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Nuclear cooling and spin properties of rhodium down to picokelvin temperatures

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Abstract

The lowest temperatures ever measured have been produced by cascade adiabatic nuclear demagnetization of copper and rhodium. Ultimately, spontaneous antiferromagnetic ordering of rhodium nuclei is anticipated. High-sensitivity SQUID-NMR measurements at high nuclear polarization in low magnetic fields have been used to study the mutual interactions between the nuclear spins of rhodium in the metal. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nuclear demagnetization cooling has been developed to its extreme at the Low Temperature Laboratory of Helsinki University of Technology by operating two nuclear stages in cascade. In the long series of experiments with our collaborators, we have investigated the magnetic properties and spontaneous ordering of nuclear moments at the record-low temperatures first in copper, then in silver, and at present in rhodium [1].

The first nuclear stage, a massive block of copper, acts as a thermal reservoir at about 100 μK during initial polarization of the sample which is the second nuclear stage. The specimen is cooled further by adiabatically demagnetizing highly polarized spins at a rate which is fast in comparison to the spin-lattice relaxation time. Only the temperature of the nuclear spins is lowered, while the lattice and the conduction–electron system remains in thermal equilibrium with the first nuclear stage. This feature is very favorable when investigating a nuclear-spin system, since most of the heat leak deposited to the sample is absorbed by the first-stage refrigerant. The drawback is the single-shot nature of the cooling and the limited measuring time available, since the nuclear-spin system is unavoidably warming up towards thermal equilibrium with the lattice due to the spin-lattice relaxation. The time constant τ_1 may, however, be as long as 20 h at the lowest temperatures in silver and rhodium.

Studies of nuclear magnetism are motivated by the ideality of the nuclear-spin systems as models for testing general theories of magnetic ordering. The nuclear spins are perfectly localized, they are thermally isolated from the lattice at low temperatures, and the mutual interactions are well understood.

A wealth of information upon the behavior of a polarized nuclear-spin system at low magnetic fields can be gained by low frequency SQUID-NMR, which is the procedure used in our laboratory. In addition, more details of the magnetically ordered spin structures can be acquired by neutron diffraction. We have conducted such experiments on copper and silver, whose nuclear antiferromagnetic states have been investigated in collaboration with the Risø National Laboratory in Denmark and with the Hahn-Meitner-Institut in Germany [2–4]. It is unlikely that any neutron-diffraction experiment would be initiated on Rh, because relatively strong neutron absorption together with rather poor thermal conductivity would heat up the sample rapidly after exposure to the neutron beam.

2. Copper, silver, and rhodium

A short survey of the three extensively investigated metals, copper, silver, and rhodium, will be made here

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emphasizing the similarities and differences between the materials.

All three metals have a face-centered cubic (FCC) lattice, in which an antiferromagnetic coupling is geometrically frustrated. This is because the lattice consists of tetrahedra, so that an antiparallel arrangement of all spins is not possible. This is expected to reduce the ordering temperature and in some cases the long-range order may be suppressed altogether.

In metals the relevant interaction mechanisms are the dipolar coupling and the conduction-electron mediated indirect-exchange interaction. Their relative strength determines the ordered spin structures, and is described by the parameter $R = \sum_j J_{ij}/(\mu_0 \hbar^2 \gamma^2 \rho)$. The dipolar force alone would align spins ferromagnetically in an FCC lattice, but the indirect exchange is antiferromagnetic in all cases considered here. The competition of the interactions adds an interesting ingredient to the collective behavior.

Copper with $R = -0.42$ is just barely antiferromagnetic, which results in the surprisingly complicated phase diagram found experimentally. Silver, on the other hand, with $R = -2.5$, is a relatively good model for the nearest-neighbor Heisenberg antiferromagnet in an FCC lattice. Rhodium, with $R = -0.9$, falls in between the other two. However, it is somewhat more problematic to describe the exchange interactions in rhodium with just one parameter, because its conduction–electron system has a considerable non-s contribution making anisotropic exchange relevant as well [5].

Experiments on rhodium were chosen to succeed the work on the two noble metals because Rh is a superconductor with the lowest known transition temperature, $T_c = 325$ μK. Also the critical field is very low, $B_c = 5$ μT [6]. It should be possible to drive the system into a state either with magnetically ordered nuclei or with a superconducting conduction–electron system or with both at the same time by varying the magnetic field and, independently, the nuclear or the conduction–electron temperature. Because the electrons mediate in part the mutual interactions between the nuclear spins, their pairing is expected to alter the behavior of the spin system. Also the polarized nuclei in the ferromagnetic or paramagnetic state are known to affect the superconductivity [7,8].

Silver and rhodium have a nuclear spin $I = \frac{1}{2}$, for copper $I = \frac{3}{2}$. Ag and Rh are thus prominent quantum-spin systems, whereas by far simpler classical theories may be applied on Cu with some caution. No quadrupolar interaction needs to be considered in Ag or Rh due to $I = \frac{1}{2}$, and in Cu the quadrupolar terms are quenched by the cubic symmetry of the lattice. The magnetic moments of Ag and Rh are comparable, $\mu_{Ag} = -0.12\mu_N$ and $\mu_{Rh} = -0.088\mu_N$, but that of Cu is much larger, $\mu_{Cu} = 2.3\mu_N$. This does not make any fundamental difference, however, implying only that the relevant temperature scale is much higher for Cu and the experiments are therefore technically somewhat easier.

Natural copper and silver have two isotopes, whereas rhodium is pure ^{103}Rh. If two isotopes exist, the indirect exchange can be deduced experimentally by observing the interaction of the isotopic NMR lines at intermediate magnetic fields, when the lines are still distinct but begin to overlap with each other. The exchange term causes a so called suppression–enhancement effect of the line intensities [9]. At lower magnetic fields, relevant for spontaneous magnetic ordering, the isotopic lines merge into just one single peak, and the small difference of the magnetic moments becomes irrelevant. With a single isotope, the exchange term can be determined by observing a weak double-spin flip resonance, which is made possible by the dipolar interaction between the spins [9,10].

An important factor in all work on nuclear magnets is the presence of small amounts of electron-paramagnetic impurities. They can be harmful even in concentrations at the ppm level by speeding up the spin-lattice relaxation at low magnetic fields. The metallurgy and chemistry of various combinations of host and impurity elements differ considerably. Early work on copper suffered from enhanced relaxation in zero field, being in the worst case as much as about 100 times faster than in high fields (> 10 mT). The cure for this problem was a selective oxidation of the magnetic impurities near the melting temperature of the host in a low-pressure oxygen atmosphere [11]. Silver, on the other hand, is much easier in this respect, since most of the magnetic elements do not dissolve in silver [12]. Simple oxidation treatment has been sufficient to quench the enhanced relaxation through impurities altogether [13]. Rhodium is a more problematic host, since it is chemically very similar to some magnetic elements, so that the starting material is already usually of higher impurity. Also the heat treatment is more difficult due to the high melting temperature of Rh, 2239 K. The samples investigated so far had 70, 12, and finally, for our sample, three-fold increase of the zero-field relaxation rate due to the remaining magnetically active impurities [14].

The first NMR experiments on copper were performed on thin wires and foils, where eddy currents do not distort the NMR results [15,16]. Antiferromagnetic ordering was found below 60 nK [16]. Later, low-frequency susceptibility measurements on a single crystal revealed a richer phase diagram than had been anticipated [17]. The different ordered phases were then investigated by neutron diffraction in an isotopically enriched single crystal [2,3]. At the same time, NMR measurements on natural silver foils were performed in Helsinki. Silver ordered antiferromagnetically at 600 pK and ferromagnetically at -2 nK [18,19]. This experiment was complemented by a neutron-diffraction work on isotopically enriched ^{109}Ag [4]. At present, NMR measurements on

a rhodium single crystal are under way. The spin system has been cooled to a record-low temperature, 250 pK in zero field, but no sign of nuclear order has been observed.

3. SQUID-NMR technique

Here, we will describe some ideas implemented on the SQUID-NMR technique for our work on rhodium. The challenge in the case of nuclear magnets is to obtain a sufficient signal to noise ratio at low frequencies with a very small excitation field.

Modern DC-SQUIDs operate at a very low flux-noise level of $(2–5)\mu\phi_0/\sqrt{\text{Hz}}$ in a frequency range from about 1–10 kHz. We used a commercial Oxford DC-SQUID, whose flux to current conversion constant was about $0.25\,\mu\text{A}/\phi_0$ with an input inductance of 0.7 μH. We operated the SQUID in a very hostile environment, where a maximum field of 7.5 T was acting upon the pick-up loop. Therefore, the base-level noise of our SQUID system was somewhat higher than under ideal conditions, about $10\mu\phi_0/\sqrt{\text{Hz}}$.

The pick-up coil design has to meet many criteria, e.g., good filling ratio by the sample, gradiometric construction to cancel background disturbances, matched inductance to the SQUID input, small resistance for wide enough high-pass band, and if resistive, the resistance must be at the lowest possible temperature to reduce thermal noise currents.

Most of the earlier SQUID-NMR experiments on demagnetized spin systems were made using a resistive pick-up coil of copper or silver, in order to prevent large supercurrents from circulating in the SQUID-input loop due to changes in the magnetic field. One must use thick wire, of the order of 0.5 mm, in order to keep the high-pass frequency, $f_h = R/(2\pi L)$, below 100 Hz at the inductance level of about 1 μH. The pick-up coil has traditionally been wound as an axial astatic pair and it has usually been thermally anchored to the mixing-chamber shield at about 10 mK. The filling factor has been unavoidably rather poor, since the coil must not touch the sample.

We were able to eliminate some of the problems mentioned above by making the coil itself from a thin superconducting wire and by using a separate filtering resistor, which was anchored thermally to the copper nuclear stage (see Fig. 1). We used 50 μm multifilamentary wire in a Cu–Ni matrix. The coil could be placed very close to the sample, because a touch would not have been disasterous due to the low thermal conductivity of the wire. In addition, the coil was shaped to a planar second-order gradiometer adapted to the dimensions of the slab-shaped sample. This geometry eliminates uniform and gradient disturbances, and is optimal for measuring the magnetization of the sample penetrating through the central loops, since the return field of the magnetized sample is opposite just outside of the sample and thus adds to the total signal picked up by the oppositely wound side loops.

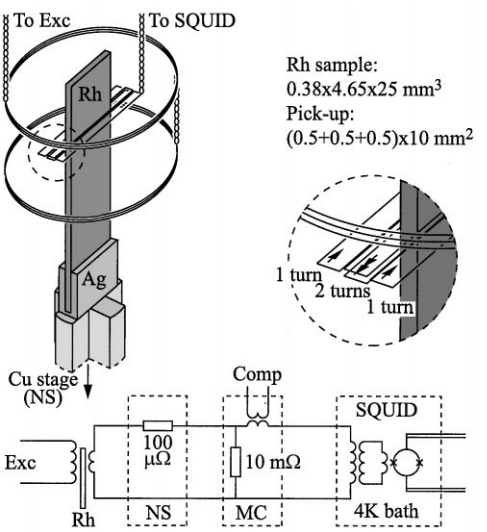

Fig. 1. The pick-up coil geometry in our experiment. The lower part depicts the coupling to the SQUID. The resistors form a band-pass filter from about 10 Hz to 1 kHz.

The inductance of our pick-up coil was estimated to be 0.12 μH. In addition, the twisted-pair wiring between the pick-up coil and the SQUID had an inductance of about 1 μH. Matching with the SQUID was not ideal, but for practical reasons the number of loops in the pick-up coil was not increased.

It was easy to adjust the separate filtering resistor to compromise between the optimal high-pass band and the thermal noise it would give rise to. A 100 μΩ resistance implies a high-pass cut off at about 10 Hz and, if it could be cooled down to 1 mK, the white thermal noise below this frequency would be about $10\mu\phi_0$ for an Oxford SQUID. In practice, the thermal noise power was proportional to T, as expected, down to about 10 mK, below which the noise level saturated to about 4 mK, probably due to insufficient thermal contact of the resistor to the nuclear stage. Nevertheless, the achieved noise level was less than $10\ \text{pA}/\sqrt{\text{Hz}}$ even below 10 Hz. The susceptibility measurements could be extended easily down to 3 Hz, which is essentially in the static limit on Rh, whose resonance frequency at zero field is about 50 Hz.

4. Low-frequency NMR on rhodium

All thermodynamic quantities of the nuclear-spin system, polarization, entropy, temperature, etc., can easily

be deduced from the NMR line at magnetic fields much higher than the internal fields representing the mutual interactions between the spins, i.e., in the ordinary paramagnetic state. The area of the absorption peak is proportional to the nuclear polarization, which can be used to calculate the other quantities of interest.

We made the polarization measurements on Rh at a frequency of 431 Hz, so that the resonance field was about 320 μT. The polarization scale was calibrated at relatively high temperatures between 0.3–1.5 mK, where the platinum-NMR thermometer on the copper-nuclear stage was still at very good thermal equilibrium with the sample. The highest polarization measured was $p = 0.86$.

The polarization of the spin system could be reversed by flipping a small magnetic field rapidly, i.e., faster than the spin–spin relaxation time, about 10 ms in Rh. Eddy-current screening in our single-crystal sample prevented the magnetic field from changing much faster than this but, nevertheless, we obtained $p = -0.49$ by turning a field of 400 μT in about 1 ms.

The nuclear spin temperature in zero magnetic field, where ultimately antiferromagnetic ordering is expected, could be determined by applying a heat pulse and measuring the resulting entropy change, as $T = \Delta Q/\Delta S$. First, the entropy was measured in 320 μT, next the field was swept adiabatically to zero, heat was applied by an ac-magnetic field close to the absorption–resonance frequency, then the field was swept back to 320 μT, and finally the entropy was measured again. The adiabaticity of the field sweeps was separately confirmed and the heating power could be calculated from the imaginary part of the nuclear susceptibility. The lowest temperature achieved in zero field was about 250 pK.

The onset of nuclear antiferromagnetic ordering was searched by measuring the static susceptibility after demagnetization to low magnetic fields. The measuring frequency was 3 Hz, where absorption is nearly zero and the signal is essentially dispersion in the static limit. Antiferromagnetic order is expected to lower the static susceptibility, whereby one would observe an initial increase, a maximum, and finally a paramagnetic decay of the signal during the warmup of the spin system. Such behavior was very clear in copper and silver [16,18], whereas in rhodium we see only a monotonous decay of the static susceptibility after the demagnetization (see Fig. 2). It was unexpected that the system did not show any signs of magnetic order, although the initial conditions should be well sufficient for that. This observation evidently calls for a more refined theoretical treatment based on the best knowledge of the interaction parameters in rhodium. As mentioned before, an exceptionally low T_N could be caused, in part, by geometrical frustration, competing interactions, and quantum fluctuations associated with spin $\frac{1}{2}$.

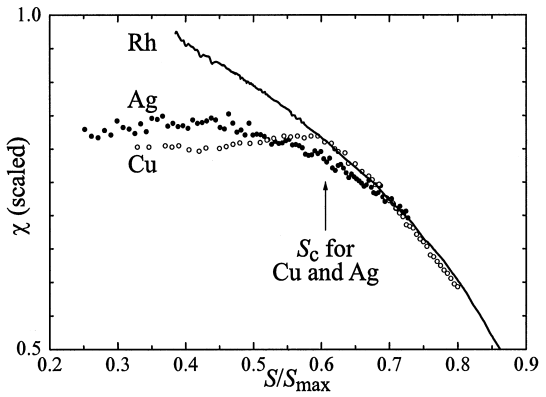

Fig. 2. Static nuclear susceptibility (scaled) of Cu, Ag, and Rh as a function of the nuclear entropy (data on Cu and Ag are from Ref. [20]). The antiferromagnetic order saturates the susceptibility at low entropies in Cu an Ag, whereas Rh shows no sign of nuclear order.

5. Superconductivity of rhodium

Very recently, we observed the superconducting transition in our rhodium sample. The found $T_c = 210$ μK and $B_c = 3.4$ μT are somewhat lower than reported for Rh earlier [6]. During the measurements on polarized nuclei, we did not reach the superconducting state due to strong supercooling. Above 150 μK the normal state supercools all the way down to zero magnetic field, and at the lowest electronic temperatures achieved, about 50 μK, the magnetic field must be below 150 nT in order to trigger the transition. This condition is extremely severe, since our sample is in the bore of a 7.5 T superconducting magnet, where the remanence fields are typically of the order of few mT. We use a high-permeability magnetic shield around the sample, reducing the stray fields by about a factor of 1000, but the remanence is still in the μT regime. If we can overcome this problem and are able to produce the superconducting state with polarized nuclei, very interesting results may await.

6. Double-spin flip resonance

To better understand why the nuclear-spin system of rhodium does not order even at a nuclear polarization $p = 0.86$, one needs to know the mutual interactions between the spins. For this purpose, we performed a study of the double-spin flip resonance, which arises from the dipolar coupling between the nuclei. The details of these measurements are described in another contribution to this conference [10]. It suffices to mention here that the dipolar term and the isotropic-exchange term can be determined separately by measuring the frequency shifts of the normal Larmor line and of the double-spin

mode. We obtained an exchange parameter $R = -0.9$, which will result in an antiferromagnetic order, and an effective magnetic moment $|\mu| = 0.10\mu_N$, of which the excess 15% is attributed to anisotropic indirect exchange mediated by the conduction electrons. Apparently, the concept of a pseudo-dipolar exchange discussed in Refs. [5,21] is not sufficient for describing the anisotropic exchange in Rh, since such short-range interaction with a dipolar form would not produce the observed additional shift of the Larmor resonance due to the cubic symmetry of the lattice.

7. Conclusions

In conclusion, the nuclear-spin system of rhodium is interesting in many respects, in particular if the interplay of nuclear magnetism with superconductivity can be studied. We have cooled the spin system down to the record-low temperature of 250 pK without observing spontaneous magnetic order. To help understand this, experimental information about the mutual interactions between the spins was deduced by examining a weak double-spin flip resonance. The superconducting state of rhodium was reached only recently, and up to this writing it has been observed with $p = 0$ only.

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