Phase diagram of YBa$_2$Cu$_3$O$_{7-y}$ at T<T$_c$ based on Cu(2) transverse nuclear relaxation

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(October 31, 2018)

Two maxima in transverse relaxation rate of Cu(2) nuclei in YBa$_2$Cu$_3$O$_{7-y}$ are observed, at T =35 K and T = 47 K. Comparison of the $^{63}$Cu(2) and $^{65}$Cu(2) rates at T = 47 K indicates the magnetic character of relaxation. The enhancement at T = 47 K of fluctuating local magnetic fields perpendicular to the CuO$_2$ planes is connected with the critical fluctuations of orbital currents. Maximum at T = 35 K is connected with the appearance of inhomogeneous superconducting phase. Together with data published to date, our experimental results allow to suggest a qualitatively new phase diagram of the superconducting phase.

PACS: 74.25.Nf, 74.72.Bk, 74.25.Dw, 76.60.Gv
Anomalous behavior of copper nuclear transverse relaxation rate in CuO$_2$ planes of YBa$_2$Cu$_3$O$_{7-y}$ superconductors had been discovered at the beginning of the HTSC history. The sharp increase of the transverse relaxation rate at $T = 35$ K occurring in the superconducting samples with the doping level close to optimal is considered by the authors as an indication of the phase transition. Okahara interpreted this transition as the second superconducting transition in the copper bilayer of YBa$_2$Cu$_3$O$_{7-y}$. Krämer and Mehring connect it with the transition of YBa$_2$Cu$_3$O$_{7-y}$ to the state with the charge density waves (CDW). As the authors of have pointed out, this interpretation needs to be checked on the samples with another oxygen doping level. It was criticized recently [10] and new measurements for a slightly overdoped YBa$_2$Cu$_3$O$_{7-y}$ samples with $T_c$=89.5 K had been presented with the well-defined Cu NQR linewidth maximum not at 35 K, but at 60 K.

Our studies of Cu(2) NQR in a series of YBa$_2$Cu$_3$O$_{7-y}$ samples confirm the existence of a transverse relaxation maximum at $T = 35$ K. The new result of our study is the discovery of one maximum more, at $T = 47$ K. Moreover, a maximum of this kind appeared to be reported already in few papers [11], but no proper attention had been payed to it. However, the existence of two maxima in some cases might indicate, to our mind, in favour of two phase transitions below $T_c$.

Specifications we suggest for the recently discussed in schematic diagram of coexistence of phases in the superconducting state near optimal doping is shown in Fig.1. In addition to the phase of spontaneous currents or, in other words, phase of charge density waves with the imaginary order parameter (id-CDW) suggested earlier, we suppose the existence of at least one more phase in the superconducting state, namely, a phase of the Cooper pairs with a non-zero total momentum or, in other words, an inhomogeneous component of the superconducting $d$-phase (d-SC). The possibility of coexistence of few phases in underdoped cuprates is connected with a Peierls instability of a quasi-2D system and was discussed in. The scenario of competition between id-CDW and $d$-type superconducting (d-SC) phases explains fairly well the non-monotonous behavior of the effective gap near $T_c$. It was used recently for explanation of neutron scattering data and anomalous behavior of spin-lattice relaxation in superconducting cuprates at low temperatures.

The dashed line in Fig.1, just as in separates the id-CDW phase, the continuous dome-like line is a boundary of the d-SC phase. The behavior of the phase boundary depicted by the dashed line in Fig.1 differs from that published in [12] and is obtained according to the calculations of. The existence of the phase boundary depicted by a dash-dotted line we assume according to the transverse nuclear relaxation data discussed below. The behavior of this boundary at small doping levels is not established in the present work and needs further investigation. The right-hand edge of this boundary is drawn in agreement with data discussed in.

Two samples of YBa$_2$Cu$_3$O$_7$ (YBCO7) made by a solid-state reaction were used in our studies. The critical temperatures ($T_{c-onset}$) were measured on a SQUID and were equal to 91.6 K and 91.2 K for the samples #1 and #2, respectively. Home-built pulsed coherent NMR/NQR spectrometers were used for copper NQR measurements.

The transverse Cu(2) nuclear relaxation was studied in the temperature range 4.2-77 K. The decay curves were fitted to a following expression:

$$M(\tau) = M_0 \cdot \exp \left(-\frac{(2\tau)^2}{2T_{2G}^2}\right) \cdot \exp \left(-\frac{2\tau}{T_{2L}}\right).$$

(1)

The first exponent in this expression represents the well-known Gaussian decay of the magnetization due to indirect Cu(2) nuclei interaction, the second one accounts for a possibility for an additional transverse relaxation channel. The Redfield contribution to the transverse relaxation becomes significant only at $T>$60-70 K and was not taken into account. The measured transverse relaxation rates, $T_{2G}^{-1}$ and $T_{2L}^{-1}$, are shown in Fig.2. As is seen in Fig.2 the Gaussian contribution to the total rate does not depend on temperature below $T_c$, and the additional Lorenzian one exhibits one maximum, at $T = 35$ K, for the sample #1 and two maxima, at $T = 35$ K and $T = 47$ K, for the sample #2.

The Cu(2) nuclear spin-lattice relaxation was studied in the temperature range 4.2-300 K by the saturation-recovery method. The recovery curves were fitted to an expression:

$$\frac{M(t) - M_0}{M_0} = \exp \left(-\frac{t}{T_1}\right)^N,$$

(2)

with $M_0$ an equilibrium magnetization, $M(t)$ a magnetization after a saturating $\pi/2$-pulse, and the parameter $N$ characterizes the relaxation rate distribution: $N=1$ for a homogeneous system for which all nuclei have the same relaxation rate, and $N<1$ for an inhomogeneous system for which the fluctuating fields causing the relaxation are different for different nuclei.

The temperature dependence of Cu(2) nuclear spin-lattice relaxation rate is shown in Fig.3. The dependence is the same for both samples between 10 and 300 K. Below $T_c$ the rate decreases rapidly which is known to be due to a superconducting gap appearing in the excitation spectrum of a superconductor. The spin-lattice relaxation kinetics gradually becomes non-exponential below 35-40 K ($N<1$). No any peculiarities of the relaxation rate are observed at $T = 35$ K and 47 K.

One can see in Fig.1 that near optimal doping the phase boundaries are crossed twice when decreasing temperature along the line 1. Since the phase boundary depicted by a dashed line in Fig.1 depends strongly on a
doping level, the small changes of it leave only one crossing of the phase boundary (for example, when the temperature is decreasing along the line 2). This crossing can be naturally connected with a $T_{2}^{-1}$ maximum at $T\approx35$ K.

The longitudinal nuclear magnetic relaxation is known to be produced by the fields fluctuating at a NMR frequency and directed perpendicularly to the quantization axis which coincides with the electric field gradient in the case of NQR. The transverse relaxation is caused by the low-frequency fluctuating fields directed along the quantization axis. Since two copper isotopes, $^{63}\text{Cu}$ and $^{65}\text{Cu}$, have different gyromagnetic ratios and quadrupolar moments ($^{63}\gamma/^{63}\gamma=0.933$, $^{65}Q/^{65}Q=1.081$), the measurements for different isotopes allow to distinguish between the relaxation caused by fluctuating magnetic or electric fields. Moreover, if the transverse relaxation is caused by interaction between like nuclear spins it should be 1.3 times slower for $^{65}\text{Cu}$ than for $^{63}\text{Cu}$ due to bigger concentration (natural abundance) of the latter.

Orbital currents circulating in CuO$_2$ planes create fluctuating magnetic fields at Cu(2) sites directed along the c-axis of the crystal. Since the electric field gradient at Cu(2) sites is also directed along the c-axis, the changes in the spontaneous currents phase will lead to the critical acceleration predominantly of the transverse nuclear relaxation leaving the spin-lattice relaxation unchanged. This corresponds to the experiment fairly well (see Fig.3a). The comparison of the relaxation rates for the $^{63}\text{Cu}$ and $^{65}\text{Cu}$ isotopes confirms the magnetic character of an additional channel of transverse relaxation at $T=47$ K and indicates that it is not connected to the interaction between like nuclear spins: $^{63}T_{2L}^{-1}/^{65}T_{2L}^{-1}=0.89\approx(63\gamma/65\gamma)^2$.

We could not definitely determine the character of additional relaxation channel at $T=35$ K due to insufficient temperature stability during the long signal acquisition time. According to the additional relaxation at 35 K in the underdoped YBCO7 is caused by fluctuations of electric field gradient at Cu(2) sites. This could be explained if one assumes that almost nothing happens to the spontaneous currents phase while crossing the phase boundary along the line 2 in Fig.1, but that an inhomogeneous superconducting phase with a spatially modulated concentration (natural abundance) of the latter.

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Strong dependence of the position of the second maximum in $T_{2}^{-1}$ on the oxygen deficiency (see Table 1) corresponds fairly well to the strong doping dependence of the temperature at which the phase of spontaneous currents disappears. The incline of the line separating the $d$-SC and the mixed ($d$-SC+id-CDW) phases to the left in Fig.1 indicates the tendency of expulsion of the spontaneous currents phase from the superconducting phase. This tendency has been already theoretically predicted in.

Finally, let us give an additional argument in favour of inhomogeneous superconducting phase. Already at $T>T_c$ the chain structures of YBCO7 exhibit the behavior typical for the systems with CDW (see, for example,5)). Hybridization of the chain and plane energy bands promotes the inhomogeneous superconductivity also in the planes. It becomes clear in this connection why there are no anomalies in the transverse nuclear relaxation rate of copper in La$_{2-x}$Sr$_x$CuO$_4$ at about 30 K.

The work is supported by the Russian program ”Superconductivity”, under Grant No.98014-1.

I. FIGURE CAPTIONS

Fig.1. The schematic phase diagram of YBa$_2$Cu$_3$O$_{7-y}$.

As in, $p$ denotes the hole concentration per one Cu(2) position.

Fig.2. Temperature dependence of $^{63}\text{Cu}(2)$ transverse relaxation rates for the sample #1 (a) and #2 (b). The vertical lines correspond to $T=35$ K and 47 K.

Fig.3. Temperature dependence of $^{63}\text{Cu}(2)$ spin-lattice relaxation rate (a) and of parameter N (b, see text for details). The vertical lines correspond to $T=35$ K, 47 K and 91.4 K.

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TABLE I. Positions of maxima of Cu(2) transverse relaxation rate below $T_c$.

| Compound          | $T_c$, K | Max.1, K | Max.2, K | Reference |
|-------------------|----------|----------|----------|-----------|
| YBa$_2$Cu$_3$O$_{6.98}$ | 92       | 35       | 52       | [5]       |
| YBa$_2$Cu$_3$O$_{7-y}$ | 90       | 35       |          | [7]       |
| YBa$_2$Cu$_3$O$_{7-y}$ | 93       | 35       |          | [3]       |
| YBa$_2$Cu$_3$O$_{6.95}$ | $\approx$ 91 | 35 | 50 | [9] |
| YBa$_2$Cu$_3$O$_{6.925}$ | $\approx$ 91 | 35 |          |           |
| YBa$_2$Cu$_3$O$_{7-y}$ | 91.6     | 35       |          | Our results |
|                   | 91.2     | 35       | 47       |           |
Fig. 1 (Eremin et al.)
Fig. 2 (Eremin et al.)
Fig. 3 (Eremin et al.)