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COMPARATIVE STUDIES OF THE Tm NMR IN THULIUM 123 AND 124 COMPOUNDS: EVIDENCE FOR STRUCTURAL AND ELECTRONIC PHASE SEPARATION

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The ^{169}Tm nuclear magnetic relaxation in $TmBa_2Cu_3O_{6+x}$ ($x = 0.1 - 1.0$, $\Delta x = 0.1$) and $TmBa_2Cu_4O_8$ is studied at temperatures below 5 K. In all the samples, the Tm spin-lattice relaxation proceeds via intrinsic paramagnetic centers (PCs) like Cu^{2+} or copper-oxygen spin-polarized clusters. The experimental data for $TmBa_2Cu_3O_{6+x}$ support the idea of the structural (chemical) micro-phase separation in oxygen-deficient 123 compounds. Apparently, the samples with $x \geq 0.4$ contain hole-poor non-superconducting regions enriched with PCs and hole-rich (PC-poor) superconducting regions. The volume fraction f_n of the PC-rich phase reaches a maximum value of 0.85 at $x = 0.4$ and decreases monotonically at x increasing ($f_n = 0.5$, 0.3 and 0.25 at $x = 0.5$, 0.6 and 0.7, respectively). The Tm spin-lattice relaxation in the underdoped $TmBa_2Cu_4O_8$ compound indicates that this sample, in contrast to oxygen-deficient $TmBa_2Cu_3O_{6+x}$, has a homogeneous composition. However, the Tm spin-spin relaxation measurements reveal two sorts of the Tm nuclear spins in Tm124 having different NMR spectra and different relaxation times T_2. The latter result gives an evidence for the electronic phase separation in CuO_2 planes.

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In our earlier experiments with $TmBa_2Cu_3O_{6+x}$ samples [1-3] we have studied the ^{169}Tm NMR at liquid helium temperatures and arrived at the conclusion supporting the idea [4-6] that the superconductivity of the oxygen-deficient 123 compounds is provided by a percolative network of mesoscopic platelike OrthoI and OrthoII domains. In particular, it was suggested that the walls of percolative cluster are enriched by $Cu^{2+}(2)$ paramagnetic centers (PCs) which are characterized by a slow ($\sim 10^8$ s^{-1}) spin dynamics. The concentration of those "intrinsic" PCs was found to be strongly dependent on the oxygen content reaching a maximum value of $\sim$0.07 per unit cell at the "semiconductor-superconductor" transition ($x = 0.4$). Further investigations of the ^{169}Tm NMR in oxygen-deficient compounds ($x = 0.5$, 0.6) at temperatures from 4.5 K down to 0.7 K have revealed that the PCs are likely located in CuO_2 planes [7]. In papers [1-3,7], all the experimental data on the Tm nuclear spin-lattice relaxation (NSLR) have been interpreted on a basis of the assumption that PCs are homogeneously distributed over the crystal lattice, i.e., the PC concentration is constant over the whole volume of the sample. However, this is certainly not the case for the multi-phase 123 compounds. Having in mind to check carefully whether the micro-phase separation in oxygen-deficient $TmBa_2Cu_3O_{6+x}$ superconductors may exhibit itself

in the multi-component Tm relaxation, we have performed a new series of the Tm NSLR measurements at temperatures from 5 K down to 0.7 K. For comparison, the $TmBa_2Cu_4O_8$ compound was also studied in which the structural (chemical) micro-phase separation is known to be absent. All the TmBaCuO powdered samples were well annealed, mixed with paraffin and partially aligned in a magnetic field. The $TmBa_2Cu_3O_{6+x}$ samples ($x = 0.1 \div 1.0$, $\Delta x = 0.1$) were studied previously in [1-3], and $TmBa_2Cu_4O_8$ was studied in [8]. All the experiments were performed with home built pulsed NMR/NQR spectrometers. The temperatures from 1.2 K down to 0.7 K were obtained in a ^{3}He cryostat. The Tm NSLR times T_1 were measured at frequencies ν from 31.5 to 50 MHz, but when measuring in the field $H \perp c$ the H value always was chosen according to $H/\nu = 2\pi/\gamma_a = 0.189\,\mathrm{Oe/kHz}$ condition where γ_a is the effective gyromagnetic ratio of the thulium nuclei in the field $H \| a$ [1,9].

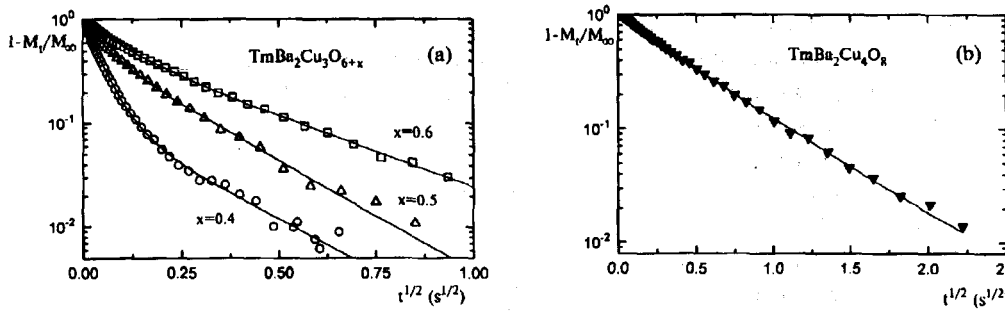

Fig.1. Tm nuclear spin-lattice relaxation in $TmBa_2Cu_3O_{6+x}$ (*a*) and $TmBa_2Cu_4O_8$ (*b*) in the field H(kOe)=0.189ν(MHz) at $T = 1.5$K. Solid lines represent (*a*) Eq.(4) and (*b*) Eq.(1): *a* - $x = 0.4$, $\nu = 48.45$ MHz, $f_n = 0.85(1)$, $1/T_{1n} = 590(20)$ s^{-1}, $1/T_{1s} = 30(5)$ s^{-1}; $x = 0.51$, $\nu = 31.55$ MHz, $f_n = 0.44(2)$, $1/T_{1n} = 383(20)$ s^{-1}, $1/T_{1s} = 27(1)$ s^{-1}; $x = 0.6$, $\nu = 47.7$ MHz, $f_n = 0.30(1)$, $1/T_{1n} = 314(29)$ s^{-1}, $1/T_{1s} = 13.0(5)$ s^{-1}; *b* - $\nu = 40.55$ MHz, $m = 0.46(1)$, $1/T_1 = 2.14(1)$ s^{-1}

The Tm NSLR kinetics in $TmBa_2Cu_3O_{6+x}$ ($x = 0.1 \div 1.0$) at temperatures 0.7–5K was found to approximately obey the relation

$$1 - M_t/M_\infty = \exp(-(t/T_1)^m), \qquad (1)$$

with M_t the magnetization at time t, and $m = 1/2 \div 1/3$ reaching the minimum value 1/3 for the $x = 0.5$ sample at $T = 0.7$K. The examples of the Tm magnetization recovery curves are shown in Fig.1*a*. The kinetics Eq.(1) are known to be valid in the absence of a nuclear spin diffusion. A strong inhomogeneous broadening is typical for all the Tm NMR spectra indicating not only the scattering of the effective γ_i-values due to local distortions of the crystal electric field at Tm sites but also the presence of the local magnetic fields produced by Cu^{2+} spins [1,2]. In this case the Tm nuclear spins having different Larmor frequencies relax directly via acceptor PCs randomly distributed in a crystal lattice, so that one has [10]

$$1 - M_t/M_\infty = \Pi_j[1 - c + c\exp(-t/T_1(\mathrm{r}_j))], \qquad (2)$$

where c is a fraction of a certain sub-lattice sites occupied at random by PCs, and $T_1^{-1}(\mathrm{r}_j)$ is the rate of the relaxation induced by the PC at site j. If the nuclear spins are coupled with PCs by a dipole-dipole interaction ($1/T_1(\mathrm{r}_j) \sim r_j^{-6}$) and the PC concentration is small ($c \ll 1$), the Eq.(2) transforms into Eq.(1) with $m = 1/2$ and $1/3$ for three- and two-dimensional distributions of PCs, respectively [7,11]. We have performed a computer simulaion of the Tm relaxation using the basic equation (2) where the relaxation rate $1/T_1(\mathrm{r}_j)$ was taken in the following simplified form:

$$1/T_1(\mathrm{r}_j) = (a_0/r_j)^6 W \tag{3}$$

where $a_0 = 3.8\mathring{A}$ and $c_0 = 3a_0$ are the lattice parameters, and W is the rate of the relaxation induced by the PC at distance a_0. This simplification could seem to be too rough. Actually, we could have taken into account the angular dependence of the rate $1/T_1(\mathrm{r}_j)$, which in the case of "ordinary" nuclei (like ^{89}Y) is expressed by $\sin^2\Theta_j \cdot \cos^2\Theta_j$ (Θ_j is the angle between H and r_j) and is more complicated for Tm nuclei characterized by the highly anisotropic γ-tensor [1,2]. However, as follows from computer simulations, in the case of non-aligned (or partially aligned) $TmBa_2Cu_3O_{6+x}$ powder the Tm relaxation kinetics calculated in this simplified way differs only slightly from the exact results obtained by angular overaging of Eq.(2) (details of the simulations will be described elsewhere [11]). Most important, the computer simulations have shown that the model of a homogeneous random distribution of PCs in the $TmBa_2Cu_3O_{6+x}$ crystal lattice can provide only the power $m \sim 1/2$ but it fails in providing the power $m \sim 1/3$ at any type of the PC location (at whether Cu(1) or Cu(2) sites). On the other hand, the simple relation

$$1 - M_t/M_\infty = f_n \exp(-(t/T_{1n})^{1/2}) + (1 - f_n)\exp(-(t/T_{1s})^{1/2}) \tag{4}$$

has been found to fit excellently all the experimental relaxation curves (including those of the two-fold coordinated Cu(1) nuclei measured at the NQR frequency of 31.55 MHz). These results shown in Fig.2 support the idea [2,5,6] of the micro-phase separation in oxygen-deficient 123 compounds. Apparently, the samples with $x \geq 0.4$ contain hole-poor non-superconducting regions (n-phase) and hole-rich superconducting regions (s-phase). The Tm nuclei characterized by the short relaxation time T_{1n} can be thought as belonging to the droplets of the n-phase enriched with PCs outside the percolative SC cluster of the s-phase. The volume fraction f_n of the n-phase reaches its maximum value of 0.85 at $x = 0.4$ and decreases monotonically at x increasing. The computer simulation of the Tm relaxation curves in $TmBa_2Cu_3O_{6+x}$ (see Fig.1a) makes it possible to estimate the PC concentrations in both n- and s-phases. For example, treatment of the experimental results for the $x = 0.5$ sample obtained at the frequency of 31.5 MHz at temperatures from 1 K to 5K gives $c_n = 0.026$ and $c_s = 0.0075$ per Cu(2) site, and the relaxation rate $W = (2 \div 3) \cdot 10^4\,\mathrm{s}^{-1}$. From the frequency dependence $T_1^{-1} \sim \tau/(1 + \omega^2\tau^2)$ of the Tm NSLR rate in the $x = 0.5$ sample at $T = 4.2\,\mathrm{K}$, it was found that the fluctuation rates ($1/\tau_n = 6(2) \cdot 10^8\ \mathrm{s}^{-1}$ and $1/\tau_s = 2.0(3) \cdot 10^8\ \mathrm{s}^{-1}$) of the local magnetic fields produced by PCs at Tm sites in n- and s-phase are roughly proportional to the PC concentrations (c_n and c_s).

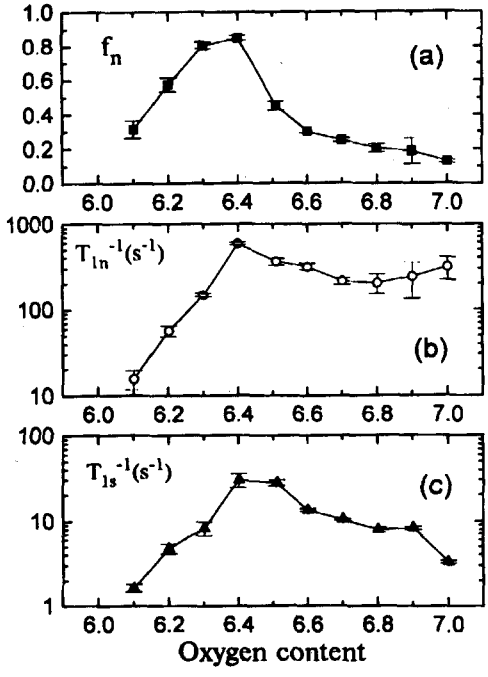

Рис.2

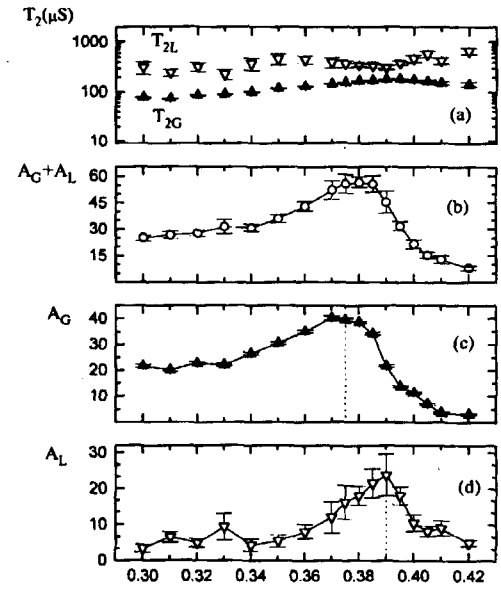

Рис.3

Fig.2. Tm spin-lattice relaxation parameters (see Eq.(4)) for $TmBa_2Cu_3O$

Fig.3. Tm NMR in $TmBa_2Cu_4O_8$ in the external field H parallel to the predominant orientation c' of the c axes of the crystallites in the partially oriented powder: $T = 1.5$K, $\nu = 22.7$ MHz, RF pulses are $1\mu s$ and $2\mu s$. (a) – field dependences of the short (T_{2G}) and long (T_{2L}) spin-spin relaxation times (see Eq.(5)), (b) - total NMR spectrum ($A_G + A_L$) *vs.* H/ν, (c) and (d) - sub-spectra of rapidly relaxing (A_G *vs.* H/ν) and slowly relaxing (A_L *vs.* H/ν) Tm nuclei. Note the 3%-difference in resonance fields.

As it was pointed out earlier [9], the Tm NMR spectrum in $TmBa_2Cu_4O_8$ is similar with that in $TmBa_2Cu_3O_{6.5}$ (OrthoII phase). However, the Tm NSLR kinetics in $TmBa_2Cu_4O_8$ at temperatures 1.5-4.2 K (for example, see Fig.1*b*) is found to obey Eq.(1) with $m = 0.50(4)$ indicating that this compound, in contrast to $TmBa_2Cu_3O_{6.5}$, has a homogeneous composition. Accordingly, the computer simulation has shown that the relatively small amount of PCs ($c = 0.001$, spin $S = 1/2$) is homogeneously distributed over Cu(1) "chain" sites.

Let us consider now the spin-spin relaxation of Tm nuclei at liquid helium temperatures. The spin-echo kinetics in $TmBa_2Cu_3O_{6+x}$ superconductors at $T = 1.5$K were previously found [2] to have the following two-component form

$$A_{2\tau} = A_G \exp(-\frac{1}{2}(\frac{2\tau}{T_{2G}})^2) + A_L \exp(- \qquad (5)$$

with $T_{2G} = 65 - 70$ μs and T_{2L} increasing monotonically from 90 μs at $x = 0.5$ to 400 μs at $x = 0.9 - 1.0$. Since the ratio A_G/A_L has been found reaching its maximum value of 2 in the optimally-doped samples [12], we have concluded that not only structural defects produced by oxygen vacancies in CuO_x layers but

also quasi-one-dimensional spin and charge correlations ("stripe correlations") in CuO_2 layers can be responsible for the two-component spin-spin relaxation of Tm nuclei. In the stripe model [12,13], two sorts of the Tm sites appear due to two types of the Cu(2) atoms, i.e. one type located at the center of the conducting (hole-rich) stripes and the other type at the edges of the stripes. The recent studies of the Cu(2) NQR spectra in $TmBa_2Cu_4O_8$ [8] have supported this idea of the frustrated electronic phase separation in CuO_2 planes [14] showing that the separation likely occurs at temperatures below $T^* = 150$ K when the so-called "spin gap" opens in the magnetic excitation spectrum. The $^{63}Cu(2)$ NQR lineshape in $TmBa_2Cu_4O_8$ was considered in [8] as resulting from two superimposed Gaussian lines characterized by different widths (~300 kHz and ~600 kHz at 4.2K). However, the very small difference in resonance frequencies (<5kHz at 4.2K and ~50 kHz at 300 K) remained up to now as a principal argument against the procedure of the decomposition of the Cu(2) NQR spectrum into two components, and consequently, against the interpretation of the experimental data given in [8]. Looking for the other nuclear probe more sensitive to local changes of a crystal electric field, we have measured the Tm spin-spin relaxation in $TmBa_2Cu_4O_8$ at 1.5 K and found it to obey the same relation Eq.(5) as in $TmBa_2Cu_3O_{6+x}$. Since the contribution of slowly relaxing Tm nuclei to the echo signal (the second term in Eq.(5)) is relatively small, the fitting of the echo decay curves without statistical weighting could not give sufficient accuracy in determining A_L and T_{2L} in Eq.(5). Thus the following fitting procedure had been accepted: (1) the preliminary fitting of the total experimental $A_{2\tau}$ curve which gave all four parameter values: A_G, A_L, T_{2G}, T_{2L}; (2) fitting the points for which $2\tau > 3T_{2G}$ by the second term of Eq.(5) and getting the A_L and T_{2L} values; (3) the final fitting of the total experimental curve by Eq.(5) with fixed A_L and T_{2L} values obtained in (2) and getting the final A_G and T_{2G} values which appeared to practically coincide with preliminary ones. When plotting the partial amplitudes A_G and A_L as functions of an external magnetic field (point by point), we have actually obtained two spectra in the field $H \| c$ and found the small (~3%) but definite difference in resonance fields of the rapidly relaxing (G-line) and slowly relaxing (L-line) Tm nuclear spins (Fig.3). The effective gyromagnetic ratio γ_c of the Tm nuclei exhibiting long T_{2L} times appears to be shifted to smaller values, i.e., somewhat closer to the γ_c-value in $TmBa_2Cu_3O_7$. In view of the fact that 124 compounds have a fairly perfect crystal structure free of planar defects [15], the observed splitting of the Tm NMR line in $TmBa_2Cu_4O_8$ seems to give evidence for the electronic phase separation in CuO_2 planes. The relative integrated intensities of the G- and L-lines in the range H/ν from 0.34 to 0.42 Oe/kHz are found to be 2.15:1 which supports again the stripe model of charge and spin correlations in CuO_2 planes [8,12,13].

In conclusion, the results of the Tm NMR studies of the thulium 123 and 124 compounds in a combination with the Cu NQR data support the principal ideas [14] about the frustrated electronic phase separation in high-T_c superconductors. Moreover, the experimental data indicate the important role played by the stripe correlations in CuO_2 planes. This work was supported in part by the Ministry of Science and Technology of Russia, the Scientific Council on Superconductivity, under Project 94029, by the NATO Scientific and Environmental Affairs Division,

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