Cu(2) nuclear resonance evidence for an original magnetic phase in aged 60K-superconductors RBa$_2$Cu$_3$O$_{6+x}$ (R=Tm, Y)

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It is widely believed that the long-range antiferromagnetic order in the RBa$_2$Cu$_3$O$_{6+x}$ compounds (R=Y and rare earths except of Ce, Pr, Tb) is totally suppressed for the oxygen index $x \geq 0.4$ (AFM insulator-metal transition). We present the results of the copper NQR/NMR studies of aged RBa$_2$Cu$_3$O$_{6+x}$ (R=Tm,Y) samples showing that a magnetic order can still be present at oxygen contents $x$ up to at least 0.7 and at temperatures as high as 77K.

I. INTRODUCTION

An enormous amount of papers, both experimental and theoretical, are devoted to the NMR and NQR studies of copper in superconducting YBa$_2$Cu$_3$O$_{6+x}$ layered cuprates. It is considered well known that in non-superconducting materials ($x < 0.4$) nuclei of copper located in the CuO$_2$ planes experience the influence of a strong internal magnetic field $H_{int} \approx 80$ kOe which is perpendicular to the $c$-axis, and that in superconductors ($x > 0.4$) such field is absent and $^{63,65}$Cu(2) nuclei with the spin $I = 3/2$ give typical NQR spectra at frequencies of $\nu_Q \approx 25 \div 32$ MHz, i.e., in the same frequency range as that for NQR spectra of two-fold coordinated "chain" copper $^{63,65}$Cu(1)\[1\]. While studying NMR of thulium in oxygen-deficient TmBa$_2$Cu$_3$O$_{6+x}$ compounds\[2\] we have discovered the wide and subtle absorption line (Fig.1) which looked like copper NMR line but could not have been attributed to the mentioned Cu(2) and Cu(1) centers with $\nu_Q \approx 25 \div 32$ MHz and $H_{int} = 0$. We consequently undertook experiments with TmBa$_2$Cu$_3$O$_{6+x}$ samples ($x = 0.51, 0.6, 0.7$) in zero external field at $T=4.2$K, which allowed us to observe a Cu(2) ZFNMR spectrum completely different from those described in the literature. The results of these experiments are presented in this paper. The analysis of Cu(2) spectra of both types corresponding to $H_{int} \neq 0$ (type I, $\nu_{ZFNMR} = 55 - 135$ MHz) and $H_{int} = 0$ (type II, $\nu_Q \approx 25 \div 32$ MHz) shows that each of them belongs to two varieties of Cu(2) centers, A and B, possessing different NQR frequencies and that $A_{I-}$ and $B_{I-}$centers differ much in the value of $H_{int}$. Similar results are obtained for one YBa$_2$Cu$_3$O$_{6.66}$ sample\[3\].

II. EXPERIMENTAL

The TmBa$_2$Cu$_3$O$_{6+x}$ samples used in these experiments were $c$-axis-oriented powders mixed with paraffin (hereafter denoted as Tm$_6$+x). They were previously used for Tm NMR studies\[2,3\]. All of them were stored at room temperature for almost 6 years after preparation. Critical temperatures ($T^{onset}_{c}$=53K, 61K and 64K for $x = 0.51, 0.6$ and 0.7, respectively) were obtained from measurements of the diamagnetic susceptibility at a frequency of 1 kHz. Home-built spin-echo NQR spectrometers were used for the Cu(2) NQR and ZFNMR measurements. Examples of the copper NQR spectra in Tm$_6$ are shown in Fig.2. Comparing the non-saturated (NS) and saturated (S) spectra (Figs.2a,b) taken at 4.2K with pulse sequence repetition rates of 1 and 200 Hz, respectively, one can distinguish two contributions with different spin-lattice relaxation times $T_1$ (Fig.2c) and separate them (Figs.2d,e) by using a simple subtraction procedure. Two narrow lines in Fig.2c corresponding to the long $T_1$ time are believed to originate from the two-fold coordinated Cu(1)$_2$ sites which belong to "empty chains" surrounded by "full chains" in the CuO$_x$ plane\[3\]. The broad spectrum in Fig.2d characterized by the short $T_1$ has a two-hump shape typical for the Cu(2) NQR spectrum of an annealed sample\[4\]. In the following it is denoted as the spectrum of type II. Computer simulations have shown that this two-hump spectrum can be obtained by adding two Gaussians (two sites, $A_{II}$ and $B_{II}$, times two isotope,
In order to clarify the origin of the LFF- and HFF-spectra, we have tried to fit the Cu(2) ZFNMR in a correct way assuming that the $A_I$- and $B_I$-sites can be characterized by different values of $\theta_Q$, $H_{int}$ and $\theta$ (angle between $H_{int}$ and the $c$-axis). Prior to fitting the experimental spectra (Fig.3) have been $T_2$-corrected by the function $f(\nu) = F_0(\nu)/F_{2\tau}(\nu)$, where $F_{2\tau}(\nu)$ is the ZFNMR spectrum shown in Fig.4 by a dotted line, and $F_0(\nu)$ is the spectrum represented by a solid line. The spectra of Tm6.51 and Tm6.6 corrected in this way are shown in Fig.5. The fitting procedure included numeric diagonalization of the two Hamiltonians and calculation of all the transitions probabilities ($\sim \nu^2$). When calculating averaged values of the probabilities in oriented powdered samples, we have taken an orientation of a radiofrequency field with respect to the $c$-axis into account ($H_1 \perp c$). In all the cases considered, the Lorentzian shape of an individual resonance line was found to fit the experimental data much better than the Gaussian one. Two versions of the fit have been considered. When the angles $\theta$ were allowed to be free, the best fit of the Cu(2) ZFNMR spectrum of Tm6.51 was obtained at the following parameters (see solid line in Fig.5a):

$$\theta = (82(4))^\circ, \quad H_{int} = 63.9(3) \text{ kOe}, \quad \nu_Q = 31(2) \text{ MHz},$$

$$\theta = (65(4))^\circ, \quad H_{int} = 58(1) \text{ kOe}, \quad \nu_Q = 31(4) \text{ MHz}.$$
$B_I$-sites, $\nu = 98 - 127$ MHz$^5$, intensity $S_{B_I} = 38(3)\%$, \\ $\theta = 64(1)^\circ$, $H_{int} = 97.7(2)$ kOe, $\nu_Q = 25(2)$ MHz, \\ linewidth $FWHM = 4.4(4)$ MHz. 
(2)

The corresponding parameters for the Tm6.6 sample have been obtained as follows (Fig.5b):

$A_I$-sites, $\nu = 55 - 98$ MHz, $S_{AI} = 66(4)\%$, \\ $\theta = 83(3)^\circ$, $H_{int} = 64.1(2)$ kOe, $\nu_Q = 30(1)$ MHz, 
(3)

$B_I$-sites, $\nu = 98 - 127$ MHz$^5$, $S_{B_I} = 34(2)\%$, \\ $\theta = 63.5(5)^\circ$, $H_{int} = 97.6(1)$ kOe, $\nu_Q = 27(1)$ MHz, \\ $FWHM = 4.4(3)$ MHz. 
(4)

In the second version ($\theta = 90^\circ$) both internal fields were assumed to lie in the $ab$ plane. The results of this fit for Tm6.6 are as follows (see solid line in Fig.5c):

$"\theta = 90^\circ"$ \\
$A_I$-sites, $\nu = 55 - 98$ MHz, intensity $S_{AI} = 66(6)\%$, \\ $H_{int} = 64$ kOe$^*$, $\nu_Q = 30$ MHz$^*$, 
(5)

$B_I$-sites, $\nu = 98 - 135$ MHz, $S_{B_I} = 34(3)\%$, \\ $H_{int} = 103$ kOe$^*$, $\nu_Q = 15.3(7)$ MHz, \\ $FWHM = 4.8(4)$ MHz. 
(6)

(* denotes the fixed parameters). The second fit seems to agree with experiment worse than the first one, but this can be due to incorrect intensities of the HFF-lines deduced from the T$_2$-correction procedure. We believe that at the present stage both versions can be considered satisfactory; more experimental work is needed to make a choice between them. In both cases the Cu(2) NMR line in Fig.1 has been identified as originating from two groups of $A_I$-lines (at 58-63 MHz and 74-79 MHz).

Then summarizing all experimental facts, one should adopt that at least a part of the two-hump NQR spectrum, which is supposed to be typical for the annealed 123 superconductors with high $T_c$, and the ZFNMR spectrum, which is observed in the 60K-superconductors exhibiting a well pronounced two-hump NQR, are actually representing a non-superconducting material. In what follows, we try to speculate about the plausible structure of this material. It is known that a structural (chemical) micro-phase separation takes place in the oxygen-deficient 123 compounds [1]. Therefore, one could naturally expect to find the defects of the crystal lattice in the form of layers (reflecting the basic property of the layered structure itself) and, following this way, could associate the two types of Cu(2) spectra with two different non-superconducting micro-phases, i.e., hole doped (type $II$) and non-doped (type $I$) layers, forming some kind of stacking sequence along the c-axis. On the other hand, the coincidence of the $\nu_Q$-values (see Eqs.(1)-(4) and Table I) in the two absolutely different phases lead us to consider that both types of Cu(2) spectra might originate from the same CuO$_2$ layers (bilayers).

To make a choice between these two scenarios, one should use the neutron scattering data which gives a direct information on a magnetic structure of the oxygen-deficient 123 compounds. The thorough studies of the neutron scattering in YBa$_2$Cu$_3$O$_{6.6}$ have resulted in a recent observation [15] of incommensurate magnetic fluctuations peaked at $\vec{Q} = (1/2 \pm \delta, 1/2 \pm \delta)$ with $\delta = 0.057 \pm 0.006$ r.l.u. It was also found that the dynamical susceptibility $\chi''(\vec{Q}, \omega)$ at the incommensurate positions first appears at temperatures somewhat above $T_c$ and then increases on cooling below $T_c$, altogether with the suppression of magnetic fluctuations at the commensurate points. These observations look similar to those for the La$_{1.6-x}$Nd$_x$Sr$_x$CuO$_4$ compounds [16] and thus can be considered as giving evidence for a formation of a static (or quasi-static) stripe pattern in the CuO$_2$ layers. The layer-by-layer separation scenario seems to be inconsistent with such a stripe model. On the contrary, the stripe-like modulation of charge and spin densities in CuO$_2$ layers resulting in an inequivalency of Cu(2) sites looks very likely. Indeed, analyzing the data of Table II, one can conclude that there could exist a certain value of $x_{pin}$ (close to 0.6) which corresponds to the following relations:

$$S_{AI}/S_{B_I} = 2, \quad S_{AI}/S_{BII} = 2, \quad S_{II}/S_I = 2.$$ 
(7)

These relations can be understood in the frame of the charge stripe model suggested in [15]. A plausible stripe pattern corresponding to the optimally doped CuO$_2$ planes (1/6 hole per CuO$_2$ unit) is shown in Fig.6a. If one takes every
third stripe away (Fig.6b), the hole concentration $p$ becomes $(2/3) \times (1/6) = 1/9$. According to the empirical formula $p = 0.187 - 0.21(1 - x)$, suggested by Tallon et al. for $x \geq 0.45$, the concentration $p = 1/9$ corresponds to $x = 0.64$ which is close to what is expected for Eq.(7) to hold. The magnetic superstructure shown in Fig.6b has a period of 18 lattice spacings. This period and the diagonal direction $[110]$ of the stripes in Fig.6b exactly corresponds to the incommensurate magnetic fluctuations observed in YBa$_2$Cu$_3$O$_{6-\delta}$: the model in Fig.6b predicts incommensurate peaks at $\mathbf{Q} = (1/2 \pm \delta, 1/2 \pm \delta)$ with $\delta = 1/18 = 0.0556$. In this stripe pattern, it is easy to distinguish four different Cu(2) sites which could be identified as sites $A_I$ (at borders of magnetic stripes), $B_I$ (at centers of magnetic stripes), $A_{II}$ (at borders of non-magnetic stripes), $B_{II}$ (at centers of non-magnetic stripes). An alternative possibility is to ascribe the $B_{II}$-sites to copper atoms located at outer borders of the non-magnetic bi-stripes allowing the $A_{II}$-sites to occupy four lines of coppers inside the bi-stripes. In any case, however, one has a problem to explain why the transferred hyperfine field from the $A_I$-copper spins does not influence the NQR spectrum of the neighboring type-II copper centers. Further experimental work is necessary to better understand the allocation of the Cu(2) centers responsible for the two-hump NQR spectrum.

It is known that the observation of the static stripe-phase order of holes and spins in La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4.44}$ has appeared possible due to pinning of the stripes by the neodymium impurities. What could be the reason for stripes to be pinned in non-stoichiometric 123 compounds? We believe that the so-called "OrthoIII" superstructure in CuO$_x$ planes could cause pinning of charge stripes in CuO$_2$ planes since this superstructure has a period $(3a_0)$ commensurate with the period of the stripe pattern shown in Fig.6b. A possibility for the OrthoIII to form a stable phase at $x = 0.65 - 0.77$ was proved by the electron, X-ray and neutron diffraction measurements. The above oxygen contents appear to be shifted to higher values than that $(x_{pin})$ expected for the condition Eq.(7) to be fulfilled. However, the value of $x_{pin}$ may happen to result from an interplay between the OrthoIII ordering of CuO$_x$ layers at $x > x_{pin}$ and an appropriate hole doping of CuO$_2$ layers $(p = 1/9$ per CuO$_2$ at $x < x_{pin}$). Experiments with an YBa$_2$Cu$_3$O$_{6.77}$ single crystal have shown that the OrthoIII phase is stable at temperatures below 75°C. Therefore, the interactions responsible for the formation of the OrthoIII phase seem to be rather weak and can be easily disturbed by thermally-activated oxygen diffusion. This feature of the T-x phase diagram allows us to understand why the Cu(2) ZFNMR was observed in our experiments only in those 123 superconductors which were subjected to a very long-term room-temperature annealing.

IV. CONCLUSIONS

The Cu(2) nuclear resonance spectra were studied at liquid helium temperatures in samples of oxygen-deficient 60K-superconductors, TmBa$_2$Cu$_3$O$_{6.5+x}$ and YBa$_2$Cu$_3$O$_{6.66}$, stored at room temperature for a long time (up to 6 years). Cu(2) ZFNMR spectra different from those known so far were observed, indicating the presence of a non-superconducting phase in the superconducting samples. The quantitative analysis of the copper resonance absorption intensities in different samples lead us to consider that both types of Cu(2) spectra (ZFNMR at 55-135 MHz and at least a part of NQR at 25-32 MHz) might originate from the same non-superconducting CuO$_2$ layers decorated by the pinned charge stripes.

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VI. FIGURE CAPTIONS

Fig.1. Tm and Cu(2) NMR spectra of the aligned Tm6+x powders with $x=0.51$ (triangles), 0.6 (light circles), 0.7 (squares) at a frequency of 70 MHz in an external field H perpendicular to the c-axis. Cu(2) NMR is particularly pronounced in the saturated spectrum of Tm6.6 (black circles) taken at a pulse sequence repetition rate of $F=100$ Hz. Inset: ac diamagnetic susceptibility of Tm6+x at liquid helium temperature (frequency of 1 kHz, $H_1 \approx 1$ Oe); circles - for 1-year aged samples, crosses - for 6-years aged samples.

Fig.2. Copper NQR spectra of Tm6.6 at a temperature of 4.2K: (a) non-saturated Cu(1) and Cu(2) spectra ($F=1$ Hz), (b) saturated Cu(1) and Cu(2) spectra ($F=200$ Hz), (c) ratio of the non-saturated to saturated echo intensity, (d) Cu(2) NQR spectrum, (e) Cu(1) NQR spectrum. Solid line in (d) is an approximation by four Gaussians (for parameters see Table I).

Fig.3. Cu(2) ZFNMR spectra of (a) Tm6.51, (b) Tm6.6, (c) Tm6.7 and (d) Y6.66 at a temperature of 4.2K. Black squares in (b) is the spectrum at $T=77$K multiplied by a factor of 10. The YBa$_2$Cu$_3$O$_{6.66}$ sample was stored at room temperature for 3 years after preparation.

Fig.4. Calculated Cu(2) NQR and ZFNMR spectra of (a) Tm6.51, (b) Tm6.6, (c) Tm6.7 and (d) Y6.66 obtained from the experimental spectra of Fig.3 as a superposition of six Gaussians: solid lines $F_0(\nu)$ - taking into account the $\nu^2$-type dependence of the spin-echo intensities and the losses of signal intensities due to spin-spin relaxation, dotted lines $F_2(\nu)$ - taking into account the $\nu^2$-dependence only (for details see text). The integrated intensities of the $S_I$- and $S_{II}$-spectra depicted by solid lines are normalized by the intensity of the Cu(2) ZFNMR spectrum of the 1 gram TmBa$_2$Cu$_3$O$_{6.1}$ sample at $T=4.2$K. For convenience of comparison, the ZFNMR spin-echo intensities are multiplied by a factor of 15.

Fig.5. Cu(2) ZFNMR spectra of (a) Tm6.51 and (b) Tm6.6 obtained from the experimental spectra of Figs.3a,b by taking into account the losses of signal intensities due to spin-spin relaxation (for details see text). Solid lines in (a) and (b) represent the results of the numerical diagonalization of the two Hamiltonians with the parameters given in Eqs.(1),(2),(3),(4); solid line in (c) represents the spectrum of Tm6.6 calculated with the parameters given in Eqs.(5), (6).

Fig.6. Plausible stripe patterns in the (a) optimally doped ($p=1/6$ hole per Cu(2)) and (b) underdoped ($p=1/9$) CuO$_2$ planes. Copper atoms carrying magnetic moments of opposite orientations are shown by big light and black circles, those carrying no magnetic moments are shown by small circles, solid lines mark the centers of the non-magnetic (hatched) and magnetic (non-hatched) stripes. The period of 18 lattice spacings of the magnetic superstructure in (b) is twice as large as the period of the charge pattern.
| Sample  | Site | $^{63}v_Q$ (MHz) | Full rms width (MHz) | Intensity |
|---------|------|-----------------|----------------------|-----------|
| Tm6.51  | $A_{II}$ | 29.44(2) | 1.35(3) | 0.65(1) |
|         | $B_{II}$ | 26.76(6) | 1.17(4) | 0.35(4) |
| Tm6.6   | $A_{II}$ | 29.69(2) | 1.75(4) | 0.69(1) |
|         | $B_{II}$ | 27.01(6) | 1.46(4) | 0.31(4) |
| Tm6.7   | $A_{II}$ | 30.36(3) | 2.02(6) | 0.68(1) |
|         | $B_{II}$ | 27.39(6) | 1.79(9) | 0.32(2) |

TABLE I. Parameters of the $^{63}$Cu(2) NQR spectra (type $II$) in Tm6+x samples at T=4.2K (with no corrections for the frequency dependence and for the spin-spin relaxation time $T_2$)

| Sample  | ZFNMR $S_{AI}/S_{BI}$ | NQR $S_{AI}/S_{BI}$ | NQR/ZFNMR $S_{II}/S_I$ |
|---------|-----------------------|---------------------|-------------------------|
|         | Lorentzian approximation with the $T_2$ corrections | Gaussian approximation with the $T_2$ corrections | Gaussian approximation with no $T_2$ corrections | Gaussian approximation with the $T_2$ corrections |
| Tm6.51  | 1.6(3) | 1.6(4) | 1.8(2) | 1.8(6) | 0.791/0.207=3.8(1.3) |
| Tm6.6   | 2.0(2) | 2.0(5) | 2.2(2) | 2.0(7) | 0.424/0.154=2.8(9) |
| Tm6.7   | 3.7(1.2) | 2.1(2) | 2.5(9) | 0.725/0.104=7(2) |
| Y6.66   | 3.3(1.2) | 2.6(9) | 3.8(1.3) | 3.7(1.3) |

TABLE II. Intensities of the Cu(2) spectra in Tm6+x (x=0.51, 0.6, 0.7) and Y6.66 at T=4.2K
Fig. 1

Spin-echo intensity vs. Magnetic field (kOe)

- Copper (Cu(2)) NMR
- Thulium (Tm) NMR

Frequency: $\nu = 70$ MHz
Temperature: $T = 4.2$ K
Fig. 2

Cu(2) and Cu(1)$_2$ NQR

T = 4.2K

(a) NS

(b) S

(c)

(d) Cu(2) NQR

(e) Cu(1) NQR

Spin-echo intensity

Frequency (MHz)
Fig. 3

(a) Spin-echo intensity

(b) Spin-echo intensity

(c) Spin-echo intensity

(d) Spin-echo intensity

Frequency (MHz)

Tm6.51
T = 4.2 K

Tm6.6

Tm6.7
T = 4.2 K

Y6.66
T = 4.2 K
Fig. 4

Spin-echo intensity

Frequency (MHz)

Tm6.51
Int.=0.791
Int.=0.207

Tm6.6
Int.=0.424
Int.=0.154

Tm6.7
Int.=0.725
Int.=0.104

Y6.66
Int.=0.15

20 40 60 80 100 120 140
Fig. 5

(a) Tm6.51

(b) Tm6.6

(c) Tm6.6

Spin echo intensity vs. Frequency (MHz)
Fig. 6