Slow order-parameter fluctuations in superconducting Pb and Ag/Nb films observed using β -detected nuclear magnetic resonance

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We report β -NMR investigations of polarized ^8Li implanted in thin Pb and Ag/Nb films. At the critical superconducting temperature, we observe a singular peak in the spin relaxation rate in small longitudinal magnetic fields, which is attributed to unexpected slow fluctuations in the superconducting order parameter. The peak is several orders of magnitude larger than the prediction based on the enhancement of the dynamic electron spin susceptibility by superconducting fluctuations. The observed peak in $\frac{1}{T_1}$ is rapidly suppressed in a small magnetic field, indicating that it is due to remarkably slow diamagnetic fluctuations which are undetectable with conventional NMR.

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Near the superconducting critical temperature T_c , thermodynamic fluctuations of the order parameter occur, leading to the appearance of pairing correlations with critically increasing lifetime on approaching T_c from above.¹ These fluctuations are easier to see above T_c in the form of excess conductivity (paraconductivity), tunnel conductivity, enhanced diamagnetism, and in many other electronic properties.² The importance of fluctuations increases in systems of lower dimensionality (on the scale of the Ginzburg-Landau coherence length) such as thin films, wires, and small particles. Unconventional superconductors such as cuprates, with their quasi-two-dimensional (2D) electronic structure, low superfluid density, and short coherence length, are even more susceptible to fluctuations.³ In these systems phase fluctuations are thought to be largely responsible for the pseudogap regime and may be connected to the presence of a quantum critical point.^{4,5}

NMR can give detailed information on the normal and superconducting electronic state and has played a pivotal role in elucidating the nature of low- and high- T_c superconductivity.⁶ In low- T_c superconductors, the observation of the Hebel-Slichter peak was an unambiguous confirmation of BCS theory. In high- T_c superconductors (HTSs) NMR measurements of the local spin susceptibility revealed the unusual pseudogap state.⁷ The nuclear spin relaxes due to time-dependent fluctuations of the local magnetic field, whose transverse components induce transitions between the nuclear spin levels. In a metal the most important contribution is from spin fluctuations of the conduction electrons which are coupled to the nuclear spins through the magnetic hyperfine interaction. This nuclear spin relaxation rate can be expressed in terms of the dynamic electron spin susceptibility χ'' and gives rise in the normal state of a noninteracting Fermi gas to the well known Korringa law $\frac{1}{T_1 T} = \text{const}$ of the longitudinal spin relaxation rate $\frac{1}{T_1}$. The effect of superconducting fluctuations on χ'' are generally calculated using diagrammatic techniques.¹ In an

s -wave superconductor without strong pair breaking effects one expects a singular peak in $\frac{1}{T_1}$ at T_c in a very narrow temperature range $\epsilon = \frac{T-T_c}{T_c}$. The singular behavior of the spin-lattice relaxation at T_c , either in conventional or in unconventional superconductors, needs to be detected. In conventional superconductors the observation of the effect of superconducting fluctuations on NMR spectra and relaxation is believed to be difficult due to the smallness of the effect on the order of the Ginzburg-Levanjuk number G_i ($\approx \frac{k_B T_c}{E_F}$).⁸ For d -wave pairing the dominant contribution, the so-called Maki-Thomson term, is suppressed.^{9,10} In HTSs, comparison with theory is further complicated by the delicate interplay of contributions with opposite sign and magnetic field dependence. Moreover, the presence of antiferromagnetic fluctuations and the unusual normal state background make it difficult to extract the fluctuation contributions, leading to controversial interpretations of the experimental data, which instead of a critical enhancement show a suppression of $\frac{1}{T_1}$ at T_c .^{11,12}

In this Rapid Communication, we report low frequency β -NMR measurements in thin films [single and normal-superconductor (NS) bilayers] of two well known low- T_c superconductors. We measured rf resonance spectra and the longitudinal spin relaxation rate $\frac{1}{T_1}$ of ^8Li implanted in a thin Pb film and in the Ag layer of Ag/Nb bilayers, where superconductivity is induced by the proximity effect. In both films we observe a large diamagnetic shift in the resonance frequency below T_c , as expected from Meissner screening of the applied field. However, there is also a well defined peak in $\frac{1}{T_1}$ in a narrow temperature range near the critical temperature T_c , which is clearly due to fluctuations of the superconducting order parameter. The fluctuations are much slower, and the region around T_c where they are observed is larger than predicted from the current theory of Gaussian fluctuations.¹ Furthermore, there is a strong field dependence.

This experiment shows that there exist unexpected slow fluctuations at the critical temperature which we attribute to diamagnetic fluctuations.

The β -NMR experiment was carried out at TRIUMF using a 28 keV beam of $^8\text{Li}^+$ produced at the isotope separator and accelerator facility (ISAC). A large nuclear polarization ($\sim 70\%$) is generated in flight using a collinear optical pumping method.¹³ The hyperpolarized beam had a beam spot of about 3 mm diam and a typical rate of 10^6 ^8Li /s. The samples were mounted on a cold finger cryostat contained in the UHV chamber of the low field β -NMR spectrometer. The spin polarization was perpendicular to the beam direction but parallel to both the sample surface and a small external magnetic field B_0 . In β -NMR the nuclear spin polarization is monitored through the anisotropic β decay of ^8Li ($S = 2$, gyromagnetic ratio 6.3015 MHz/T, electric quadrupole moment $Q = +31.4$ mb, mean lifetime $\tau = 1.2$ s). The beam energy can be chosen between 1 and 28 keV.¹³

The samples were rf sputtered onto epitaxially polished quartz and sapphire substrates. Resistivity measurements give for Pb (260 nm) $T_c = 7.12$ K, $\Delta T_c \lesssim 8$ mK with mean free path $\ell \approx 48$ nm which is less than the BCS coherence length $< \xi_0 \approx 83$ nm. For Ag(29 nm)/Nb(252 nm), the critical temperature of the entire bilayer $T_c = 9.15$ K, $\Delta T_c \lesssim 40$ mK, $\ell_{\text{Ag}} \approx 40$ nm, and $\ell_{\text{Nb}} \approx 250$ nm.

Figure 1 shows resonance curves of $^8\text{Li}^+$ implanted at 5 keV in the Pb sample with a magnetic field of 1 mT applied parallel to the surface of the film. At this energy the implantation range of $^8\text{Li}^+$ extends to ~ 100 nm with a mean implantation depth and straggle of 34 and 19 nm, respectively. The temperature dependence of the resonance frequency below T_c (the inset of Fig. 1) is an unambiguous signature of the Meissner state. Also the additional line broadening observed below T_c reflects the field distribution probed by ^8Li averaging the Meissner field profile over the stopping distribution. The frequency shift fits well to a solution of the London equation taking into account the implantation profile, yielding an effective pene-

FIG. 1. (Color online) β -NMR resonance spectrum above and below T_c for ^8Li stopped in the Pb film. The inset shows the temperature dependence of the resonance frequency and resistivity. The curve is a fit to the London model.

tration depth $\lambda_{\text{eff}}(T) = \frac{\lambda_L(0)}{\sqrt{1 - (T/T_c)^4}} \sqrt{1 + \frac{\xi_0}{\ell}}$ with $\lambda_{\text{eff}}(0) = 62.2 \pm 0.3$ nm, in good agreement with low-energy muon spin rotation (LE- μSR) measurements on this sample,¹⁴ and literature values.¹⁵ Similarly, a sharp decrease of the resonance frequency in the Ag/Nb film was observed below T_c at 4 keV. At this energy, the signal originates entirely from the Ag overlayer of the Ag/Nb bilayer (mean implantation depth and straggle 17 and 10 nm, respectively). Knight shift β -NMR measurements in elemental metals such as Ag and Au indicate that below ~ 100 K the Li is static and occupies the interstitial octahedral site.^{13,16,17} Since Pb has the same fcc structure, it is reasonable to assume that Li is mainly in the octahedral interstitial site over the temperature range of our experiment.

Spin relaxation measurements were carried out with a pulsed beam of length 1–4 s with the rf field off. The inset of Fig. 2(c) shows the time evolution of the asymmetry signal of the ^8Li stopped in Ag. The decay of the signal is a direct measure of $\frac{1}{T_1}$. Fitting the time-dependent asymmetry during and after the pulse, by taking into account the constant implantation rate during the pulse and the exponential relaxation, we obtain $\frac{1}{T_1}$.

Figure 2 shows the temperature dependence of $\frac{1}{T_1}$ for both samples. Note in particular the sharp increase at T_c within $\lesssim 50$ mK, followed by a smooth decrease below T_c . Such a peak at T_c is unambiguous evidence for critical slowing down of the fluctuations in the superconducting order parameter. Before discussing this in more detail, it is important to first understand the data in the normal state. Above T_c the relaxation rate increases linearly with temperature, as expected from Korringa relaxation [the insets of Figs. 2(b) and 2(d)]. Extensive β -NMR relaxation studies in pure elemental metals such as Ag, Au, and Nb have shown that in the normal state at sufficiently high field T_1 is dominated by the magnetic field-independent, temperature-linear Korringa relaxation due to the direct hyperfine coupling between the ^8Li and the conduction electrons. The measured slopes, $0.0028(1) (\text{sK})^{-1}$ for Ag and $0.0044 (\text{sK})^{-1}$ for Pb, are close to those found in other elemental metals.¹⁷

Spin relaxation for ^8Li in Pb at low magnetic fields involves also cross relaxation between the host Pb spins and ^8Li . In addition to the direct Korringa relaxation there is also an indirect contribution from the relaxation of the host ^{207}Pb spins ($S = 1/2$ and 22% abundant) which are coupled to the ^8Li through a magnetic dipolar interaction. The interaction produces a significant cross relaxation between ^8Li and ^{207}Pb nuclear spins in low field. As shown in Ref. 18, this process characteristically gives rise to a strong Lorentzian field-dependent $\frac{1}{T_1}$ evident in the normal state in Figs. 2(a) and 2(b). Consequently, the reduction of the local field in the superconducting state leads to a temperature-dependent enhancement of $\frac{1}{T_1}$ over the normal state values starting at T_c and extending to lower temperatures. We have calculated this contribution fitting the field dependence of the relaxation rate above T_c to determine magnitude ($\Delta B = 0.01$ mT) and fluctuation time ($\tau_c = 3 \times 10^{-5}$ s) of the ^{207}Pb dipolar fields. Below T_c , we take into account the reduction of the local field acting on the ^8Li nuclei due to the Meissner effect with penetration depth $\lambda_{\text{eff}}(T)$, as determined above from the

FIG. 2. (Color online) Spin lattice relaxation rate $\frac{1}{T_1}$ vs temperature from single exponential fits to relaxation data. (a) and (b): Pb film (260 nm) ^8Li implantation energy 5 keV. The solid curves show the contribution from the host nuclear dipole dynamics in Pb. (c) and (d): Ag(29 nm)/Nb(252 nm) bilayer ^8Li implantation energy 4 keV. Inset of (c): Typical polarization spectrum; insets of (b) and (d): extended temperature range showing the Korringa contribution.

resonance data. The solid curves in Figs. 2(a) and 2(b) show the results of the calculation including a small Hebel-Slichter contribution, due to opening of the gap and coherence effects.¹⁹ It is clear that the remaining singular peak observed at T_c cannot be due to the Hebel-Slichter effect because the latter appears as a much broader field-independent peak at $T \sim 0.85T_c$. Furthermore, the Hebel-Slichter peak represents barely a factor of 2 enhancement over the normal state Korringa value of 0.0313 s^{-1} for Pb (see also below). In contrast, the peak we observe occurs exactly at T_c , as shown in Fig. 2, and is easily suppressed in a few mT external field. This is clear evidence that the peak is due to critical fluctuations in the superconducting order parameter. Sample inhomogeneities cannot produce the observed peak. In principle, time varying fluctuations of the local field related to a temperature instability ΔT ($\lesssim 5 \text{ mK rms}$) could produce a rounded step (but not a peak) at T_c . Also, the resulting ΔB ($\lesssim 10^{-3} \text{ mT}$) from temperature fluctuations is much too small to account for the observed relaxation. Moreover, the observed peaks are much wider than the transition width from resistivity (see the inset of Fig. 1).

In terms of the mean field Ginzburg-Landau order parameter Ψ , the superconducting fluctuations are related to $\langle |\Psi|^2 \rangle \neq 0$ although $\langle \Psi \rangle = 0$. This state of local phase coherence can be represented by the presence of superconducting droplets of size $\xi(T) = 0.85\sqrt{\xi_0\ell}\sqrt{\frac{1}{\epsilon}}$ and lifetime of the order of $\tau_{\text{GL}}(T) = \frac{\pi\hbar}{8k_B T_c \epsilon}$.¹ The nonequilibrium pair density $n \propto \langle |\Psi|^2 \rangle$ leads to fluctuation induced diamagnetic susceptibility and paraconductivity. The effect of superconducting fluctuations is generally calculated in the Gaussian regime by the diagrammatic technique in a microscopic theory involving the hyperfine contact coupling. The acceleration of Cooper pairs of limited lifetime contributes directly to the conductivity with the so-called Aslamasov-Larkin (AL) term.²⁰ An additional indirect contribution [Maki-Thomson term, MT (Ref. 2)]

reflects the conductivity increase induced by fluctuations decaying into quasiparticle pairs of nearly opposite momenta that maintain their correlation and continue to be accelerated as though they were paired.¹

For NMR observables, the interplay and importance of these contributions is different than in the case of conductivity. Due to spin-singlet pairing, the direct Cooper pair AL contribution to the (static and dynamic) spin susceptibility is absent and the anomalous MT term is the only positive and dominating contribution to the relaxation rate. A physical picture of the MT relaxation process is the following. When the electron is scattered by the nucleus changing its spin orientation and momentum to the opposite value, it can pass again the previous trajectory moving in the opposite direction. Due to the retarded character of the pairing interaction, a Cooper pair can form and this turns out to be a spin relaxation mechanism.

However, the phenomenon reported here cannot be explained by the MT enhancement of the local spin susceptibility because (i) the magnitude of the peak with respect to the Korringa relaxation is much larger, (ii) it appears in a wider temperature range, and (iii) because of its strong field dependence. In the 2D limit, which is well fulfilled in the temperature interval where we observe the jump [$\xi(\epsilon) \gtrsim d$ for $\epsilon \lesssim 3 \times 10^{-2}$] and dirty case, the MT enhancement of the NMR relaxation rate over the normal Korringa value can be analytically expressed for static ($\omega \rightarrow 0$) long wavelength fluctuations to be^{10,21}

$$\frac{\frac{1}{T_1}^{\text{MT}}}{\frac{1}{T_1}^n} = \frac{\pi\hbar}{8E_F\tau\epsilon - \gamma_\phi} \ln\left(\frac{\epsilon}{\gamma_\phi}\right), \quad (1)$$

which diverges logarithmically for $\epsilon \rightarrow 0$.

The size of this contribution depends on pair breaking processes expressed by the parameter γ_ϕ . Taking for a

conservative estimate for Pb only the thermal phonon contribution $\gamma_\Phi \approx \frac{\pi^2}{4} \frac{(T_c)^2}{\theta_D^2} = 1.57 \times 10^{-2}$, and $\epsilon = 7 \times 10^{-4}$ (which corresponds to the temperature stability of our experiment), we obtain an estimate for the jump in the relaxation rate at T_c which is more than two orders of magnitude smaller than observed. For the Ag/Nb film the calculation underestimates the peak by three orders of magnitude. The discrepancy is larger if one considers that additional effects not included in Eq. (1), such as strong coupling ($\lambda_{e-ph}^{\text{Pb}} = 1.547$) (Ref. 22) and some degree of three dimensionality,¹⁰ further reduce the magnitude of the MT term. Also the existing theory does not account for the strong field dependence of the peak which is suppressed by a few mT. Such field dependence is not expected for the MT processes of the dynamic spin susceptibility.^{23,24}

The experimental results, together with the above estimates, suggest that other mechanisms that add to the direct contact interaction must be involved. There are two plausible resolutions to this puzzle. Since the order parameter is complex, phase fluctuations can generate fluctuating supercurrents and magnetic fields relaxing the probe spin even in cases where the contact term is small or zero.²⁵ However, there is no reason to expect this would be strongly field dependent as observed. Growth and decay of superconducting correlations are reflected in the additional diamagnetic susceptibility observed above T_c .^{2,26} Associated with these diamagnetic fluctuations there are local fluctuating fields which may act as the source of ^8Li spin relaxation. The sensitivity to small fields we observe supports the latter explanation. In Pb the jump in spin-lattice relaxation is strongly suppressed at $\simeq 3$ mT, the same field where the diamagnetic response, which is dominated by very-low-energy, long wavelength modes, is significantly reduced.²⁷ The suppression of $\frac{1}{T_1}$ as a function of

magnetic field indicates that there is a decrease in the size (and corresponding correlation time) of the fluctuating domains with increasing applied field. Consistent with this picture is also the observation that in a thin Pb film ($d = 45$ nm $< \xi_0$ and λ_{eff}), which displays weaker shielding supercurrents and Meissner effect and hence smaller amplitudes of supercurrents and diamagnetic fluctuations than the 260 nm film, the $\frac{1}{T_1}$ enhancement is strongly suppressed.

Summarizing, we have observed a pronounced increase of the longitudinal spin-lattice relaxation in a narrow region close to the critical temperature of low- T_c thin superconducting films. The peak is attributed to unexpected low frequency ($\sim$ kHz) critical fluctuations. The strong field dependence explains why these have not been detected with conventional NMR. Both the magnitude and the field dependence are inconsistent with the existing theory of NMR relaxation near T_c from the Fermi contact interaction. Our observation also demonstrates the sensitivity of β -NMR to low frequency dynamics in superconductors. In contrast to conventional NMR, depth-dependent β -NMR can be carried out at very low frequencies and in thin films or structures. The implantation range of the polarized nuclei makes them suitable to application in low dimensional systems where fluctuation effects are enhanced, e.g., in heterostructures containing insulating and superconducting layers, where they can be stopped in the insulating environment to act as a sensitive probe of fluctuations in the nearby superconducting layer, in high- T_c superconductors, and mesoscopic devices.⁵

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