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DECREASE OF THE HOMOGENEOUS WIDTH OF THE Tm^{3+} ELECTRON ENERGY LEVELS IN $TmBa_2Cu_3O_{6+x}$ AT THE SUPERCONDUCTING TRANSITION

A.V. Egorov[1,2], H. Lütgemeier[2], D. Wagener[3], A.V. Dooglav[1], M.A. Teplov[1]

[1] Kazan State University, 420008 Kazan, Russia
[2] Forschungszentrum Jülich, IFF, W-5170 Jülich, Germany
[3] Universität Bonn, Institut für Strahlen- und Kernphysik, W-5300 Bonn, Germany

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Enhanced NMR of ^{169}Tm (I=1/2) enhanced NMR has been studied in $TmBa_2Cu_3O_{6+x}$, x=0, 0.2, 0.4, at temperatures 1.2-40K. The nuclear magnetic relaxation rates at T>20K increase exponentially as $1/T_{1(2)} = R_{1(2)}\exp(-\Delta/kT)$, with Δ=176 K being the energy of the first excited state of the Tm^{3+} ion, while the $R_{1(2)}$ pre-exponential factors are inversely proportional to the homogeneous width Γ_o of this doublet state. The pre-exponential factors measured at the frequencies of 48 and 69 MHz show homogeneous broadening of the 4f-levels due to the decreasing dipole-dipole transfer of the electron excitations from ion to ion at increasing x because of crystal structure disordering. A sharp decrease of Γ_o (by about 0.9K) is observed in the superconducting compound with x=0.4 (T_c onset at 20K) at low temperatures and is attributed to the weakening of the 4f-electron-phonon interaction. At the temperatures around 6K the same sample displays enhancement of the transverse relaxation due to the relatively slow ($W \approx 10^9 s^{-1}$) fluctuations of the internal magnetic fields caused by Cu^{2+} ions in CuO_2 planes.

Among the rare-earths (RE) which are contituents of high-T_c compounds, praseodimium and thulium are of special interest for NMR-spectroscopy. If the 4f-shell ground state of Pr^{3+} ($4f^2$) or Tm^{3+} ($4f^{12}$) ions in a crystal electric field (CEF) is non-degenerate and the energy gap between the ground and excited states is large enough, then one can observe at low temperatures the magnetic resonance of 100%-abundant nuclei ^{141}Pr(I=5/2) and ^{169}Tm(I=1/2) [1]. The enhancement of the magnetic field by the 4f-electron shell makes the parameters of the NMR spectra and the relaxation times T_1, T_2 very sensistive to the details of the crystal and electron structure of dielectric and superconducting compounds. This was proved at liquid helium and lower temperatures [2,3,4]. However, it is obvious that the most interesting is RE NMR study at temperatures around T_c. The subject of the present work is the first enhanced NMR investigation at "high" temperatures. The method enables one to observe the sharp change in the homogeneous width of the 4f-electron energy levels at T_c.

The temperature range limitations for NMR experiments are due to relaxation of thermally excited 4f-electrons. These limitations can be easily understood by considering the following model system: (i) the crystal electric field is of axial symmetry, (ii) the first 4f-electron excited state is the doublet $|d>$ with the energy Δ, (iii) the nuclear spin is 1/2, so that the NMR spectrum is described by the nuclear spin Hamiltonian as follows:

$$\mathcal{H}_I = -\gamma_{\parallel}\hbar H_{oz} I_z - \gamma_{\perp}\hbar(H_{ox} I_x + H_{oy} I_y). \qquad (1)$$

In the external magnetic field H_0 perpendicular to the crystal c-axis the doublet $|d>$ is not split, and nuclear relaxation rates due to the fast fluctuations of the hyperfine magnetic fields are given by the following expressions [5]

$$T_1^{-1} = \left[2(A_J/\hbar)^2 a^2 + (1/2)(\omega_0 - \omega_I)^2\right] \tau_c \exp(-\Delta/kT) \quad , \qquad (2a)$$

$$T_2^{-1} = (1/2)T_1^{-1} + 5(\omega_0 - \omega_I)^2 \tau_c \exp(-\Delta/kT), \qquad (2b)$$

with A_J being the free ion hyperfine interaction constant, $a = < d \mid J_z \mid d>$ is the matrix element of the total angular momentum J of the 4f-electron shell, $\omega_o - \omega_I = (\gamma_\perp - \gamma_I)H_o$ is the difference in frequencies between