinsic dipole moments of the nuclei, the nuclear spins, while in Electronic magnetism, the electronic orbital motion contributes to the magnetic moment in addition to the electronic spin.

If a system is in equilibrium, one can define the temperature  $T$  to describe the distribution of its constituents over the possible energy states. It can happen, that a nuclear spin system reaches internal equilibrium, but remains in a non-equilibrium state with the rest of the lattice. Then, it is practical to define two different temperatures to describe the system, the nuclear spin temperature  $T_n$  and the lattice (or electronic) temperature  $T_e$ .

The high temperature state of a nuclear spin system is paramagnetic: in the absence of an external magnetic field, the spins will have no preferential alignment, and the probability of an individual spin pointing at any direction is the same. The system is then disordered, which means that it has a large entropy. The third law of thermodynamics states, however, that at zero temperature the entropy must vanish. When the system approaches zero temperature, it must develop magnetic order in order to comply with this law.

The actual type of order depends on the strength of the different interactions between the spins. The interactions may favor parallel alignment of neighboring spins, whereby a ferromagnetic order is formed. If antiparallel alignment is favored, the order is antiferromagnetic. The interactions may also favor the formation of more complicated structures, such as spiral or canted structures.

Many phenomena related to electronic magnetism belong to our everyday lives. For example, magnetism makes computers, VCR's and many other household equipment work. Even some animals are known to possess magnetic "sensors", with which they navigate in the earth's magnetic field [15]. The ordered states in many materials with electronic magnetism exist at room temperature: iron, for example, is ferromagnetically ordered at tem-

peratures below the Curie temperature  $T_C = 1024$  K. The ordering temperatures can also be much lower, like the antiferromagnetic ordering (Néel) temperature  $T_N = 12.5$  K of cerium.

The temperature scales for nuclear magnets are, however, quite different. The ordering temperature depends on the strength of the interactions between the spins. Because of the much smaller magnetic moments, the nuclear magnetic interactions are expected to be much weaker than magnetic interactions between the electrons. The different nuclear spin systems have been found to order at temperatures between the nano- and the milli-Kelvin range, roughly six orders of magnitude lower than the electronic ordering temperatures. Thus, nuclear magnetic ordering phenomena can only be investigated by using cryostat equipment capable of reaching ultra-low temperatures.

## 1.2 Interactions

In electronic magnetism, the spins interact by strong exchange forces that arise from the electrostatic coupling. The same coupling is not present between the nuclear spins in metals. Instead, these spins interact through several different mechanisms. The nuclei act as small dipolar magnets, and their magnetic moments interact through the dipolar interaction. The indirect exchange interaction arises when the nuclei couple to conduction electrons by hyperfine interaction, and the conduction electrons act as mediators between two separate spins. This interaction is called the Ruderman-Kittel (RK) interaction, according to the developers of its first theoretical model [16]. The strength of this interaction is a damped oscillatory function of the distance between the nuclei. It has short range nature, unlike the dipolar interaction. Another form of the exchange forces is direct exchange interaction, in which the interaction between the nuclear spins arises when the nuclei can actually exchange lattice sites. It occurs only in such fermionic systems, where the zero point motion of the nuclei is large, i.e. the nuclei are very light. Finally, all nuclei with spin  $I > 1/2$  possess an electric quadrupole moment which arises from the spatial distribution of the charged protons in the nucleus. If the lattice environment is not cubic, the nuclear spins interact with each

other through the quadrupolar interaction.

The interactions that an individual spin in a system experiences with the other spins in the system can be described by an average local mean field. This field  $B_L$  adds to the external magnetic field  $B$  as  $\sqrt{B^2 + B_L^2}$ .

### 1.3 History of Nuclear Magnetism

Nuclear magnetic ordering has been investigated in several materials. The first systems where spontaneous magnetic ordering was observed in the 1970's were insulators like  $\text{Ca}(\text{OH})_2$ ,  $\text{LiF}$  and  $\text{LiH}$  [17]. Both ferro- and antiferromagnetic orderings were observed, and the critical ordering temperatures were in the micro-Kelvin range. In these materials, the nuclear spins are only weakly coupled with the localized electrons, and special techniques were needed for the cooling: the spins were polarized through paramagnetic impurities and the demagnetization was performed in the rotating coordinate frame. The nuclei in these insulators interact with each other only through the dipolar interaction.

In 1974, the  $^3\text{He}$  nuclei were discovered to form antiferromagnetic order in the compressed state [18,19]. This "quantum solid" has a very high transition temperature of around 1 mK. The ordering is brought about by direct exchange interactions, which arise from the large zero point motion of the light, fermionic  $^3\text{He}$  nuclei.

The Van Vleck paramagnets of rare earth intermetallic compounds, like  $\text{PrCu}_6$  and  $\text{PrNi}_5$ , order ferro- or antiferromagnetically around the milli-Kelvin regime [20]. The nuclear spins are coupled to the paramagnetic  $f$ -electrons through the hyperfine interaction, and a strong indirect exchange interaction is formed between the nuclei.

Nuclear magnetic ordering has been observed also in some elemental metallic systems. The element investigated in this thesis, lithium, is now to be added to this list. In 1982, investigations on copper led to the discovery of antiferromagnetic ordering at 58 nK [21]. A rich phase diagram with several regions having different antiferromagnetic arrangements was discovered [22]. Silver orders antiferromagnetically at 0.56 nK [23], while at negative tem-

peratures, the ordering is ferromagnetic with  $T_C = -1.9$  nK [24]. In these materials, a competition exists between the dipolar and indirect exchange interactions, both being important. In praseodymium, the nuclear interactions are greatly enhanced by the hyperfine interaction with the conduction electrons, and the nuclear spin system orders ferromagnetically at 60 mK [25]. Indications of ordering have been observed also in the highly exchange enhanced Pauli paramagnet scandium, where the type of order is presumably ferromagnetic; the  $T_C$  has not been resolved yet [26]. In scandium, electric quadrupole interactions are quite important. The indium nuclei in the intermetallic compound AuIn<sub>2</sub> order ferromagnetically at 35  $\mu$ K [27]. Also in In [28], Tl [29], Au [30], and Rh [31, 32] such investigations have been made, but no evidence for magnetic ordering has been found.

## 1.4 Phenomenology of Superconductivity

Today, superconductivity is an important phenomenon with an increasing number of practical applications. When a material reaches a superconducting state, many of its properties change. The electrical resistivity disappears. The magnetic field is expelled from the sample; this is called the Meissner effect. The theory of conventional, low temperature superconductors is well known; it was first developed by Bardeen, Cooper, and Schrieffer in 1957 [33]. In the superconducting state, two electrons with opposite spins and equal but opposite momenta form a bound state, a Cooper pair. Having like charges, the electrons repel each other through the Coulomb interaction. This interaction is described by the electron-electron repulsion parameter  $\mu^*$ . For the formation of a paired state, an attractive interaction must exist to overcome the natural repulsion between two like charges. This attraction is created through interactions with lattice vibrations, the phonons, and it is described by the electron-phonon interaction parameter  $\lambda$ . The McMillan equation [34]

$$T_c = \frac{\theta_D}{1.45} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \quad (1.1)$$

can be used to estimate the superconducting transition temperature  $T_c$  from the two parameters,  $\mu^*$  and  $\lambda$ . Here  $\theta_D$  is the Debye temperature.



In a normal metal, the electrons can absorb any small amount of energy available to them and the inelastic scattering processes give rise to electrical resistivity. In the superconducting state, however, the possible energy levels of the electrons are restricted: there is a forbidden energy gap  $\Delta$ , describing the binding energy of a Cooper pair, in the possible energy levels of the electrons. Only excitations above  $\Delta$  can be absorbed by a single electron. If no such excitations are available, the electrons cannot scatter, and the material has no electrical resistivity.

Superconductivity was first observed in 1911, when Kamerlingh Onnes observed a sudden decrease in the electrical resistance of mercury. Since then, a numerous group of metals, alloys, compounds, and even non-metallic elements (under pressure) have been found to be superconductors. The discovery of high temperature superconductivity in 1986 [35] opened new possibilities for the application of this phenomenon in practice. The high temperature superconductors obey the same phenomenology as conventional superconductors, but a theoretical understanding of the origin of superconductivity in them remains yet to be discovered. Today, the highest transition temperatures are found in cuprate compounds, where superconductivity can be found at almost 140 K at ambient pressure [36], and at 160 K under high pressure [37]. The material with the lowest currently known transition temperature is rhodium with  $T_c = 0.325$  mK [38].

Quite many metallic, non-magnetic elements have been found to exhibit ambient pressure superconductivity at low temperatures, as illustrated in Fig. 1.1. Some elements not exhibiting ambient pressure superconductivity, do become superconductors under high pressure, or in thin films. Electronic magnetism and superconductivity are mutually excluding, competing phenomena: usually, the elements with electronic magnetism (e.g., iron, cobalt) do not show superconductivity. But, for example, when the electronic magnet iron is compressed, it reaches a non-magnetic hexagonal close packed phase above 10 GPa, and it can become a superconductor [39]. There are two interesting areas in the periodic table, where non-magnetic metals not showing bulk superconductivity are concentrated: the noble and platinum group metals Ag, Au, Cu, Pt and Pd, and the alkali and alkaline earth metals (except beryllium). In the noble metals, the electron phonon interaction

The figure shows a periodic table with elements shaded to indicate their superconducting properties. The legend below the table defines the shading patterns:

- Light gray: Nonmetallic or not stable
- Dark gray: Electronic magnetism
- White with an asterisk (\*): Superconducting only under special circumstances
- Dark gray with a wavy border: Superconducting

H																				He
Li*	Be												B*	C*	N	O*	F			Ne
Na	Mg												Al	Si*	P*	S*	Cl		Ar	
K	Ca*	Sc*	Ti	V	Cr*	Mn	Fe*	Co	Ni	Cu	Zn	Ga	Ge*	As*	Se*	Br*			Kr	
Rb	Sr*	Y*	Zr	Nb	Mo	Tc	Ru	Rh	Pd*	Ag	Cd	In	Sn	Sb*	Te*	I*			Xe	
Cs*	Ba*	Lu*	Hf	Ta	W	Re	Os	Ir	Pt*	Au	Hg	Tl	Pb	Bi*	Po	At			Rn	
Fr	Ra																			
		La	Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb					
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No					

Figure 1.1: Superconducting elements in the periodic table.

is very weak and the electronic density of states is low. These factors presumably suppress the occurrence of superconductivity below temperatures achievable with today's cooling methods. In the alkali and alkaline metals, superconductivity has not yet been observed, but many of these metals are expected to be superconductors at low enough temperatures [6]. Lithium is considered the most likely candidate of the alkali metals to become a superconductor, since the electron phonon attractions are largest in it.

Magnetic impurities in a sample can suppress superconductivity. This problem has been studied theoretically, e.g., by Abrikosov and Gor'kov [40] and later by Müller-Hartmann and Zittartz [41]. The impurities may be magnetically inactive in certain host materials, but active "Kondo impurities" in others. The Kondo impurities act as scattering centers for the Cooper pairs, and the scattering processes can prevent the formation of a superconducting state.

## 1.5 Properties of Lithium

In this thesis, we concentrate on experiments on lithium. This apparently simple metal has several specific features which are presented in this section. Some basic properties are shown in Table 1.1. For comparison, the same information for copper is also presented there.

Lithium is the third element, lightest of the alkali metals. It is a silvery, soft metal, easily cut with a knife. It is mainly used in batteries, heat transfer applications, alloys, and it also has an important pharmaceutical use in drugs used as mood stabilizers. In larger doses, it is considered toxic. Like the other alkali metals, lithium is reactive as well. It reacts, e.g., with nitrogen, oxygen and water, even though the reactions are less violent than in the heavier alkali metals. It is also corrosive. An experimentalist investigating lithium is then faced with challenges in protecting the sample from reactions with its surroundings.

Lithium has two natural isotopes,  ${}^6\text{Li}$  and  ${}^7\text{Li}$ . Some properties of these isotopes are shown in Table 1.2 along with the same data for the copper isotopes. The isotope  ${}^7\text{Li}$  dominates the nuclear magnetic properties of lithium both because of its large abundance and a much larger magnetic moment than that of the minor isotope,  ${}^6\text{Li}$ .

In lithium, the coupling between the nuclear spins and the conduction electrons is very weak. If the nuclear spin system is cooled down to a lower temperature than the lattice, the nuclear spins will warm up towards the lattice temperature very slowly because of this weak coupling between the two subsystems, i.e. the spin lattice relaxation time is very long. In metals with nuclear spin  $I \neq 1/2$ , as in lithium, the nuclear relaxation is not exponential. However, one can define a momentary relaxation time  $\tau_1$  [51]. At fields  $B \gg B_L$ , it is given by

$$\tau_1 T_e = \kappa. \quad (1.2)$$

The Korringa constant  $\kappa$  describes the time scale of spin relaxation. For lithium, it is  $\kappa = 44$  sK [44]. For example, at a lattice temperature  $T_e = 0.3$  mK, the relaxation time  $\tau_1$  of the lithium nuclei in high field is as long as 41 hours.

At room temperature, the lithium lattice has body centered cubic (bcc)

	natural Li	natural Cu
Element number	3	29
Mass (amu)	6.94	63.55
Lattice symmetry at 298 K	bcc [42]	fcc
Lattice constant at 298 K (nm)	0.351 [42]	0.362
Density at 298 K ( $\text{kg}/\text{m}^3 \cdot 10^3$ )	0.534	8.96
Number density at 298 K ( $1/\text{m}^3 \cdot 10^{28}$ )	4.63	8.49
Number density at 78 K ( $1/\text{m}^3 \cdot 10^{28}$ )	4.76	
Electrical resistivity at 298 K ( $\Omega\text{m} \cdot 10^{-8}$ )	9.47	1.712
Local field at 4.2 K ( $\mu\text{T}$ )		340 [43]
Curie constant (nK)	606	566
Saturation magnetization $\mu_0 M_{\text{Sat}}$ (mT)	0.93	1.2
Melting point ( $^{\circ}\text{C}$ )	180.5	1084.6
Boiling point ( $^{\circ}\text{C}$ )	1342	2562
Linear expansion coefficient ( $1/\text{K} \times 10^{-6}$ ) at 298 K	46	16.5
Korringa constant $\kappa$ (sK)	44 [44]	1.2 [45]
Spin-spin relaxation time $\tau_2$ (ms)	$\sim 1$ [46]	0.15 [47]
Debye temperature $\theta_D$ (K)	344 [48]	343 [48]
Density of states at the Fermi energy (states/eV per atom per spin)	0.536 [11]	24.5 [49]

Table 1.1: Properties of Li and Cu metals. Most of the information was taken from Ref. [50].

	<sup>6</sup> Li	<sup>7</sup> Li	<sup>63</sup> Cu	<sup>65</sup> Cu
Natural abundance (%)	7.5	92.5	69.2	30.8
Atomic mass (amu)	6.015	7.016	62.930	64.928
$I$	1	3/2	3/2	3/2
$\mu/\mu_N$	0.822	3.256	2.223	2.382
$\gamma/2\pi(\text{Hz}/\mu\text{T})$	6.266	16.548	11.298	12.103
$Q$ (barn)	-0.0008	-0.041	-0.211	-0.195

Table 1.2: Properties of the isotopes <sup>6</sup>Li and <sup>7</sup>Li, <sup>63</sup>Cu and <sup>65</sup>Cu: Natural abundance, atomic mass, nuclear spin  $I$ , nuclear magnetic moment  $\mu/\mu_N$ , gyromagnetic ratio  $\gamma$ , and quadrupolar moment  $Q$ . Most of the information was taken from Ref. [50].

structure, but around 70 - 80 K it undergoes a martensitic structural phase transition. The low temperature lattice structure of lithium is not simple: competition between the cubic and hexagonal ordering tendencies causes the coexistence of several different structures. The low temperature structure is mostly close-packed rhombohedral  $9R$  [52] with a small amount of face centered cubic (fcc) order. In addition to these long range ordered forms, a part of the lattice forms a disordered polytype with short range ordering tendencies of the hexagonal close packed (hcp), fcc and  $9R$  types [53]. The  $9R$  structure, illustrated in Fig. 1.2, has a nine-layer repeat sequence (ABCB-CACAB) of close packed hexagonal planes with lattice parameters (at 78 K) of  $a_{9R} = 3.0986 \text{ \AA}$  and  $c_{9R} = 22.735 \text{ \AA}$  [54].

On compression, the lithium lattice gains a cubic fcc order at a pressure of around 20 GPa [55]. When it is further compressed, a new structural phase transition into a cubic polymorph with 16 atoms per unit cell is observed at around 39 GPa [56]. The material may undergo further structural phase transitions with increasing pressure [57].

The interactions between the lithium nuclei are governed by dipolar forces. The indirect exchange is expected to be small, since the coupling between the conduction electrons and the nuclear spins is weak. The non-cubic lattice

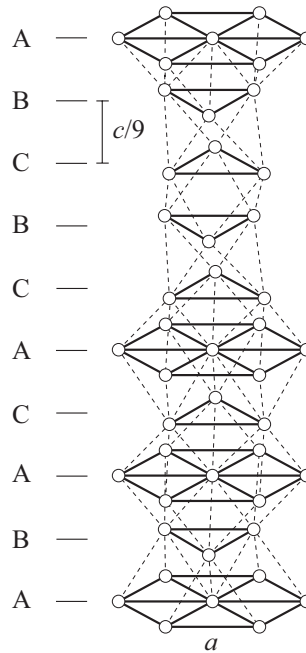


Figure 1.2: Close packed rhombohedral 9R structure.

environment at low temperatures gives rise to quadrupolar interaction, but this interaction is expected to be much smaller than the dipolar interaction.

The lightness of the lithium nuclei facilitates a considerable zero point motion and the direct exchange interaction for  ${}^7\text{Li}$  may have a non-vanishing magnitude. For comparison, in solid  ${}^3\text{He}$ , the amplitude of the zero point vibrations is about  $1/3$  of the interatomic distance. The amplitude is large enough to allow substantial exchange of lattice positions between the nuclei, which results in a considerable direct exchange interaction. In lithium, the zero point vibration amplitude is about 10 % of the nearest neighbor distance; the overlap of the wavefunctions of two neighboring nuclei is then drastically smaller in lithium than in helium, and the direct exchange interaction must be much smaller. It may, however, have some importance.

### 1.5.1 Superconductivity and Lithium

The superconducting transition is expected in lithium at ambient pressure according to many theoretical predictions [6–9, 11, 12], but no indications of superconductivity have been observed down to 4 mK [13, 14]. Like many other materials not showing ambient pressure superconductivity, lithium becomes a superconductor under altered conditions: in thin films [58] and under compression. The pressure induced superconductivity in lithium has raised a lot of interest in the recent years. The first observation of it is from almost twenty years ago [55], but its recent confirmation [57] inspired further studies in the pressure range 20 - 80 GPa [59, 60]. One set of experiments suggested a critical temperature as high as 20 K at 48 GPa [57], which would be the highest  $T_c$  observed in any pure element so far. More reliable experiments suggest a lower highest critical temperature,  $T_c = 14$  K at 30 GPa [60], which is still one of the highest critical temperatures ever observed in pure elements. The appearance of the superconducting state around 20 GPa is apparently associated with the simultaneous structural phase transition to the cubic fcc order [55, 60].

According to simple arguments, the ambient pressure superconductivity in lithium should appear at around 1 K. These calculations assume an electron-electron repulsion parameter  $\mu^* = 0.12$ , often accurate for simple metals, and use this value together with an estimate for the electron-phonon interaction parameter  $\lambda \sim 0.3 - 0.4$  in the McMillan equation, Eq. (1.1). The transition temperature so obtained ( $\sim 1$  K) is several orders of magnitude too high.

The structural disorder of lithium may influence superconductivity. The low temperature structure of lithium is mostly the rhombohedral 9R structure, interspersed with some fcc structure and short range ordered polytypes. As seen in the high pressure experiments, the superconducting state appears only after a structural phase transition to the cubic fcc form. Many of the calculations involving ambient pressure superconductivity are performed for a lattice with bcc symmetry, thereby omitting the structural disorder effects. According to other calculations, the existence of superconductivity in the 9R phase is slightly less likely than in the cubic bcc form [8], but it should still

appear above the milli-Kelvin regime. The effect of structural disorder on superconductivity in the short range ordered polytype forms has not been studied.

Spin fluctuations have been suggested to cause the absence of superconductivity in lithium [61], but the credibility of such calculations is in doubt because they are in some respects inconsistent with experiments [8]. In systems where the superconductivity is not of the conventional (s-wave) type, the spin fluctuations may, in fact, be responsible for the formation of a superconducting state [62, 63].



# Chapter 2

## METHODS

### 2.1 Nuclear Cooling

In a system of nuclear spins, changes of magnetic field  $B$  can be performed *adiabatically*, i.e., the entropy  $S$  is not altered. Two conditions have to be fulfilled in order for the field change to be adiabatic: firstly, the spin system should not exchange energy with its surroundings during the field change. This condition is satisfied if the changes occur much quicker than the spin lattice relaxation time  $\tau_1$ . Secondly, the spin system must be in internal equilibrium during the field change, i.e. one must be able to describe the system with a single spin temperature  $T_n$  at all times. This requirement is satisfied, if the field is changed in a time much longer than the spin-spin relaxation time  $\tau_2$ . For the case of paramagnetic lithium at ultralow temperatures, both conditions are easy to satisfy. The spin lattice relaxation time is very long, on the order of several days, while the spins reach internal equilibrium in a time on the order of one milli-second.

When such adiabatic changes are applied to a spin system, its temperature and magnetic field are directly related to each other. The entropy is a function of  $\sqrt{B^2 + B_L^2}/T_n$ ; since the entropy is conserved, a change of field from  $B_i$  to  $B_f$  imposes a change of the initial temperature  $T_i$  to

$$T_f = T_i \sqrt{\frac{B_f^2 + B_L^2}{B_i^2 + B_L^2}}. \quad (2.1)$$

This phenomenon is used as a basic tool in nuclear cooling: a nuclear stage, containing a set of nuclear spins with a large heat capacity, is magnetized in a high field  $B_i$ . The system is then cooled down to  $T_i$  by using an external cooling device. Then, the heat transfer between the cooling device and the spin system is stopped by a special heat switch, and the field is turned adiabatically to  $B_f$ . The nuclear spin temperature is then reduced to  $T_f$  according to Eq. (2.1). After cooling down, the nuclear spins absorb energy from the electronic system, and if the spin-lattice relaxation time is short enough, and the heat capacity of the nuclei large enough, the electronic system is cooled by the nuclei. This cooling method is a central tool in the experiments described in this thesis.

The same principle can be used if one wishes to cool another set of spins even further down. The spins, kept in a high field, are cooled down by the nuclear stage through the electronic systems. An adiabatic demagnetization to zero field can then cool the nuclei to much below the electronic temperature. The spins exchange energy with the electronic system, and the strength of these interactions determines the time scale of reaching equilibrium between the two subsystems. If the spin-lattice relaxation time is long enough, the cold nuclear spin system can be investigated during the time it warms up towards the electronic temperature. This method of cooling was used to study the lithium nuclei in the present experiment. The electronic temperatures were around 0.1 – 0.5 mK, at which temperatures the equilibration of the lithium nuclei to the electronic temperature takes several days.

## 2.2 Nuclear Magnetic Resonance

Today, nuclear magnetic resonance (NMR) methods are basic tools in biology, biochemistry, chemistry, medicine and physics. In the work presented in this thesis, NMR methods play an essential role in obtaining information of the behavior of the nuclear spins. With the method of nuclear magnetic resonance, one may select a desired component, even a very weak one, of the total magnetic susceptibility for detailed study.

In NMR, the spins are held at a constant field  $B$ , whereby they obtain

a magnetic energy proportional to their magnetic moments, spins and the magnetic field. An alternating field, transverse to the constant field, is then applied on the system. If the energy of the photons ( $hf$ ) of the alternating field equals the difference in the magnetic energies of two possible energy levels in the system, the system absorbs energy from the field at this resonance frequency  $f$ . If several spin species with different magnetic moments exist in the system, each spin species can then be investigated individually because the resonances occur at different frequencies. Actually, interactions between the spins change the possible energy levels of the individual spins slightly, and the spins resonate at slightly different frequencies, that on average occur on a common resonance frequency. Thus, the absorption resonance is widened and possibly shifted due to spin-spin interactions. The shape and position of the NMR peak can then be used to extract information on the interactions in the system.

There are several different ways of performing NMR measurements. In this thesis work, continuous wave NMR methods were used. The spectra were measured by sweeping the frequency and keeping the magnetic field constant, or vice versa. Other schemes of NMR are the pulsed wave methods: pulses of ac-fields are applied on the system, and the decay of the nuclei from this perturbed state towards equilibrium is recorded.

Multiple resonances occur when one photon excites two or more separate spins. The probability of such a transition is naturally much lower than that for a single spin excitation, but such resonances may still be observed. The double resonance, for example, occurs at around twice the frequency of the single spin flip peak, or at half the magnetic field.

For lithium, the NMR spectra consist of several different components: the resonances for both lithium isotopes, and also, within the limits of resolution, possibly the multiple spin flip resonances for both isotopes. The resolution in the present experiment was high enough to resolve the double spin resonance of  ${}^7\text{Li}$ , and also a trace of the triple spin resonance was observed.

## 2.3 Computational Methods

If the interactions between the nuclear spins are well known, it is possible to use computational methods to extract information on the behavior of the spin system in the paramagnetic phase. In exact diagonalization, the energy levels of a small cluster of spins are calculated by diagonalizing the spin Hamiltonian. The knowledge of the energy levels allows the computation of all thermodynamical properties of the system. Because of the finite size of the spin cluster, no long range order can exist. Instead, short range correlations in this small cluster can give hints about the behavior of a real spin system.

Other methods of studying nuclear spin systems include the high temperature expansions (HTE). They rely on the series expansion of the partition function around a small  $\beta = 1/(k_B T)$ . These expansions provide excellent approximations for the system at high temperatures but they eventually break down at low temperatures. Including more terms in the expansion extends its region of validity. The Padé approximant of a high temperature expansion can be used to remove its divergence.

In rhodium, the interactions between the nuclear spins are well known and these kinds of calculations are feasible. Publication [P2] describes the calculation of the exact diagonalization data for a system of 16 rhodium spins, and the results are compared with experimental data and high temperature expansions up to the third or fourth order. Excellent agreement with experimental data was obtained for the high temperature expansions and their Padé approximants down to  $\sim 1$  nK, but the accuracy of the exact diagonalization suffered from the finite size of the cluster.

In lithium, less information exists presently about the spin-spin exchange interactions, and the same kinds of calculations are not possible. The local field  $B_L$  and the exchange parameter  $R$ , which were used for the extraction of the nearest- and next nearest neighbor exchange interaction parameters in rhodium, have large error margins in lithium [P7]. Determining the interaction parameters from  $B_L$  and  $R$  is then not sensible. Also, the lattice disorder in lithium handicaps the exact diagonalization calculations, which rely on lattice symmetries. Simple second order high temperature expansions for lithium can, however, be determined. They can be used as a tool

in verifying the experimental results [P7].

## 2.4 Experimental Samples

The two phenomena investigated here, superconductivity and nuclear magnetic ordering (NMO), require quite different experimental conditions: if the superconducting transition temperature is low, the critical field will be low as well. Also, supercooling of the normal state may occur. For superconductivity, the sample then needs to be carefully protected from external magnetic fields. For NMO, on the other hand, the sample needs to be polarized in a large ( $\sim 1$  T) magnetic field, and less strict requirements are posed on the magnetic shielding of the remanent fields after the demagnetization. The NMO sample has to be thin such that the alternating fields on the order of 10 kHz used in the NMR will penetrate the sample. Only low frequencies are needed for the observation of superconductivity, and a more bulky construction is beneficial for the signal to noise ratio. For these reasons, two different sets of samples were prepared, one for the superconductivity experiment, and another one for the nuclear ordering experiment.

The reactivity of lithium poses severe restrictions on sample preparation: the samples must be prepared in an inert atmosphere and protected from deterioration by a capsule, since the samples will necessarily be exposed to air while setting up the cryostat. A possible encapsulating material had to be non-superconducting and non-magnetic, and, naturally, not reactive itself. Also, a good thermal contact between the encapsulating material and lithium had to be ensured. The practically suitable group of possible encapsulating materials consisted of only three metals: copper, silver and gold. The primary candidate for encapsulation was silver since the large difference in the magnetic moments of Li and Ag would render the NMR measurements easier. Several test samples were produced to find out the quality of the thermal contact between lithium and these metals. In publication [P3], the characterization of these samples is described, and the conclusion was definite: it was not possible to obtain a good thermal contact between lithium and silver or gold in any of the samples, apparently due to the formation of

Li-Ag and Li-Au alloys. Also other authors have suspected such Li-Au alloying [55]. However, excellent contact resistances were achieved with copper in every sample. Copper was then chosen for the encapsulating material, even though the magnetic moments of the copper isotopes are close to those of the lithium isotopes. This causes some problems in the NMR measurements, but, fortunately, the measurements are still possible.

The different thermal expansion coefficients of lithium and copper may cause some stress on the lithium lattice. On cooling from room temperature (where the samples are made) to below 1 K, the lithium lattice contracts about 0.5% more than the copper lattice. Since lithium is more pliant than copper, the lithium lattice will be deformed rather than the copper lattice. It is difficult to estimate, what kind of effects this stress could have on the sample as a whole; however, the low temperature structure of lithium is not very regular in any case, and this stress may be a minor source of irregularity compared to the inherent disorder present in the lattice.

The samples were fabricated in an argon filled glove box. They were cooled down in the two stage adiabatic nuclear demagnetization cryostat of the YKI group in the Low Temperature Laboratory at Helsinki University of Technology [64]. Its dilution unit is capable of maintaining a constant temperature of 3 - 8 mK, while the massive copper nuclear stage can be cooled down to around 100  $\mu$ K. In the nuclear ordering experiment, the sample itself acted as the second nuclear stage. It was polarized with a superconducting magnet which could in practice reach a field of 3 T.

## Chapter 3

# RESULTS

### 3.1 Search for Superconductivity

The samples for the experiment on superconductivity were two half spheroidal disks of lithium. Their preparation and the measurement setup has been described in publications [P6] and [P7]. An efficient magnetic shield made of two concentric high permeability cylinders with a superconducting layer of lead between them was protecting the sample from external magnetic fields. Its shielding factor was about 25000.

The samples were cooled down to  $(105 \pm 10)\mu\text{K}$  in several separate cool-downs. The magnetic field was estimated to be on the order of a few nano-Teslas. The static susceptibility of the sample was monitored; in the case of superconductivity, the emergence of the Meissner effect would have caused a clear decrease in the susceptibility. No such decrease was observed.

Instead, a small, unexpected susceptibility signal with a Curie-Weiss temperature dependence was observed. The signal was not of nuclear origin, and neither was it produced in the copper capsule [P7]. It may have arisen from magnetic impurities, the electronic system of lithium, or from the interfacial layer between lithium and copper. This peculiar susceptibility signal will be investigated in another sample in the future.

One cause for the suppression of superconductivity may be the paramagnetic impurities. The sample investigated in this work had less than 4 ppm of possible magnetic impurities (iron). If these atoms acted as magnetic

Kondo impurities, this concentration could cause a relatively large reduction of the critical temperature. The amount of this reduction is difficult to estimate, since values of the Kondo temperature for the dilute Li-Fe alloy are not available. The nuclear ordering experiment, however, gives evidence of a magnetically clean sample [P7]: the zero field spin lattice relaxation time agrees with the theoretical estimate [65]. If the sample were severely contaminated by Kondo impurities, this relaxation time could be considerably shortened [66,67]. Since the lithium used in both experiments came from the same batch, the iron impurities are not expected to have much importance in suppressing superconductivity in the bulk sample either.

## 3.2 Nuclear Ordering Experiment

The samples for the nuclear ordering experiment consisted of 24 thin ( $50\ \mu\text{m}$ ) spots of lithium pressed inside a copper foil of  $25\ \mu\text{m}$  thickness. The thermal path to the nuclear stage consisted of copper foils of different thicknesses. The preparation of the samples is described in publications [P5] and [P7].

The nuclear spin system of lithium was investigated by measuring the quasistatic (13 Hz) susceptibility, determining the spin temperature, and measuring the NMR spectra. A SQUID was used in the detection. The measurements were performed at nuclear polarizations up to 90 %. In addition to the standard features expected to be seen in low field NMR, the NMR spectra revealed an anomalous peak growing at low frequencies and high polarizations for low magnetic fields. Also, irreversible effects were observed in the static susceptibility at high polarizations. These facts provide evidence for the existence of magnetic ordering in the spin system, and the effects will be discussed in subsections 3.2.2 and 3.2.3. The main results of this experiment are presented in publication [P6], while publication [P7] gives a detailed description of the experimental procedures, data analysis and results. The NMR frequency spectra at high polarizations are described in publication [P5].

The nuclei were in general polarized by a superconducting magnet in fields up to 2 T at lattice temperatures 0.1 – 0.5 mK. The polarization times varied



from a few hours to a few days. The resulting maximal nuclear polarizations were nearly 100 %. After a suitable time of polarization (typically 10 – 48 hours), the nuclei were adiabatically demagnetized to zero field in 40 minutes. Then, the measurements could be started.

The nuclei of the encapsulating material, copper, have a magnetic moment of their own, and these nuclei were polarized along with the lithium nuclei. The polarized copper nuclei created a signal which was mixed with the signal from the lithium nuclei. A balancing loop in the pickup circuit was designed in order to considerably reduce the signal from the copper nuclei [P7], but some copper signal was still observed. At low frequencies, the copper signal was much smaller than that from lithium, and it could hardly be detected. At higher frequencies, however, the copper signal was enhanced in comparison to the lithium signal because of eddy current effects. The true signal from lithium could be obtained with some patience: the relaxation time of the copper nuclei was considerably shorter than that of the lithium nuclei. At zero field, the rate of relaxation of the copper nuclei was more than 100 times the corresponding rate for lithium [P7]. After waiting for about one hour after a demagnetization, the copper nuclei had no polarization left, while the lithium nuclei were still highly polarized. When doing high frequency measurements, some time was spent after a demagnetization before starting to collect data, just to suppress of the copper signal.

The polarization  $p$  of a spin system (i.e., its net magnetization) is related to entropy; the relationship between these quantities will be shown in Fig. 3.1. In the paramagnetic state,  $p$  can be obtained from the high field static susceptibility according to a simple law. Since  $p$  is an easily accessible parameter of the system, it is mostly used here to quantify the state of the system, rather than entropy or temperature. The polarization at small fields ( $B < B_L$ ) is not a well defined quantity, but one can measure the polarization at a high field and after an adiabatic change to the small field, one can use the measured  $p$  to describe the entropy at low fields as well.

The NMR measurements suffered from eddy current effects. At high frequencies, both copper and lithium screen the alternating magnetic fields. The copper capsule also distorts the signal generated by the lithium nuclei. These effects cause changes in the signals at frequencies above  $\sim 10$  kHz.

For example, the NMR frequency sweeps require a nontrivial background correction because of the eddy current effects [P5].

A system similar in some respects to the nuclear spin system of lithium is that of rhodium nuclear spins. It is the material used previously by the YKI group in the Low Temperature Laboratory for studies of nuclear magnetism [P1], [68–71]. In those experiments, the zeroth moments of the NMR spectra were used for determining the polarization. Numerical calculations revealed that the eddy current effects distorted the assumed linear relationship between  $p$  and the measured zeroth moments [P1]; the first and second moments were affected as well. Since such distortions could arise in the case of lithium as well, other means were used for the determination of polarization in the present experiments on lithium to avoid the need for such numerical corrections [P7].

### 3.2.1 Entropy and Static Susceptibility

The temperature of a nuclear spin system at ultralow temperatures cannot be measured by using any conventional thermometers, if the spin system is not in thermal equilibrium with the electronic system. This is the case for the lithium nuclear spins after a demagnetization in the present measurements. Instead, the temperature is obtained by using the second law of thermodynamics: applying a heat pulse and measuring the change in entropy caused by the pulse. This method has been described in detail, e.g., in Ref. [47]. We performed these kinds of measurements on the nuclear spin system of lithium at several different fields.

Figure 3.1 shows the reduced entropies and polarizations of the lithium spin system as a function of temperature for fields 0, 0.05, 0.2, 1, 1.5, and 2 mT. The data follow their second order high temperature expansions down to a certain temperature (open circles). Below this point, the entropy decreases rapidly until slowing down at the solid circles.

Figure 3.2 displays the static susceptibility as a function of polarization at some fields 0 - 60  $\mu$ T. At very low polarizations, the susceptibility follows the paramagnetic relation  $\chi'(0) = \mu_0 p M_{\text{sat}} / [B + \mu_0 (D_z - D_x) p M_{\text{sat}}]$  [P7]. Here  $M_{\text{sat}} = 0.93 \text{ mT} / \mu_0$  is the saturation magnetization of lithium,  $B$  is

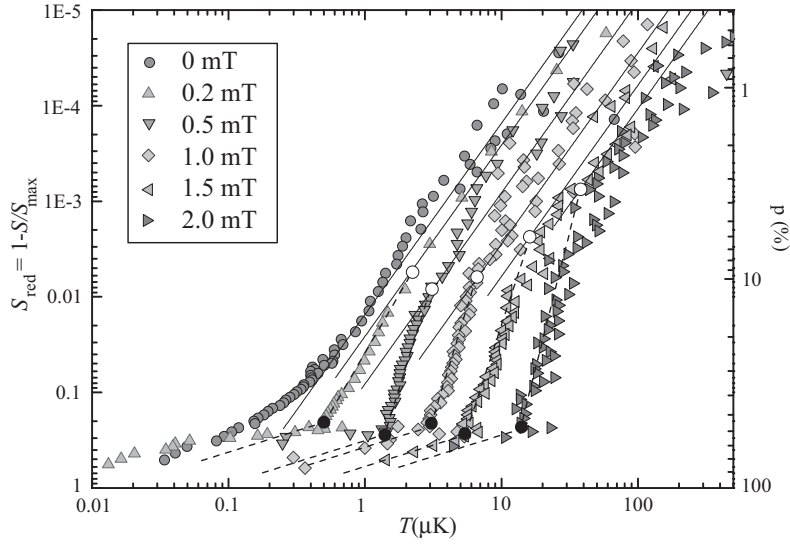


Figure 3.1: Reduced entropy  $S_{\text{Red}}$  and polarization  $p$  at fields 0, 0.2, 0.5, 1, 1.5 and 2 mT as a function of temperature.

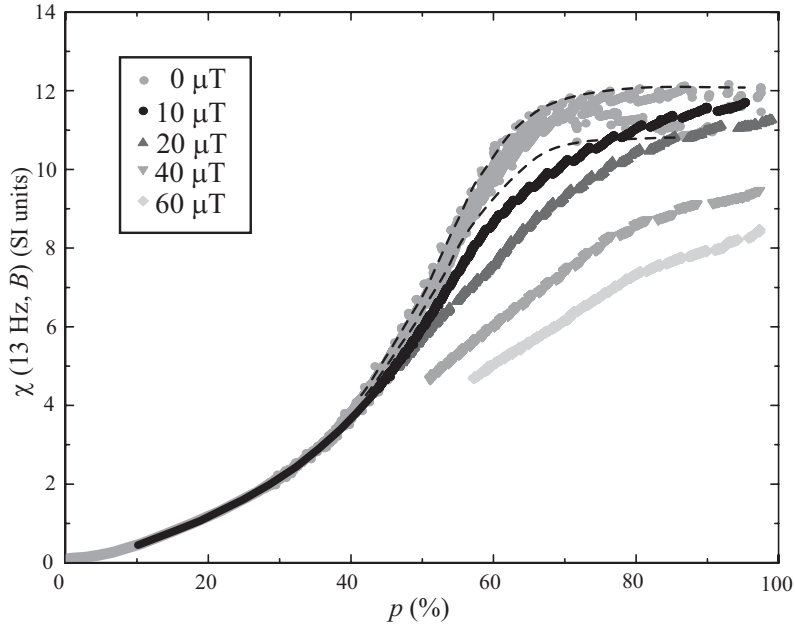


Figure 3.2: Static susceptibility at fields 0, 10, 20, 40, and 60  $\mu\text{T}$ . The dashed lines show the spread of possible paths of the zero field susceptibility.

the field, and  $D_z$  and  $D_x$  are the demagnetization factors in the directions of the excitation and static fields, respectively. The susceptibility data at high fields,  $B > 1$  mT, follow this relation up to the highest polarizations, but at lower fields, above a polarization of 5 – 20%, the susceptibility grows faster than this linear relationship [P7]. The zero field data saturate above 60 – 70 % to form a plateau at  $\chi(13 \text{ Hz}, 0) = 11 - 12$  (SI units). The low field data do not clearly indicate such a plateau, but weaker signs of saturation can be seen as well. The zero field susceptibility is not single valued above  $\sim 40\%$  polarization, but rather follows different routes, apparently depending on the preparation of the initial state and other experimental circumstances.

### 3.2.2 NMR Measurements

The NMR spectra were measured using two methods: by sweeping the frequency and keeping the magnetic field constant, or vice versa. It is interesting to investigate the frequency sweep spectra, since such data have often provided the first clue and final evidence for the existence of an ordered state [17]. On the other hand, the field sweep spectra are interesting as well, since their analysis is more straightforward, and they can be used in analyzing the interactions between the spins.

The frequency sweep NMR spectra were measured at fields 0 – 2.5 mT at polarizations up to 70%. Figure 3.3 shows some such spectra. Many standard features of low field NMR can be identified: when the field is much higher than the local field, the positions of the peaks at low polarizations are proportional to the field, while at low fields the positions are dictated by the internal local field. The spectra are narrowed with increasing polarization and shifted towards higher frequencies. The low frequency and low field region, however, revealed unexpected features: an anomalous peak appears at high nuclear polarizations. The ordinary paramagnetic resonance, originating from individual spin excitations, is expected at  $\sim 5$  kHz in zero field. At highest polarizations, however, the absorption maximum was observed as low as at 0.2 kHz.

Such an anomaly is obviously associated with the existence of an ordered state and arises from some kind of collective excitations, such as spin waves.

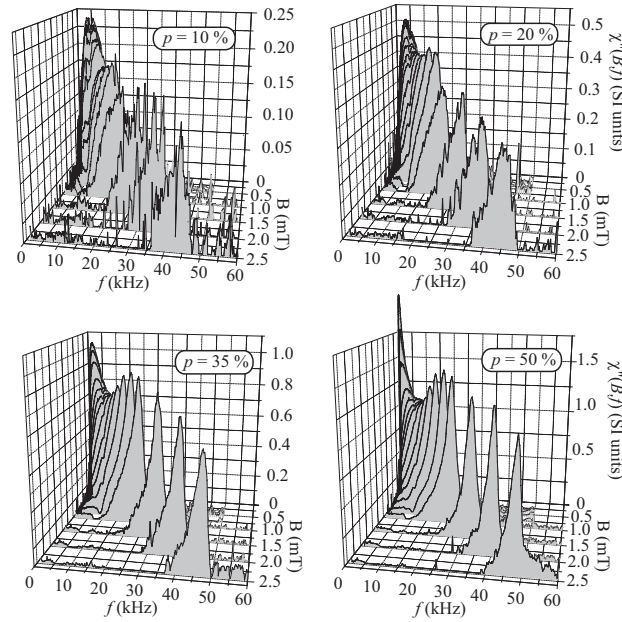


Figure 3.3: NMR absorption spectra for lithium at different nuclear spin polarizations  $p$  in fields of 0 – 2.5 mT.

To investigate its development, one can determine the first moments of the NMR spectra, i.e., their positions. Any extra intensity at a low frequency is reflected as a shift in the positions towards lower values. In order to emphasize the low frequency behavior, the moments were calculated on a logarithmic frequency axis. Figure 3.4 displays these moments as a function of polarization. At high fields ( $B > 0.25$  mT), the data have a positive slope. For lower fields, the slope is clearly negative, i.e., the low frequency anomaly forms. Its development is a gradual process: the zero field data (black boxes), for example, have a negative slope already at the lowest polarizations. One cannot then point out a single position, where the anomaly emerges.

Figure 3.5 shows the same data as a contour diagram of field and polarization. The figure is clearly divided into low- and high-field regions: the horizontal lines at high fields convert into downwards bending curves at small fields.

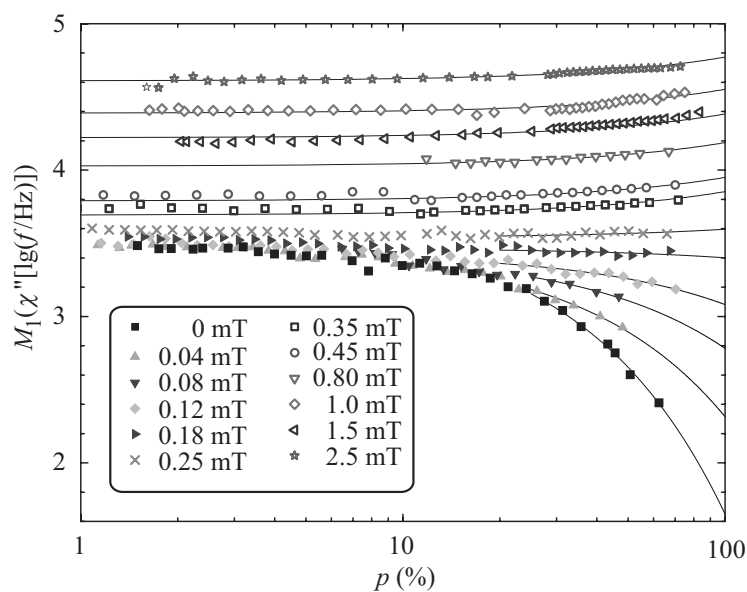


Figure 3.4: First moments (position of resonance) of the lithium NMR spectra as a function of nuclear spin polarization.

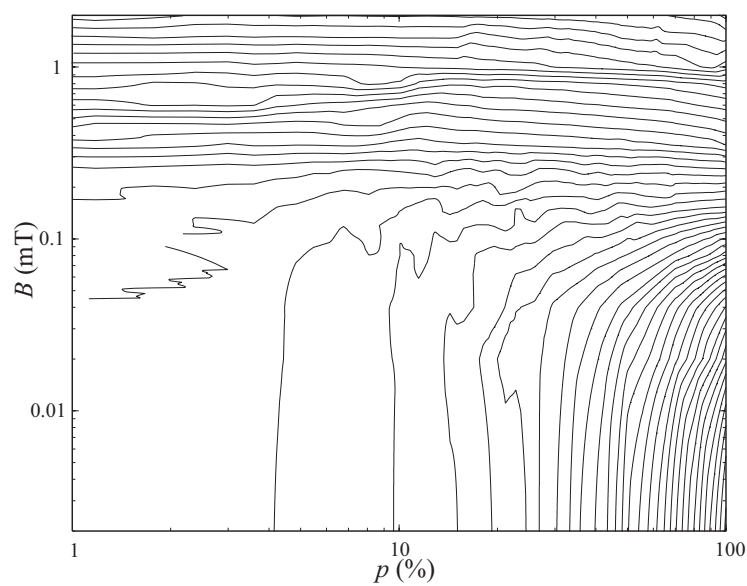


Figure 3.5: Contour diagram of the first moments of the NMR peaks calculated on a logarithmic frequency scale.

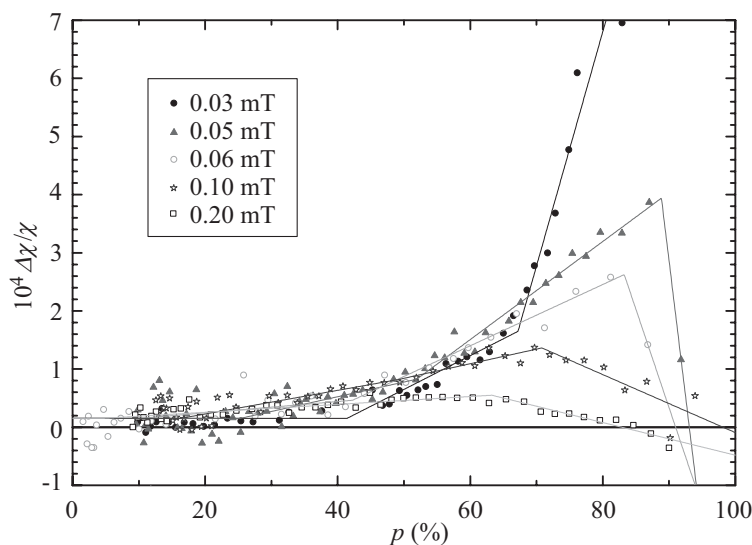


Figure 3.6: Change of susceptibility associated with the application of a transverse field at fields 0.03, 0.05, 0.06, 0.1, and 0.2 mT. Solid lines are fits to the data.

### 3.2.3 Irreversible Effects

In the paramagnetic state, a system of nuclear spins should follow all slow enough (and quick enough) changes of field adiabatically and reversibly, as discussed in section 2.1. However, when magnetically ordered structures are in question, irreversible behavior may occur. This kind of irreversible behavior was seen in the nuclear spin system of lithium at low magnetic fields and high polarizations: when the field was changed even very slightly, and then returned to its original value, the static susceptibility changed [P6],[P7]. Often, the susceptibility decreased, but in some cases, at the very highest polarizations, the susceptibility was observed to increase. The changes were, in general, at largest for the lowest fields, and decreased with increasing field. Above 0.25 mT, the signals were below resolution. To obtain quantitative information of these effects, a systematic set of measurements was conducted. A slowly changing transverse field was applied on the system at different fields  $B = 0.01 - 0.25$  mT, and the change of susceptibility  $\chi(13 \text{ Hz}, 0.05 \text{ mT})$  associated with each application of the transverse field was recorded.

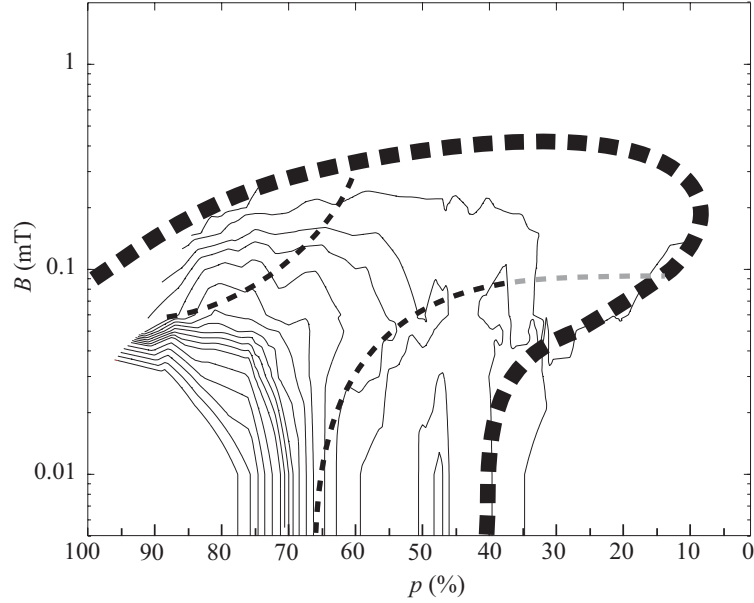


Figure 3.7: Contour diagram of the irreversible effects. The thick dashed lines separates the region where irreversible behavior is observed. The thin dashed lines indicates the change of slope for the irreversible effects (Fig. 3.6).

Figure 3.6 displays the change in susceptibility at several different fields.

All changes in the susceptibility vanish below a certain polarization (only a small offset remains). At the lowest external fields this occurs at  $p \sim 40\%$ . This polarization corresponds to a temperature of  $\sim 350$  nK, which can be deduced from the relationship between  $p$  and  $T$ , shown in Fig. 3.1. For higher polarizations, the data show piecewise linearity. The data at the lowest fields ( $B < 0.05$  mT) always display a positive slope; at higher fields  $B > 0.05$  mT one observes a point where the slope of the data turns negative. At the highest polarizations, the irreversible effects then disappear, or are seen as an increase of the susceptibility. In addition, the slope of the data at fields  $B < 0.1$  mT turns steeper at intermediate polarizations, like the data at 0.03 mT in Fig. 3.6 at around  $p \sim 65\%$ .

A contour diagram of the irreversibility data is shown in Fig. 3.7. The contours tend to stretch towards the upper right corner of the figure. The region where irreversible behavior was observed is surrounded by the thick



dashed line. The upper thin dashed line in the figure denotes the points where the slope turns negative at high polarizations and fields, while the other thin dashed line marks the first change of slope at small fields.

### 3.2.4 Phase Diagram

The results described above provide strong evidence for the existence of a magnetically ordered state in lithium. The irreversible behavior and the low frequency anomaly in the NMR spectra are unnatural features for a paramagnetic system, and nuclear magnetic order is necessarily present. A tentative phase diagram for this system is shown in Fig. 3.8. The construction of a phase diagram, however, is not simple: for example, the low frequency NMR anomaly appears in a gradual manner, and no critical points can be singled out. The onset of the irreversible effects is, however, abrupt, and the emergence of these effects can be taken as the onset of a long range ordered state. This region is surrounded by the thick dashed line in Fig. 3.8, and marked as O1. The thin dashed black lines denote the inflexion points where the irreversible effects change slope. Obviously, the nature of the irreversible effects changes there, but the character of these transitions remains unclear.

At lower polarizations, the low frequency anomaly appears, but one cannot trace its emergence to a single point. This may be due to the development of short range ordered regions, which then form the long range ordered state O1 when the irreversible effects appear. Hints on the termination of the paramagnetic state can, however, be obtained by looking at the susceptibility: it deviates from a simple paramagnetic relationship in the polarization range  $p \sim 10\%$  for fields  $B < 0.5$  mT. This deviation is marked by the grey dashed line with outline in Fig. 3.8, and it is taken as the onset of the precursory short range ordered state.

Some further lines may be added to the phase diagram as well, even though the data leading to them is less conclusive than for the lines discussed already. At high fields, the entropy deviates from its second order high temperature expansion abruptly at the open circles of Fig. 3.1. Eventually, a deviation from a high temperature expansion is expected at a low enough temperature for all systems. The data in Fig. 3.1, however, seems to change

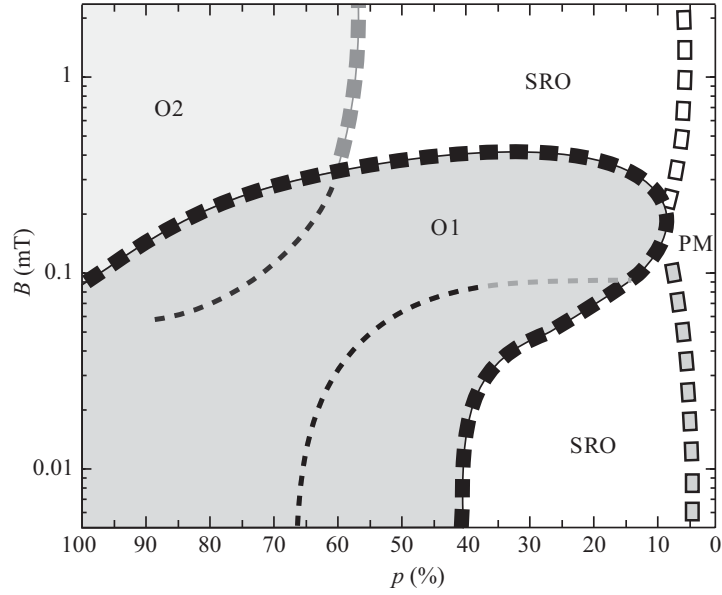


Figure 3.8: Tentative phase diagram for the magnetically ordered phases of nuclear spins in lithium.

slope abruptly at these points, especially at the highest fields; the deviation may then be associated with a real change in the system, instead of a failure of the expansion. For this reason, the dashed white line with outline in the upper right corner of Fig. 3.8 is marking these points.

The high polarization region where irreversible effects have either disappeared, or changed sign, obviously has a different nature than the region marked as O1. This region is designated as O2 to distinguish it from the strongly non-adiabatic region O1. To mark its onset, one can look at the entropy vs. temperature curves in Fig. 3.1: at the solid circles, the rapid decrease of entropy slows down. These points would, in fact, correspond to a maximum in the heat capacity of the system. It is suggested that these points mark the onset of the second ordered phase O2. The dashed white line with outline may be interpreted to denote the onset of a precursory short range ordered phase that later leads to the formation of the ordered phase O2.

## Chapter 4

# DISCUSSION AND CONCLUSIONS

In the research presented in this thesis, two possible new low temperature phase transitions in lithium metal were investigated. The electronic ground state of lithium is expected to become superconducting, but its experimental confirmation is still lacking. The first part of the work was aimed at searching for ambient pressure superconductivity in lithium at ultralow temperatures. The other part of the experiment concentrated on investigating the behavior of the nuclear spin system of lithium in the highly polarized state. These two effects were investigated in two separate sets of samples, each designed to suit the experimental requirements.

These experiments established a new upper limit for the transition temperature of ambient pressure superconductivity in lithium, as no superconductivity was observed at temperatures down to 0.1 mK and fields less than 10 nT. The new upper limit of 0.1 mK is more than an order of magnitude lower than the earlier upper limit of 4 mK. Several theoretical estimates predict superconductivity in the milli-Kelvin temperature regime, while simple arguments would indicate a transition already around 1 K. The persistent absence of superconductivity in this region becomes ever more puzzling with the new experimental result for the upper limit. Magnetic impurities may suppress the superconductivity, but spin-lattice relaxation time measurements indicate a magnetically clean sample.

An unexpected susceptibility signal was observed in the superconductivity sample. Its origin remained unclear, but it was confirmed that neither the copper capsule nor the nuclear spins in lithium did produce it [P7]. Another sample will be cooled down for further investigation of this signal.

The present work also shows that the lithium nuclei order magnetically at around 350 nK at zero external magnetic field. A suggestive phase diagram was constructed, based on the low frequency anomaly in the NMR spectra, the irreversible behavior at low fields and high polarizations, the susceptibility, and the measured entropy versus temperature curves. The non-adiabatic region clearly has a distinguishing, ordered character. The high polarization region where the irreversible effects disappear cannot be considered to belong to the same type of order, and it is separated as its own region. The low frequency NMR anomaly appears at lower polarizations than the irreversible effects, and it is suggested that its appearance is due to the development of short range order, which later develops into the non-adiabatic long range ordered phase. Less conclusive arguments can be presented about the character in the other regions of the phase diagram. It may be, that the deviation of the entropy from its second order high temperature expansion denotes the development of another short range ordered region, which later develops into the high-polarization, adiabatic ordered region.

The type of nuclear order was not resolved unambiguously. Often, the Weiss parameter is a good indicator of the ordering tendency of the system. Its sign is positive for a system with a ferromagnetic ordering tendency, while for an antiferromagnetic system, it is negative. Unfortunately, not even the sign of this parameter could be reliably estimated from the measured susceptibility [P7]. Some of the observed features, however, point to a ferromagnetic scenario, while no features contradicting this kind of order are seen. For example, the static susceptibility has the very large value of 11 – 12 (SI units) at high polarizations, which is typical for ferromagnets.

The element lithium is now added to the group of pure metallic elements exhibiting nuclear magnetic order. The two metals in this group most closely resembling lithium in regard to their nuclear spin-spin interactions are copper and silver. In them, the ordered structures are observed at much lower temperatures: at 58 nK in copper and at 0.56 nK in silver, compared to the

350 nK now measured in lithium. The exchange forces play an important role in the formation of the ordered states in these two materials, while in lithium, dipolar forces are expected to dominate over both the indirect and direct exchange interactions. Based on the examination of the Ruderman-Kittel formula for indirect exchange interactions, one would expect a positive and small exchange parameter  $R$ . However, the measured value for lithium was negative, and its magnitude was larger than expected, similar to that for copper [P7].

The high pressure superconductivity in lithium may open up new possibilities for studies of the interplay between superconductivity and nuclear magnetism. If the critical superconducting temperature in lithium can be realized in the temperature region where nuclear magnetism can be observed, the interplay phenomena will be interesting to study. The lowest observed critical temperature in the high pressure form is 5.47 K at a pressure of 20.3 GPa [60], but lower critical temperatures may yet be discovered.

The current setup for the superconductivity measurement would easily allow the experimentation on other reactive materials as well. The space taken up by the measurement setup is rather small, and one can cool down the superconductivity sample when doing another experiment. If one is able to ensure a good thermal contact with an encapsulating material, it would be easy to prepare similar samples of sodium or potassium, for example, to search for their superconductivity. They are considered less likely than lithium to become superconducting, but are still possible candidates for its occurrence.

The positions and widths of the NMR peaks can yield interesting information on the spin-spin interactions. For example, the direct exchange interaction will have no effect on the bosonic  $^6\text{Li}$  nuclei, while the more abundant isotope  $^7\text{Li}$ , being fermionic, will experience it. Analyzing the NMR peaks could then provide information on the relative strengths of the different interactions. Work on this problem will continue.



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