Zeeman Perturbed $^{63}$Cu Nuclear Quadrupole Resonance Study of the Vortex State of YBa$_2$Cu$_3$O$_{7-\delta}$

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We report a $^{63}$Cu nuclear quadrupole resonance (NQR) study of the vortex state for an aligned polycrystalline sample of a slightly overdoped high-$T_c$ superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ ($T_c \sim 92$ K) at a low magnetic field of 96 mT along the c axis, near a lower critical field $H_{c1}$. We observed the frequency distribution of the nuclear spin-lattice relaxation time $^{63}T_1$ in the Zeeman-perturbed $^{63}$Cu NQR spectrum below $T_c$. The characteristic behavior of $1/^{63}T_1$, taking the minimum values with respect to temperature and frequency, indicates the significant role of antiferromagnetic spin fluctuations in the Doppler-shifted quasiparticle energy spectrum inside and outside vortex cores.

74.25.Nf, 74.72.Bk, 76.60.-k

Strong correlation effects on the electronic state inside and outside vortex cores in the mixed state of type-II superconductors have attracted great interests, because an interplay between magnetic correlation and unconventional superconductivity could be observed at quasi-normal cores [1]. Scanning tunneling spectroscopy [2] and muon spin rotation technique [3] have been applied to study the local quasiparticle density of states and the disorder of superconducting Sr$_2$RuO$_4$ to estimate a large Ru Knight shift [11].

In this Letter, we report a Zeeman-split plane-site $^{63}$Cu NQR study of the vortex state of a slightly overdoped high-$T_c$ superconductor Y123 ($T_c \sim 92$ K) at a low magnetic field of 96 mT along the c axis. The sample is a $^{63}$Cu-isotope enrich powder, already used in Ref. [12], mixed with Styac 1266 epoxy and magnetically aligned along the c axis. An intervortex distance at 96 mT is $\sim 1800 \AA$, slightly larger than the penetration depth $\lambda_{ab}(T \rightarrow 0) = 1100 - 1300 \AA$ [7]. For $\delta \sim 0.05$, $H_{c1}$ is about 110 mT at $T \rightarrow 0$ K [13]. We observed the effect of Zeeman-perturbed magnetic field distribution on the split NQR spectrum, the characteristic temperature and frequency dependence of the $^{63}$Cu nuclear spin-lattice relaxation time $^{63}T_1$ below $T_c$. It turned out that the antiferromagnetic spin fluctuations develop at the vortex cores on a dilute vortex lattice.

A phase-coherent-type pulsed spectrometer was utilized to perform the NMR/NQR experiments. All the NMR measurements were done while cooling in a magnetic field of 96 mT. The pure NQR spectra and the Zeeman-split frequency spectra were measured with quadrature detection, where integrations of the nuclear spin-echoes were recorded as functions of frequency $\nu$ while $\nu$ was changed point by point. The power spectra of the spin-echo signals will be shown below, because the spectra include weak signals over a broad frequency region. Throughout the present measurements, the frequency window excited by rf pulses was $\nu_1 \sim 83$ kHz, which was estimated from the first exciting $\pi/2$-pulse $t_w = 3 \mu$s and the relation of $\pi/2 = 2\nu_1 t_w$. The nuclear spin-lattice relaxation curves $p(t) \equiv 1 - M(t)/M(\infty)$ (re-
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Field against the magnetic field. From the observed shift but also the superconducting diamagnetic shift.

Field along the c-axis. The dashed line is $H_0=96$ mT. The scale of the spectrum is not realistic. The actual diamagnetic shift is superimposed on the original broad NQR lines.

FIG. 1. (a) Zeeman-split $^{63}$Cu (a spin $I=3/2$) NQR spectra at $T=10$ and 100 K. (b) Zeeman-split $^{63}$Cu NQR lines (solid lines with $\nu_{Q1}$ and $\nu_{Q2}$) as functions of an external magnetic field along the c-axis. The dashed line is $H_0=96$ mT. (c) A model illustration of the diamagnetic field distribution of the Zeeman-split NQR spectrum of a spin $I=3/2$. The scale of the spectrum is not realistic. The actual diamagnetic shift is superimposed on the original broad NQR lines.

covery curves) of the nuclear spin-echo amplitude $M(t)$ were measured by an inversion recovery technique, as functions of a time $t$ after an inversion pulse.

Figure 1(a) shows a zero-field $^{63}$Cu NQR power spectrum at 100 K ($> T_c$) and the Zeeman-split NQR spectra at 100 K and 10 K ($< T_c$). The magnetic field of $H_0=96$ mT was applied along the c-axis, the maximum principle axis of electric field gradients. The applied magnetic field splits the $^{63}$Cu NQR spectrum with a peak frequency $\nu_{\text{NQR}}$ into two lines with lower and higher frequency peaks ($\nu_{Q1}$ and $\nu_{Q2}$) [14,15]. Using definition of $^{63}g_n=|1+K_c|^{63}g_n$ $^{63}g_n=11.285$ MHz/T and the c-axis Knight shift $K_c$, the transition lines of $\nu_{Q1}$ ($I_z=3/2\leftrightarrow1/2$) and $\nu_{Q2}$ ($I_z=-3/2\leftrightarrow1/2$) are expressed by

$$
\begin{align*}
\nu_{Q1} &= \nu_{\text{NQR}} + ^{63}g_n H_0,
\nu_{Q2} &= \nu_{\text{NQR}} - ^{63}g_n H_0.
\end{align*}
$$

One should note that $K_c$ includes not only the Knight shift but also the superconducting diamagnetic shift. Figure 1(b) illustrates a diagram of the resonance frequency against the magnetic field. From the observed $\nu_{Q1}$ and $\nu_{Q2}$, one can estimate the quadrupole frequency $\nu_{\text{NQR}}(H)$ at a magnetic field $H$ and the local magnetic field $\delta h[≡(1 + K_c)H_0]$ by

$$
\begin{align*}
\nu_{\text{NQR}}(H) &= (\nu_{Q1} + \nu_{Q2})/2,
\delta h &= (\nu_{Q1} - \nu_{Q2})/2^{63}g_n.
\end{align*}
$$

The origin of the linewidth at 100 K is primarily electric, i.e. the distribution of the electric field gradients. The split $^{63}$Cu NQR lines broaden at 10 K. The local field due to the Knight shift of 1.27 % [16] is negligible at the magnetic field of $H_0=96$ mT. Therefore, the line broadening at 10 K must be due to the superconducting diamagnetic shift $^{63}K_{diam}$ or due to the distribution of the electric field gradient $\nu_{\text{NQR}}(H)$ in a mixed state.

In order to determine whether the broadening at 10 K is magnetic or electric, we measured the frequency dependence of $^{63}$Cu nuclear spin-echo decay curves $^{63}E(2\tau)$ ($\tau$ is a delay time between $\pi/2$- and $\pi$-pulses) at 10 K and 100 K. As shown in Fig. 2, the transverse relaxation is slower at 10 K than at 100 K and no appreciable frequency dependence of $^{63}E(2\tau)$ is observed. The slower transverse relaxation in the superconducting state indicates the occurrence of a detuning effect on the nuclear spin-spin coupling [17]. The local field distribution due to the vortices shifts the resonance frequency of the neighboring nuclei out of the excited frequency region of $\nu_1 \sim 83$ kHz. A part of the like-spin (resonant) nuclei at 100 K becomes the unlike-spin (nonresonant) ones at 10 K. The in-plane $^{63}$Cu nuclear spin-spin coupling is expressed by $a_{ij}I_zI_z$ ($i$ and $j$ are the nuclear sites), where $a_{ij}$ is enhanced via an antiferromagnetic spin susceptibility [18]. The slow nuclear spin-spin relaxation in Fig. 2 is not consistent with the zero field $^{63}$Cu NQR results [12], and then it should not be intrinsic in the local antiferromagnetic correlation. The detuning effect on the transverse relaxation confirms that the diamagnetic field distribution results in the additional broadening at 10 K.

First, we estimated $31.54 \leq \nu_{\text{NQR}}(96\text{mT}) \leq 31.58$ MHz at 10 K. We have already measured the $T$-dependence of $\nu_{\text{NQR}}(0)$, e.g. $\nu_{\text{NQR}}=31.54$ MHz at 10 K. We estimated the upper limit of the field-induced quadrupole frequency

$$
0 \leq |\nu_{\text{NQR}}(96\text{mT}) - \nu_{\text{NQR}}(0)| \leq 40\text{kHz}.
$$

This is slightly smaller than the reported values for charged vortices at 9.4 T [19]. The low magnetic field of 96 mT does not enhance the vortex charge for Y123.

Second, we estimated $\delta h=90\pm1$ mT at 10 K. The value of $\delta h$ is smaller than the applied field $H_0=96$ mT, so that the peaks of the split lines are affected by negative shift of -6 mT. One may suppose the Redfield pattern in the field distribution superimposed on the split NQR lines.
The peak lines are regarded as the saddle points in the diamagnetic field distribution on a vortex lattice [20–23]. The highest and the lowest frequency edges are regarded as the vortex core positions. In this assignment, the site-selective NMR at a low field is possible for the present Y123 after Ref. [4]. The superconducting parameters of the penetration depth $\lambda$ and the coherence length $\xi$, however, could not be estimated from Fig. 1(a), because it is difficult to model the inhomogeneous NQR lines and then the actual distribution of diamagnetic field. The line profile of the split NQR spectrum at 10 K in Fig. 1(a) just imitates the Redfield pattern and results predominantly from the inhomogeneous distribution of electric field gradients.

Figure 3 shows the frequency distribution of $^{63}$Cu nuclear spin-lattice recovery curves $^{63}p(t)$ (right panels) in the Zeeman-perturbed Cu NQR spectra (left panels) at $T=100$ K (upper panels) and $T=10$ K (lower panels). The solid curves in the right panels are best fits by eq. (4). The frequency dependence of $1/^{63}T_1$ are shown in the left panels.

The frequency dependence of $1/^{63}T_1$ is similar to those of the plane-site $^{17}$O(2, 3) and the apical $^{17}$O(4) at high magnetic fields of $H_0=9-37$ T [4, 5]. The plane-site Cu directly probes the in-plane antiferromagnetic correlation, but the plane-site oxygen does not. The frequency dependence of $1/^{117}T_1$ is understood primarily by change in quasiparticle excitations around the vortex cores due to Doppler shift [20, 24]. The supercurrent around a vortex core induces Doppler shift in the local quasiparticle energy spectrum [25]. Therefore, the frequency dependence of $1/^{63}T_1$, similar to that of the high field $1/^{117}T_1$, indicates the importance of the Doppler-shifted quasiparticle energy spectrum and the absence of the static antiferromagnetic vortex cores at 96 mT. Coexistence of vortex solid with liquid is reported at higher magnetic fields [26]. The coexistence could be expected just below $T_c$ at a low field but was not clear in this study.

Figure 4(a) shows $1/^{63}T_1$ as a function of temperature across the split NQR spectrum and at the zero field NQR frequency. The signals at 30.4-30.6 MHz and at 29.5 MHz in the split NQR spectrum come from the nuclei close to the saddle points and close to the vortex cores, respectively. The zero field $1/^{63}T_1$ is consistent with the results in Ref. [27]. The dashed line is a function of $1/^{63}T_1T \propto T^2$ due to a $d$-wave superconducting gap with line nodes. The temperature dependence of $1/^{63}T_1T$ at each selected site can be understood primarily by the spatial dependence of the local density of states with the Doppler-shifted quasiparticle energy spectrum [20]. The minimum of $1/^{63}T_1T$ at 10 K for nuclei at 29.5 MHz, however, is not understood simply by the local density of states.

Figure 4(b) shows $1/^{63}T_1T$ as a function of frequency the site-selective measurement of $1/^{63}T_1$ in the Zeeman-split NQR spectrum and for the less effect of nuclear spin diffusion.
at $T=5$ and 10 K. The increase in $1/63T^1T$ from the saddle points to the vortex cores can be understood by the Doppler-shifted quasiparticle energy spectrum. But, the minimum behavior around the saddle points is not understood only by the Doppler shift effect.

The superconducting order is locally destroyed by the field-induced supercurrent, and then the competing fluctuations develop in the vortex cores. The supercurrent-induced scattering process via the antiferromagnetic spin fluctuations in the Doppler-shifted quasiparticle energy spectrum plays a significant role around the vortex cores [24]. The local antiferromagnetic spin fluctuations cause competition between thermal quasiparticle scattering and the creation/annihilation of two quasiparticles in a spin-fermion model [24]. The minimum behavior of $1/63T^1T$ with respect to temperature and frequency is an evidence for such a competition mechanism inside and outside the vortex cores with the antiferromagnetic spin fluctuations.

To conclude, the effect of antiferromagnetic spin fluctuations on the low-lying excitation inside and outside vortex cores was observed in the $^{63}$Cu nuclear spin-lattice relaxation measurements for Y123 at 96 mT near $H_{c1}$.

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