Relaxation of Polarized Nuclei in Superconducting Rhodium

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(Received 8 March 2000)

Nuclear spin lattice relaxation rates were measured in normal and superconducting (sc) rhodium with nuclear polarizations up to $p = 0.55$. This was sufficient to influence the sc state of Rh, whose T_c and B_c are exceptionally low. Because $B_c \ll B_{\mathrm{loc}}$ and the short-range spin-spin interaction is unchanged, the nuclear spin entropy was fully sustained across the sc transition. The relaxation in the sc state was slower at all temperatures without the coherence enhancement close to T_c. Nonzero nuclear polarization strongly reduced the difference between the relaxation rates in the sc and normal states.

PACS numbers: 74.25.Nf, 74.25.Ha, 76.60.Es

Most of the natural isotopes possess a nuclear spin, whose interaction with the surrounding electrons can be used as a sensitive indicator of the physical properties and structure of superconductors [1]. The early spin-lattice relaxation measurements by Hebel and Slichter in superconducting aluminum actually provided one of the first convincing results supporting the BCS theory of superconductivity developed at that time [2]. At present, similar concepts are applied mostly on studies of exotic superconductors, such as high-T_c materials [3], heavy-fermion compounds [4], alkali fullerides [5], and candidates for unconventional pairing states [6].

So far, nuclear-spin–electron interaction in superconductors has been investigated under circumstances where the nuclear magnetism does not influence the superconductivity. The opposite condition requires extremely low temperatures owing to the smallness of the nuclear magnetic moments. Only recently, the effects of nuclear magnetism on the superconducting phase in $AuIn_2$ and in Al were reported [7,8]. In those cases no relaxation measurements were made in the superconducting state.

In this paper we describe the spin-lattice relaxation measurements in rhodium with nuclei polarized to the extent that their magnetization and collective magnetic behavior *does* affect the superconductivity. Rhodium is a type-I superconductor with the lowest known T_c of pure elements, 325 μK, and a very low critical field $B_c = 4.9$ μT [9].

Our sample was a slab-shaped single crystal with dimensions $0.4 \times 5 \times 25$ mm^3. The nominal purity of the rhodium was 99.99% and the residual resistivity ratio was increased to 740 by careful annealing and selective oxidation of magnetic impurities [10].

The lattice temperatures in the microkelvin regime were produced by a copper nuclear demagnetization refrigerator [11]. The temperature was measured by a Pt pulsed NMR thermometer fixed to the copper nuclear stage. A firm thermal and mechanical connection to one end of the sample was made by diffusion welding. A possible difference between the sample temperature and the thermometer reading was checked by spin-lattice relaxation measurements in magnetic fields sufficiently high to assure ordinary Korringa behavior. We obtained $\kappa_{\mathrm{Rh}} = \tau_1 T = 8.0$ s K, which was obeyed to the lowest temperatures [12]. In the superconducting (sc) state, where the thermal conductivity decreases rapidly towards lower temperatures, it was more difficult to assure a uniform temperature throughout the sample. In low magnetic fields, however, the external heat leak to the sample was unmeasurably low ($\ll$0.1 nW), so that a thermal conductivity of $>1/10$ of the normal state value, satisfied when $T_c/T \leq 3$, was still sufficient for preventing a notable thermal gradient from developing.

The sample was located in the bore of a superconducting solenoid with a maximum field of 7.5 T for polarizing the Rh nuclei. However, we were limited to a maximum applied field of 2 T by the requirement of having submicrotesla control of the remanence field after the demagnetization. Typically, the flux trapped in the windings of a large superconducting magnet produces a field of the order of a few millitesla. Such residual field was screened out from the sample position by a cylindrical high-permeability shield [13]. The shielding factor was better than 1000 and the material saturated in an external field of about 10 mT. The demagnetization from 2 T was followed by an experimentally determined optimal degaussing cycle, which reduced the ambient field below 1 μT. This field was practically parallel to the solenoid and was compensated by a small copper coil inside the magnetic shield. It was found necessary to avoid superconducting wiring inside the shield, where trapped flux would have lead to an uncontrollable field distribution.

The primary measured quantity was the ac susceptibility at a frequency well below the zero field absorption maximum of Rh nuclei, which is at about 50 Hz [14]. We chose a measuring frequency of 3 Hz, at which the nuclear response is almost purely dispersive: $\chi(3\ \mathrm{Hz}) \approx \chi'(0)$ to a good approximation. Therefore, a relatively high excitation amplitude, 180 nT, could be used without speeding up the nuclear relaxation. The signal was coupled to a dc SQUID by a 4 + 4 turn astatic pair pick-up coil wound of 0.5 mm copper wire. The condition $\chi' = -1$ in the fully superconducting state was used to obtain the absolute scale of the susceptibility. This simple choice was in good

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agreement with the anticipated field and temperature dependencies of the paramagnetic nuclear contribution. The nuclear signal in the normal state will be denoted by χ_n.

The contribution of electronic paramagnetic impurities to the static susceptibility was unobservable within our resolution of $\sim 10^{-3}$. This was verified by varying the electronic temperature with zero nuclear polarization.

When determining the critical magnetic field of superconductivity we used a higher excitation frequency of 431 Hz to enable faster field sweeps and a lower excitation amplitude of 0.5 nT in order not to smear out the transitions. Both ac and dc magnetic fields were applied along the longest dimension of the sample.

The lowest lattice temperature achieved was $T \approx 60$ μK. On the other side, the superconducting transition could not be detected above 140 μK owing to strong supercooling of the normal state. The measured critical field $B_c(T)$ as a function of temperature followed the usual dependence $B_c(T)/B_c(0) = 1 - (T/T_c)^2$, extrapolating to $B_c(0) = 3.4$ μT and $T_c = 210$ μK. These are somewhat lower than the values given by Buchal *et al.,* $B_c(0) =$ 4.9 μT and $T_c = 325$ μK [9]. This difference will be discussed later in this paper. The supercooling field was 0.25 μT at the lowest temperature. The long thermal settling times of several hours reported by Buchal *et al.* were not observed.

For the spin-lattice relaxation measurements, the sample was first polarized in 2 T for 40–60 h ($2-3 \times \tau_1$) at $T_e =$ 70–140 μK. The subsequent adiabatic demagnetization was performed in about 0.5 h, i.e., rapidly in comparison with the spin-lattice relaxation time. At the lowest fields, the nuclear entropy was maintained by the mutual interactions of the spin system. The highest measured initial nuclear susceptibility in zero external field (≈ 1 μT) was $\chi_n = 0.47$. This corresponds to an initial nuclear polarization $p = 0.55$, as deduced from a separate calibration run [12], or to a nuclear spin temperature of $T_n \approx 1$ nK, using the results from an earlier experiment [14]. Over the investigated range, the susceptibility (at $B = 0$) is a practically linear function of the polarization (at $B \gg B_{\mathrm{loc}}$), $\chi_n \approx 0.9p$, so that the decay of either of them can be monitored to deduce the spin-lattice relaxation time τ_1.

The sample could be switched between the normal and superconducting states by minute changes of the magnetic field. Cycling through the transition did not result in any noticeable change in the normal state susceptibility, indicating that the nuclear entropy was conserved. This is understandable since in rhodium the critical field $B_c = 4.9$ μT is much lower than the internal local field, $B_{\mathrm{loc}} = 34$ μT [14], which is a measure of the spin-spin interactions. The condition $B_c \ll B_{\mathrm{loc}}$ must be fulfilled so that a sample with polarized nuclei can be switched between the normal and sc states adiabatically, as the leading nonconstant term of the entropy of the spin system is proportional to $(B^2 + B_{\mathrm{loc}}^2)$ and B is changed abruptly to zero at the sc transition. B_{loc} remains essentially constant, since the mutual nuclear spin interactions are unaffected by the sc transition within the coherence length $\xi \approx (\xi_0 l)^{1/2} \approx 0.1$ mm, where the dirty limit estimate was used for our sample with the BCS coherence length $\xi_0 \approx 1$ mm and the mean free path $l \approx 5$ μm [9].

Typical data are shown in Fig. 1. It can immediately be seen that the relaxation in the sc state was much slower than in the normal state. The data were analyzed by fitting each normal state segment by an exponential decay, $A_0 e^{-t/\tau_{1,n}}$, and interpolating the value for $\tau_{1,\mathrm{sc}}$.

During some runs, such as in Fig. 1, the sc signal level was only about -0.9 and some relaxation was observed also in the sc state. The relaxing component in the sc state was initially about 10% of the magnitude of the normal state signal, which suggests that $1/10$ of the sample always remained normal during these runs. We believe, though, that the remanence field throughout the specimen was well below the critical field of superconductivity and that the normal region was in the supercooled state. In any case, the nuclei of the 10% normal part obviously kept relaxing at the same rate during the complete run. To correct for this contribution, all superconducting segments of a run were fitted together to a single exponential decay, which was subtracted from the normal segments before further analysis. The data in the main frame in Fig. 1 have been corrected in this way.

The ratio of the relaxation times in the sc and normal states is plotted in Fig. 2 at different temperatures as a function of nuclear susceptibility. The sc relaxation time $\tau_{1,\mathrm{sc}}$ is the interpolated value and $\tau_{1,n}$ was taken as the average before and after the sc segment. Finite nuclear polarization reduced appreciably the difference between the relaxation rates. The effect is remarkable since a similar reduction due to noninteracting electronic paramagnetic impurities would be accompanied by a suppression of T_c

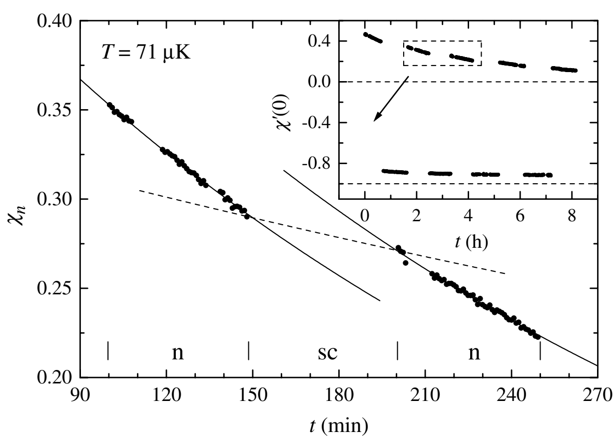

FIG. 1. Relaxation measurement at $T = 71$ μK and $p_i =$ 0.55. The inset shows all data, while the main frame displays an enlargement of one section. The solid lines are the fitted exponential decays, and the dashed line shows the interpolation for the relaxation in the superconducting state. The gaps in the data are caused by unlocking of the SQUID.

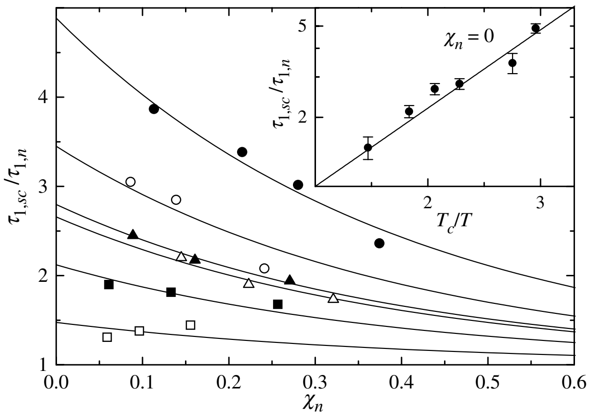

FIG. 2. The ratio of superconducting and normal state spin-lattice relaxation times as a function of nuclear susceptibility measured at different electronic temperatures (from the top: 71, 76, 92, 102, 114, and 143 μK, respectively). The solid lines show fits of the form $e^{-\chi_n/c}$ with the same decay constant $c = 0.4$ for all data sets. The inset shows the ratio of the relaxation times at the limit $\chi_n = 0$ as a function of T_c/T. The straight line is an exponential fit crossing the point (1, 1).

by as much as 60%–80% [1,15,16]. The nuclear paramagnetism *did* reduce B_c by 20%–30% but should not affect T_c; see below. However, it was not possible to measure T_c directly due to the supercooling.

For extracting the ratio $\tau_{1,\mathrm{sc}}/\tau_{1,n}$ at the limit of zero nuclear susceptibility, the data at each temperature in Fig. 2 were fitted by an exponential. One common decay constant was used. This fitting is, of course, arbitrary without reference to any physical model, but the outcome was not very sensitive to the particular choice of the fitting function. This uncertainty is included in the displayed error margins of the resulting data shown in the inset in Fig. 2.

Well below the critical temperature, the ratio $\tau_{1,\mathrm{sc}}/\tau_{1,n}$ for conventional superconductors behaves as e^{Δ/k_BT}, where Δ is the BCS energy gap [1,2]. Such a dependence describes our data well giving $\Delta/k_BT_c = 0.79$, which is, however, much less than the BCS value 1.76. Furthermore, the data in the inset in Fig. 2 show no indication of a Hebel-Slichter coherence peak, i.e., a local minimum in the τ_1 ratio just below the critical temperature due to a sharp peak in the electronic density of states at the superconducting gap edge. In other instances, several possible explanations have been proposed for such smearing out of the Hebel-Slichter peak; see, e.g., Refs. [1,17]. This can occur, for example, due to an anisotropic energy gap or non-s-wave pairing [6,18] or due to pair breaking by paramagnetic impurities [16].

It has been argued that very pure Rh is a good candidate for p-wave pairing [19]. This scenario is unlikely here, however, since the critical temperature of a p-wave superconductor should vary strongly as a function of the residual resistivity [20], but no such tendency was observed by Buchal *et al.,* who studied several Rh samples.

The temperature dependence in the inset in Fig. 2 resembles closely that of the theoretical results describing the influence of electronic paramagnetic impurities with concentrations x close to the critical value x_c, where they would suppress the host superconductivity altogether [1,16]. The best correspondence is obtained at $x/x_c \approx 0.8$, which would imply a true T_c of $\approx$0.5 mK for pure Rh [15,21,22]. The absolute suppression of T_c by a few hundred μK can be produced by an active paramagnetic impurity concentration of the order of 1 ppm. We cannot exclude such a possibility. In that case the gap value given above would be an underestimate, since the impurities tend to flatten the temperature dependence of $\tau_{1,\mathrm{sc}}/\tau_{1,n}$.

More insight into this question can be obtained by looking at the normal state relaxation in low magnetic fields, which is also sensitive to paramagnetic impurities due to direct or indirect impurity-nucleus interactions [23]. The polarization and field dependence of $\tau_{1,n}$ in Rh has been studied earlier [24]. In our case, at zero field ($\approx$1 μT), $1/\tau_{1,n}(T)$ had a temperature independent contribution, $1/\tau_{1,n}^i$, and a term directly proportional to temperature, T/κ_0 (Korringa behavior), viz., $1/\tau_{1,n}(T) = 1/\tau_{1,n}^i + T/\kappa_0 = 1/(29 \times 10^3\ \mathrm{s}) + T/(2.6\ \mathrm{s\,K})$. The zero-field Korringa value $\kappa_0 = 2.6\ \mathrm{s\,K} = \kappa/3.1$ practically fits the theoretically justifiable range $\kappa/\kappa_0 = 2$–3 [25]. The temperature independent term can be attributed to impurities. $\tau_{1,n}$ had a weak polarization dependence, decreasing by 10%–15% to $p = 0.5$. Within the investigated temperature range, it was not possible to resolve whether this change was due to $1/\tau_{1,n}^i$ or κ_0.

The impurity-nucleus coupling is expected to depend only weakly on the onset of superconductivity [1]. This is because both the dipolar and RKKY contributions are essentially unmodified within the coherence length [26]. However, this contradicts our observations, since the longest relaxation times in the sc state $\tau_{1,\mathrm{sc}} \approx 4\tau_{1,n} \approx 64 \times 10^3$ s were much longer than $\tau_{1,n}^i = 29 \times 10^3$ s. The validity of the preceeding simple argumentation has been discussed in [27], where the impurity contribution was found to be affected by the sc state.

The most interesting question to address is the observed strong nuclear polarization dependence of $\tau_{1,\mathrm{sc}}$. There is no obvious way to explain this by the presence of magnetic impurities. Since $\tau_{1,n}$ also showed a weak p dependence, it is natural to check if this contribution could simply be amplified in the sc state by the inhibition of all the other relaxation mechanisms. At $T_c/T = 3$, the proper order of magnitude of this effect would be obtained by assuming that the Korringa component had practically died out, the impurity contribution was reduced by a factor of about 3, but the polarization enhancement of $1/\tau_{1,n}$ still operated at its full strength. Such a set of assumptions does not seem appropriate and a more delicate theoretical treatment is obviously needed.

An idea of how much the finite nuclear magnetization disturbed the superconducting state macroscopically

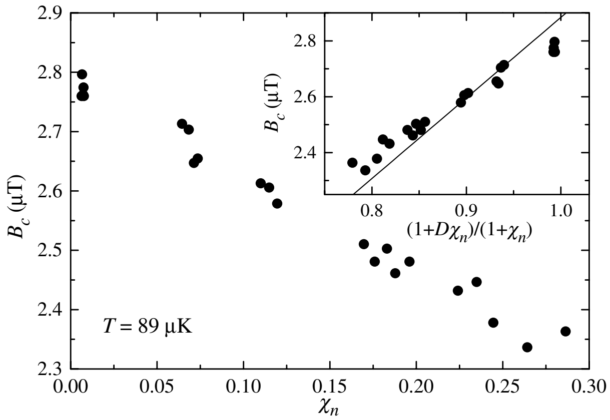

FIG. 3. Critical field vs nuclear susceptibility at 89 μK. The axes in the inset were chosen so that the expected behavior is linear and intersects the origin (the solid line).

can be obtained by measuring B_c as a function of χ_n at a constant temperature. Such data are shown in Fig. 3. The nuclear magnetization enhances the magnetic field inside the sample and a basic treatment leads to the relation $B_c(\chi_n) = B_c(\chi_n = 0)(1 + D\chi_n)/(1 + \chi_n)$. The estimated demagnetization factor for our sample was $D = 0.01$ along the longest dimension. The expected dependence was reproduced fairly well; see the inset in Fig. 3. It is evident that this effect is too small to explain the observed χ_n dependence of the spin-lattice relaxation.

In conclusion, we investigated the spin-lattice relaxation in Rh both in the normal and the superconducting state. We observed no change in nuclear entropy upon sweeping through the sc phase transition, confirming that the short-range spin-spin interactions are unaffected by the transition. The relaxation in the sc state was slower at all temperatures, and no indication for the Hebel-Slichter coherence enhancement close to T_c was observed. In addition, we found an unexpectedly strong dependence of the sc relaxation time on the nuclear polarization. This remains an open issue. The dependence cannot be explained simply by considering the nuclei as magnetic scattering centers or by the presence of electronic impurities. Neither a change in the mutual spin interactions in the sc state nor a change in the sc state itself due to the magnetic behavior of the nuclei consistently explain all our observations.

As a further development of the current experiment it would be extremely interesting to study similar effects at *negative* nuclear polarization, the possibility of which has been demonstrated experimentally [14,28]. Unfortunately, the required flip of the field to create $p < 0$ could not be produced by the present resistive coil system.

We wish to acknowledge useful discussions with M. Paalanen and P. Hedegård. This work was supported by the ULTI II grant of the European Union.

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