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SHAPE OF THE Cu(2) NQR SPECTRA IN $YBa_2Cu_3O_7$, $TmBa_2Cu_3O_7$ and $TmBa_2Cu_4O_8$

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We present a study of shape of the Cu(2) NQR spectra in $YBa_2Cu_3O_7$, $TmBa_2Cu_3O_7$ and $TmBa_2Cu_4O_8$ compounds at temperatures of 4.2–300 K. The results of the quantitative analysis lead us to conclude that the shape of the Cu(2) NQR spectra in all the samples studied can be described in the frame of the "motional narrowing" model implying the Cu(2) nucleus to possess two different NQR frequencies between which it can rapidly jump. The difference in frequencies seems to be related to the charge-stripe-correlations in CuO_2 planes resulting in a dynamical modulation of the electric field gradients at the Cu(2) nuclei.

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In the present study an attempt was undertaken to analyse quantitatively a resonance line shape of so-called "planar" copper nuclei belonging to CuO_2 planes. The main problems preventing the correct studies of the planar copper NQR/NMR line shape are widely believed to arise from an enormously strong inhomogeneous broadening of spectral lines due to great many defects of a crystal lattice (oxygen vacancies and interstitials, twin boundaries, impurity phases, stacking faults, etc.) typical for the layered cuprates. These difficulties finally seemed to result in a loss of basis for cooperative studies of the line shape problem since the Cu(2) NQR/NMR spectra of the same compounds prepared in different laboratories usually appeared to be very much different and "sample-dependent". In order to minimize the problems of the inhomogeneous broadening due to crystal lattice defects, we have studied nominally pure stoichiometric 123 and 124 compounds. Furthermore, by measuring the Cu(2) NQR spectra (i.e., in a zero external magnetic field), the additional complications resulting from an inhomogeneous broadening due to the vortex lattice in a superconducting state have been avoided. The principal finding of the paper is that the shape of the Cu(2) NQR spectra in all the samples studied can be described in a frame of the "motional narrowing" model [1–3] implying the Cu(2) nucleus to possess two different NQR frequensies between which it can rapidly jump.

All three samples studied in the present work were previously used in our NMR/NQR experiments, those are $YBa_2Cu_3O_7$ (Y1237) [3], $TmBa_2Cu_3O_7$ (Tm1237) [4], and $TmBa_2Cu_4O_8$ (Tm1248) [5]; the critical temperatures T_c(onset) of 92.5 K, 91.5 K and 80.0 K, respectively, have been obtained in the ac susceptibility vs. T measurements at a frequency of 1 kHz (amplitude$\approx$ 1 Oe). A home-built spin-echo coherent pulsed spectrometer was used for the Cu(2) NQR spectra measurements. Both of the 1237 compounds were found to be in a slightly overdoped state. The example of the Tm1237 spectrum is shown in Fig.1. It is seen that, except relatively narrow ^{63}Cu(2) and ^{65}Cu(2) NQR lines, the spectrum of Tm1237 (similar with that of Y1237 [3]) have a broad "pedestal" (P).

It has been recently suggested [3] that the spectrum P arises from copper nuclei wich are located in areas with a partly disordered oxygen sublattice of basal CuO planes (for example, in the areas of twin boundaries) and, respectively, with a reduced and locally inhomogeneous hole concentration in the CuO_2 planes. In the spectrum of the Tm1248 sample such a pedestal is absent. Subtracting P from the observed "raw" spectrum, we obtain the spectrum of a "good" 1237 superconductor, free (or almost free) of crystal structure defects. In fact, this refinement procedure makes possible a subsequent quantitative analysis of the Cu(2) NQR lineshape of the 1237 superconductor having an undistorted or slightly distorted orthorhombic structure. Fitting of the Cu(2) NQR spectra of Y1237 by using a superposition of Gaussian-type lines has shown [3], that the spectrum P can be satisfactorily described by a single Gaussian with a temperature-independent rms width of 1.5(1) MHz. The corresponding width of the Tm1237 pedestal appeared to be somewhat bigger (1.9(1) MHz), whereas the relative intensities of the P-spectra in both Y1237 and Tm1237 samples were found approximately equal to 1/3.

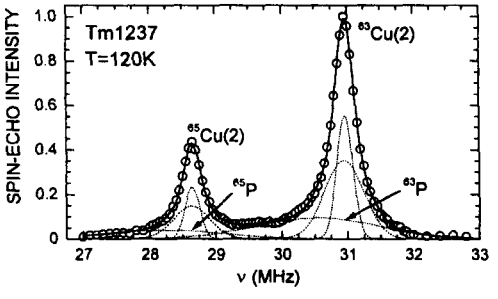

Fig.1. The Cu(2) NQR spectrum in Tm1237 at $T = 120$ K; the solid line is a best fit by six Gaussians (dotted lines, for detailes see Ref.[3])

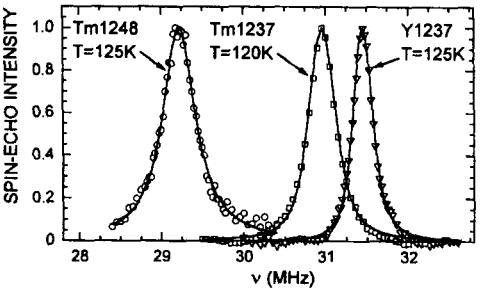

Fig.2. The ^{63}Cu(2) NQR lines in Y1237, Tm1237 (as obtained by subtracting of a "pedestal" P from the experimental spectra, see Fig.1 and text for details), and in Tm1248. The solid lines are a best fit by Eqs.(1),(2) with $k = 2$, $l = 2$; for other parameters of the model see Fig.3

The refined spectra of Y1237, Tm1237 (experimental spectra minus "pedestals") and the "raw" spectrum of Tm1248 are shown in Fig.2 for the ^{63}Cu isotope. The common property of all the lines in Fig.2 is that their shape is intermediate between Gaussian and Lorentzian. Such a shape being non-typical for resonance lines in the rigid-lattice solids can be regarded as a hint that some kind of a charge motion takes place in the CuO_2 planes. Assuming this motion to be the case for high-T_c cuprates, one can immediately find a qualitative explanation for two puzzles existing from the very beginning of the high-T_c story. First, the striking fact that the electric field gradient at the orthorhombic Cu(2) sites has an axial symmetry ($\eta \approx 0$) can be understood just as a result of the motional averaging. Second, a strong inhomogeneous broadening of the Cu(2) NQR lines which is observed at low temperatures can be then considered as resulting not only from an appearance of some excess distortions of a crystal lattice but also from changes in the characteristics of the charge motion. In what follows, we try to analyse the shape of the Cu(2) NQR lines (Fig.2) using a model of two NQR frequencies (ω_1, ω_2) between which the Cu(2) nucleus can rapidly jump. When applying the "motional narrowing model", we expect to find it capable to take hold of an essential difference in the Cu(2) NQR parameters at temperatures above and below T_c. For this simplest version of the model,

the shape of the Cu(2) NQR spectrum can be described by the following expressions [3]:

$$S(\omega) \sim \int I(\omega, \Omega) \exp[-(\Omega - \omega_0)^2/2\sigma^2] d\Omega, \quad (1)$$

$$I(\omega, \Omega) \sim [(\omega_2 - \omega_1)^2 (W_2 + W_1)]/[(\omega - \omega_1)^2 (\omega - \omega_2)^2 + (W_1(\omega - \omega_2) + W_2(\omega - \omega_1))^2]. \quad (2)$$

Here $\omega_1 = \Omega + l \times D$, $\omega_2 = \Omega - \Delta$, the frequency shifts $(+l \times \Delta)$ and $(-\Delta)$ are due to fluctuations of a hole density in the 1-st and 2-nd states, respectively, $1/W_i$ is the lifetime of the i-th state, $W_1 = k \times W$, $W_2 = W$. The individual NQR line is assumed to be inhomogeneously broadened due to crystal lattice defects, so its shape is Gaussian with the rms halfwidth σ, and $\omega_0 = <\Omega>$ is the mean NQR frequency over the sample volume. One may regard the above model as being oversimplified since the crystalline defects should also result in a random distribution of the other parameters, i.e., Δ, W, k and l. However, it was shown recently [3] that the Cu(2) NQR spectrum shape in the Pr-doped Y1237 compound can be well fitted by Eqs.(1),(2) at the values $k = l = 2$ corresponding to the particular conformation of charge stripes in the CuO_2 planes [6]. Therefore, we start with the same model $k = 2$, $l = 2$ which is expected to give some averaged values of Δ and W.

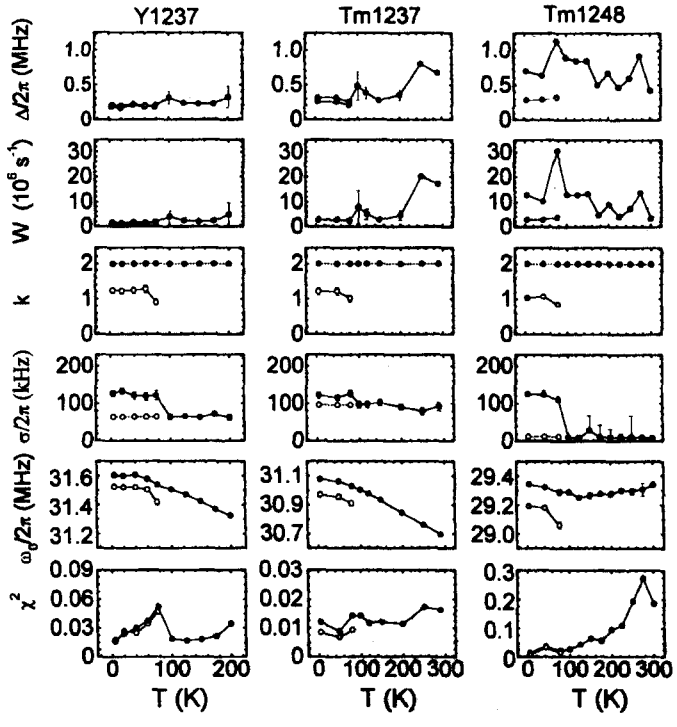

Fig.3. The temperature dependences of the parameters $\Delta/2\pi$, W, k, $\sigma/2\pi$ and $\omega_0/2\pi$ of the Eqs.(1),(2) as obtained from fitting of the "refined" ^{63}Cu(2) NQR lines in Y1237, Tm1237, and of the "raw" ^{63}Cu(2) NQR line in Tm1248. Filled circles correspond to the model: $k = 2$, $l = 2$, σ-variable; light circles correspond to the model: k-variable, $l = 2$, $\sigma = \text{const}$ $(\sigma_n = \sigma_s)$

The temperature dependences of the parameters $\Delta/2\pi$, W, $\sigma/2\pi$, and $\omega_0/2\pi$ for the ^{63}Cu(2) NQR lines in all three samples are shown in Fig.3 by solid circles, and the examples of calculated line shapes are illustrated by solid curves in Fig.2. For all the samples, the case of an intermediate jumping rate is realized,

$$(\omega_1 - \omega_2)/W \sim 1, \quad (3)$$

and the rate itself, W, appears to be rather low: $W = 2 \cdot 10^6 \div 2 \cdot 10^7$ s^{-1}. In fact, by the Eq.(3), the jumping rate is closely coupled with the frequency difference $\omega_1 - \omega_2 = 3\Delta$. It is interesting to notice here that the values of $(\omega_1 - \omega_2)/2\pi$ appear to lie in the frequency range from 0.7 MHz (separation of the ^{63} Cu(2) NQR lines in the Pr-doped Y1237 [3]) to 2.2 MHz (separation of the A- and B-lines in $La_{2-x}Sr_xCuO_4$, $La_2CuO_{4+\delta}$ [7]). In two of three samples studied, Y1237 and Tm1237, the difference $(\omega_1 - \omega_2)$ seems to exhibit a sharp decrease at the superconducting transition. However, the most striking result is that in all the samples under study the inhomogeneous linewidth σ undergoes a sharp increase at T_c, so that one actually has two different values of σ, i.e., σ_n for $T > T_c$ and σ_s ($> \sigma_n$) for $T < T_c$, which seem to be temperature-independent. The small width σ_n in Tm1248 is close to that usually observed in the ^{63}Cu(2) NMR spectra of the crystallographically-perfect materials in a high external magnetic field. For the 1237 compounds, which are known to have many structural defects, the σ_n-values appear to be rather large. As to the σ_s-value, it is found to be the same for all three samples, $\sigma_s \approx 0.8 \cdot 10^6$ s^{-1}. The latter fact can be regarded as a hint that the broadening of the Cu(2) NQR line at $T < T_c$ reflects some intrinsic property of high-T_c cuprates. In principle, the broadening of the copper NQR lines can originate from disordering of both atomic positions and charges of ligands. Since the values of σ_n in 1237 compounds are much bigger than that in Tm1248, they can be naturally attributed to a disorder of oxygen positions in CuO basal planes. It is known [8] that even in the almost stoichiometric Y123-6.98 single crystal the chain oxygen is statically displaced in the a-direction by 0.074(10) Å. Starting from this point, we then arrive at the conclusion that the same type of oxygen displacements should exist in Tm1248 below T_c. In fact, the dynamical displacements of chain oxygens in the a-direction by 0.1 Å resulting in a formation of ferroelectric domains were found to be present in the Y1248 compound [9]. If those displacements are indeed responsible for broadening of the Cu(2) NQR line in Tm1248, one can conclude from the static nature of the linewidth σ_s that the oxygen motion in CuO chains slows down or even freezes at $T < T_c$. The modification of charge motion in CuO chains at $T = T_c$, if exists, may have an indirect effect onto electronic state of CuO_2 planes via an abrupt re-distribution of holes between chains and planes.

Alternatively, the broadening of the Cu(2) NQR spectra at $T < T_c$ can be explained as arising from an abrupt re-distribution of charges in CuO_2 planes. In the particular conformation of charge stripes [3 – 6], two types of Cu(2) ions are distinguished (see Fig.2b, c in Ref. [6]) – those located at the center of the stripe (type 1, the hole density on the nearest oxygen ligands is high) and those at the stripe boundaries (type 2, the hole density is low). At the optimal doping of the CuO_2 planes by holes (i.e., for close packing of the stripes in rows -2-1-2-2-1-2-) the number n_2 of centers 2 appears to be twice as large as that of centers 1 (n_1), for which case $k = W_1/W_2 = n_2/n_1 = 2$. Fitting of the experimental ^{63}Cu(2) NQR lines by Eqs.(1),(2) with k and l being free parameters (along with Δ, W, σ) has shown the parameter l to be temperature-independent and close (in average) to the value of 2. When performing the subsequent fits with the constant $l = 2$ and variable k, we have obtained a striking result: it appeared that the experimental data for $T < T_c$ can be well described (light circles in Fig.3) by using a constant value of $\sigma_s = \sigma_n$, the only condition necessary for this being $k \sim 1$. At $T < T_c$ the parameter χ^2 for the model $k = 1$, $l = 2$ is definitely smaller than that for $k = 2$, $l = 2$. In the frame of the model under discussion the latter result can be interpreted as a hint for a modification of

a stripe pattern at the superconducting transition. In particular, the stripe conformation of the -1-2-1-2-1-2- type or the checkerboard pattern can be deduced from the above condition $k = 1$. The decrease of k from 2 (above T_c) to 1 (below T_c) may actually mean that the lifetime of Cu(2) ions in the state with a high NQR frequency (corresponding to a high local density of holes at neighboring oxygen ions in CuO_2 plane) becomes longer in a superconducting state. Moreover, the frequency difference $(\omega_1 - \omega_2)$ appears to be smaller at $T < T_c$ which, perhaps, indicates that the charge-stripe modulation in a superconducting state is weaker than that in a normal state or that, in other words, charge-density-waves in CuO_2 planes coexist but compete with superconductivity.

When interpreting the experimental results on the Cu(2) NQR in the framework of the stripe model [6] we do not rule out the possibility of other modifications for charge-density-waves in the CuO_2 planes. It should be noted, however, that the above model seems to get an indirect confirmation in the inelastic neutron scattering studies of $YBa_2Cu_3O_{6.6}$ [10–13]. Indeed, if one takes every third hole-rich stripe in Fig.2*b* of Ref.6 away, the mean hole concentration p becomes equal to $(2/3) \times (1/6) = 1/9$ per CuO_2 unit, and, according to the empirical formula $p = 0.187 - 0.21 \times \delta$ [14], the oxygen index $7 - \delta = 6.64$ appears to be close to 6.6. The resulting stripe pattern should give rise to the magnetic neutron scattering not at $\mathbf{Q}_{AF} = (1/2, 1/2)$, but instead at $(1/2 \pm \delta, 1/2 \pm \delta)$ with $\delta = 1/18 = 0.0556$. The very recent INS experiments with the $YBa_2Cu_3O_{6.6}$ single crystal have revealed such an incommensurate structure with $\delta = 0.057 \pm 0.006$ [13].

In conclusion, the analysis of the shape of ^{63}Cu(2) NQR spectra in Y1237, Tm1237 and Tm1248 compounds performed on a basis of a simplified model of motional narrowing supports the idea that the Cu(2) nucleus possesses two different resonance frequencies between which it can jump. The plausible cause of this difference in frequencies seems to be related to charge-density-waves (or dynamical charge-stripe-correlations) in CuO_2 planes resulting in a dynamical modulation of the electric field gradients at Cu(2) nuclei.

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