Nuclear spin–lattice relaxation of thulium in $TmBa_2Cu_3O_{6+x}$ at low temperatures

O. N. Bakharev, A. G. Volodin, A. V. Duglav, A. V. Egorov, O. B. Marvin, V. V. Naletov, and M. A. Teplov
Kazan University, 420008 Kazan, Russia

D. Wagner
Bonn University, Bonn W-5300, Germany

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"Amplified NMR" of thulium has been utilized to determine the positions of the paramagnetic Cu^{2+} centers in the crystal lattice of $TmBa_2Cu_3O_{6+x}$ ($x=0$–1). Analysis of the measured rate of spin–lattice relaxation of thulium nuclei in oriented TmBaCuO powders at low temperatures (to 40 mK) shows that in superconducting compounds ($x=0.4$–1.0) the paramagnetic copper centers are localized at walls between superconducting and nonsuperconducting microdomains. The average length of the segments of the CuO chains is estimated (~ 90 Å at $x=1.0$). The density of the paramagnetic $Cu^{2+}(2)$ centers is also estimated (2.4×10^{19} cm^{-3} at $x=1.0$).

The test samples were ceramic TmBaCuO samples, prepared by the method described in Ref. 1, ground into a powder, and oriented in a field of 94 kOe (Refs. 2 and 3). The diamagnetic susceptibility $\chi(T)$ was measured with an ac bridge (1 kHz, in a field $H_1=1$ Oe directed perpendicular to the c axis of the sample). The measurements revealed that the transition temperatures of six samples with $x=0.4$–1.0 were essentially the same as the T_c's of corresponding $YBa_2Cu_3O_{6+x}$ samples.[4] The $\chi(T)$ curve for $TmBa_2Cu_3O_{7.0}$ has two steps near 90 K (at 91.5 and 88.5 K). These steps are characteristic of overdoped 1–2–3 compounds.[4–7]

The NMR spectra of ^{169}Tm (spin $I=1/2$, natural abundance of 100%), "amplified" by the hyperfine interaction of the nuclei with $4f$ electrons,[2,8,9] are very sensitive to the structure of the crystal lattice. They are described by the Hamiltonian $\mathcal{H}=-\hbar\Sigma\gamma_i H_i I_i$, whose parameters $|\gamma_b/2\pi|$ and $|\gamma_c/2\pi|$ at $T\leqslant 4.2$ K have the following values[8,9] (in kHz/Oe): 6.8(1) and 2.20(5) in the ortho-I phase ($x=1$), 6.1(1) and 2.56(5) in the ortho-II phase, and 5.3(1) and 3.05(5) in the tetragonal phase ($x=0$). A particular feature of these spectra is that the parameter $|\gamma_a/2\pi|$ remains at the value 5.3(1) kHz/Oe in all three main phases. We made use of this circumstance in the present study. In the experiments described below, with various test samples, the frequency of the pulsed NMR spectrometer ranged from 42 to 50 MHz, but the strength of the field $H\perp c$ was in all cases chosen from the condition $H/\nu=2\pi/\gamma_a=0.189$ Oe/kHz. Here the resonant effect of the rf field $H_1=100$ Oe is felt by those particles whose a axes are nearly parallel to H. The spin–lattice relaxation time of thulium was measured by a $\pi/2-\pi-t-\pi/2-\pi$ pulse sequence, on the basis of a reconstruction of the amplitude of spin echo A_t with increasing time interval (t) between the pairs of pulses. We found that at $T<4.2$ K the kinetics of the

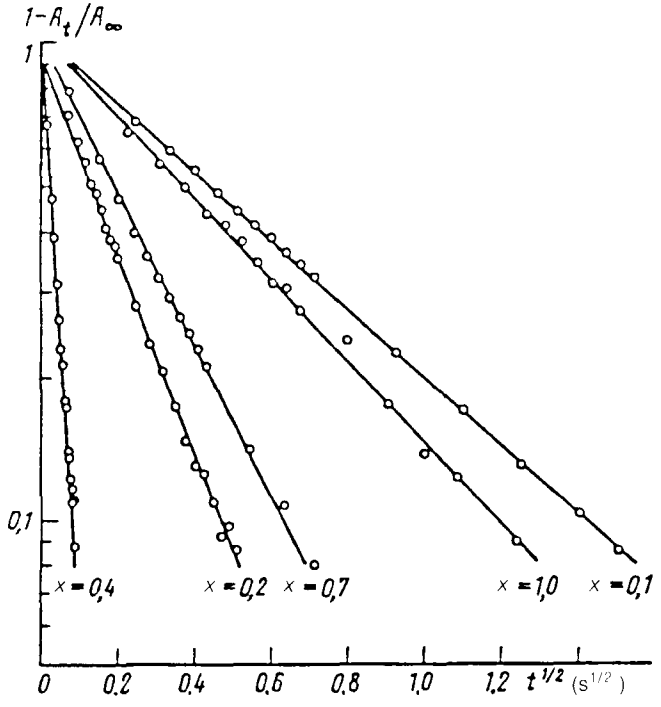

FIG. 1. Reconstruction of the longitudinal nuclear magnetization of thulium in oriented $TmBa_2Cu_3O_{6+x}$ powders in a field $H \parallel a$ at a temperature of 1.5 K. The straight lines are approximations by Eq. (1). From left to right: $T_1 = 1.3$ ms ($x = 0.4$, $\nu = 45$ MHz), 39 ms (0.2, 46 MHz), 75 ms (0.7, 47 MHz), 300 ms (1.0, 48 MHz), 385 ms (0.1, 48 MHz).

restoration of the longitudinal magnetization of the thulium can be described fairly well for all the samples by

$$1 - A_t/A_\infty = a \exp(-\sqrt{t/T_1}). \quad (1)$$

Because of the large nonuniform width of the NMR lines of the individual crystallites (even in a sample with $x = 0$ the line half-width is greater than[8] 300 Oe), the longitudinal component of the magnetization could not be rotated through a complete 90° by the rf pulses. For this reason, the value of a was < 1 in all cases; it varied from sample to sample, in the interval 0.65–0.85. For convenience in comparison of the results, we are using $a = 1$ in all cases in Fig. 1.

An $\exp(-\sqrt{t/T_1})$ kinetics is known[10,11] to be characteristic of disordered systems in which there is a pronounced nonuniform broadening of the NMR lines, and nuclear spin diffusion is hindered by the difference between the Larmor frequencies of the nuclear spins in neighboring lattice sites. At low temperatures in such systems, the nuclear spins transfer energy directly to paramagnetic centers, which are coupled well with phonons. For a random distribution of paramagnetic centers with a spin $S = 1/2$ in the crystal lattice, the rate of spin–lattice relaxation of the nuclei is given by[11]

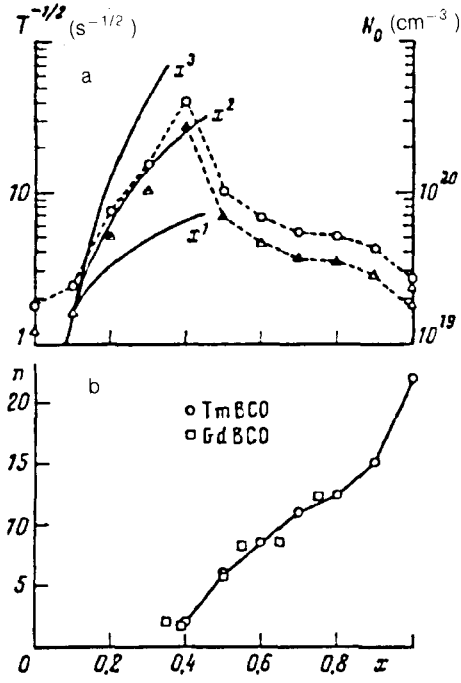

FIG. 2. a: Triangles—Square root of the rate of spin–lattice relaxation of Tm nuclei versus the oxygen content ($T=1.5$ K, $H \parallel a$, $\nu = 42$–48 MHz). The solid curves show x^n ($n=1,2,3$); the circles are explained in text proper. The dashed lines are drawn to aid the eye. The filled and open triangles for $x=1.0$ show the value of $\sqrt{1/T_1}$ at the beginning and end of the 5-month series of experiments. b: Average length of the segments of CuO chains in the $TmBa_2Cu_3O_{6+x}$ samples (data from the present study) and $GdBa_2Cu_3O_{6+x}$ samples (Ref. 20).

$$\frac{1}{T_1}=\frac{32}{15}\pi^3\mu_B^2N_0^2\gamma_\perp^2 g_\parallel^2\frac{\tau_c}{1+\omega^2\tau_c^2}\left(1-\tanh^2\frac{g_\parallel\mu_B H}{2kT}\right), \qquad (2)$$

where μ_B is the Bohr magneton, N_0 is the concentration of paramagnetic centers, $\omega = \gamma H$ is the NMR frequency, and τ_c is the correlation time of fluctuations in the local fields at the nuclei due to paramagnetic centers. Equation (2) holds when the nuclear spins and the paramagnetic centers are coupled exclusively by the magnetic dipole–dipole interaction. The quantities $g_\parallel$ and $\gamma_\perp$ should be understood as components of the g- and γ-tensors corresponding to directions along and across the spin quantization axis, i.e., along and across the external field H.

Figure 2a shows the results on the spin–lattice relaxation in a field $H \| a$ at $T=1.5$ K. In the interval $x=0.1$–0.4 there is an approximately quadratic dependence of $\sqrt{1/T_1}$ on x. If we set $\tau_c=\text{const}$ in (2), we find $N_0 \propto x^2$ in the interval $x=0.1$–0.4. It is natural to suggest that paramagnetic centers bound with $Cu^{2+}(1)$ ions in CuO chains are serving as acceptors in the spin–lattice relaxation of thulium, since the concentration of the latter increases with increasing x. However, if the paramagnetic-center–acceptors were bound to all the $Cu^{2+}(1)$ ions, including those in Cu–O–...–O–Cu chains, then we would have[12] $N_0 \propto x$. An $N_0 \propto x^2$ dependence is characteristic of the concentration of pairs formed by atoms distributed sparsely and at random in the lattice. In this case it might be suggested that the paramagnetic-center–acceptors localize near pairs of $Cu^{2+}(1)$ ions at the ends of chains. This assumption would make it possible to explain the peak in the rate of spin–lattice relaxation at the interface between tetragonal and orthorhombic phases ($x=0.4$): Only short segments of chains

form at $x<0.4$, while at $x>0.4$ they are combined into long segments, so the concentration of "end" $Cu^{2+}(1)$ ions and pairs formed by them decreases sharply (and the material goes superconducting).

To verify the condition $\tau_c=\text{const}$, we first find the quantity $\tau_c/(1+\omega^2\tau_c^2)$, making use of the measurements of the time T_1 in a sample with $x=0.4$. To pursue this analysis, we must correctly evaluate the average length ($n_{0.4}$) of CuO chains in our sample with $T_c=23$ K (Ref. 8). Superconductivity can arise only when the CuO_2 planes are doped with holes, and the doping is performed by segments of CuO chains with a length $n\geqslant 4$ (Ref. 13; here n is the number of oxygen atoms). However, the relative amount of superconductor in the samples with $x=0.4$ is small.[4,14] It is thus reasonable to assign $n_{0.4}$ a value of 2; this value (Fig. 2b) was extracted from measurements of nuclear quadrupole resonance of Cu(1) in a series of GdBaCuO samples,[15] related to our own samples in terms of preparation procedure. In a chain of length $n=2$, two Cu(1) atoms of the three are end atoms. Their relative number in the sample with $x=0.4$ is $(2/3)\times 0.4=0.27$. The concentration of pairs of such atoms should be $(0.27)^2$ of the total Cu(1) concentration, i.e., $N_0=4.1\times 10^{20}$ cm^{-3}. Substituting this value into (2) along with $\gamma_1^2=(\gamma_b^2+\gamma_c^2)/2$, $g_\parallel=2$, and the measured time $T_1=1.3$ ms, we find the equation $\tau_c/(1+\omega^2\tau_c^2)=1.1\times 10^{-9}$ s in the high-temperature approximation. With $\omega/2\pi=48$ MHz, this equation has the two roots $\tau_c=8.7\times 10^{-9}$ s and 1.3×10^{-9} s. Another possibility for evaluating τ_c arises from the results of a series of low-temperature measurements of T_1 in a sample with $x=0.8$ in a field $H\|c$. These measurements were carried out with the help of a ^{3}He–^{4}He dissolution refrigerator (Fig. 3). Comparing (2) with the measured relation $[T_1(39\text{ MHz})/T_1(24\text{ MHz})]_{T=4.2\text{ K}}=2$, we find a time $\tau_c=8.9\times 10^{-9}$ s, which is essentially the same as one of the values found above.

Armed with a constant value of τ_c, we can use the rates found for the nuclear spin–lattice relaxation (Fig. 2a) to estimate the average chain length in the superconducting samples. These estimates are based on the assumption that the measured value of $(1/T_1)^{1/4}$ is proportional to the number (p) of end $Cu^{2+}(1)$ ions in the given sample. Denoting by q the number of internal Cu(1) atoms in the CuO chains, we find a segment length[15] $n=1+2q/p$. As the origin of the scale we again adopt an average chain length $n_{0.4}=2$ in the sample with $x=0.4$. For this sample we have $(p+q)/p=3/2$. In a sample with $x>0.4$ the chain length is then

$$n_s=1+2\left[\frac{3}{2}\frac{c(x)}{c(0.4)}\left(\frac{T_1(x)}{T_1(0.4)}\right)^{1/4}-1\right], \tag{3}$$

where $c(x)$ is the relative number of $Cu^{2+}(1)$ ions. Figure 2b shows the average chain length in the superconducting TmBaCuO samples calculated from expression (3) with the help of experimental values[12] of $c(x)$ for YBaCuO. The good agreement between the values of n_x for TmBaCuO and GdBaCuO in the interval $x=0.4$–0.75 can be taken as indirect confirmation of the validity of the assumptions underlying our analysis. Under the condition $\tau_c=\text{const}$ we can also estimate the concentration of paramagnetic copper centers in our test samples, using the simple relation $N_0(x)\approx N_0(0.4)\cdot[T_1(0.4)/T_1(x)]^{1/2}$ (Fig. 2a). Again setting $N_0(0.4)=4.1\times 10^{20}$

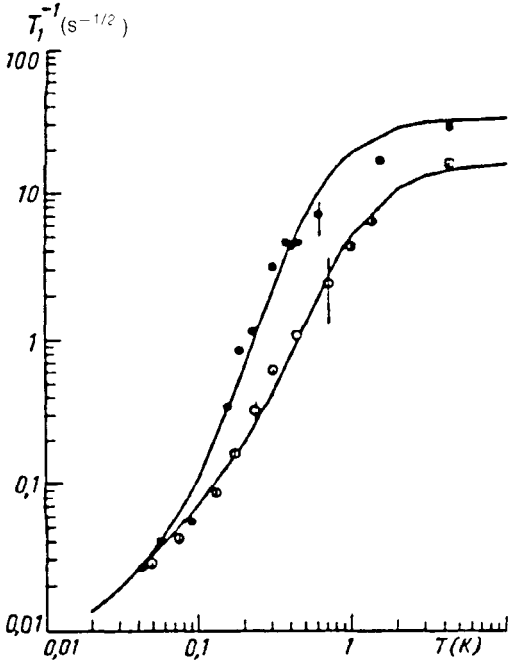

FIG. 3. Temperature dependence of the rate of spin–lattice relaxation of thulium nuclei in a $TmBa_2Cu_3O_{6.8}$ sample in a field $H \parallel c$. Open circles) $\nu = 39.3$ MHz, $H_0 = 16.0$ kOe; filled circles) 24.3 MHz, 9.5 kOe; solid lines) approximation by Eq. (4) with the parameter values $\Delta = 2.93$ kOe and $B = 13.5$ s^{-1} (upper curve) and 5.87 kOe and 6.58 s^{-1} (lower curve).

cm^{-3}, we find, in particular, a concentration $N_0 = 2.4 \times 10^{19}$ cm^{-3} for a superconducting sample ($x = 1.0$). This figure agrees well with data reported by other investigators.[16,17]

We turn now to the correlation time τ_c. Estimates show that this time is independent of x and N_0 and has a value of about 10^{-8} s. The origin of this time is not completely clear to us. It may be determined by the interaction energy (E_p) of the end $Cu^{2+}(1)$ ions in a pair along the c axis. Under the assumption that the Cu(1) moments are coupled by a purely dipole interaction, we use the relation $\tau \sim \hbar/E_p = \hbar r^3/S(S+1)g^2\mu_B^2$ to estimate the distance between $Cu^{2+}(1)$ spins in a pair. With $\tau = 8.9 \times 10^{-9}$ s, $S = 1/2$, and $g = 2$ we find $r \sim$ 13 Å ; i.e., the distance does indeed turn out to be close to the value of the lattice constant c. We should stress here that the experimental results at $T < 1$ K can be approximated by expression (2) only if we assume that the paramagnetic-center–acceptors are being influenced by nonuniform internal magnetic fields which are strong (on the order of several kiloersteds). Under the assumption that the distribution of local fields can be described by a Gaussian curve with a standard deviation Δ , we approximate the temperature dependence of the spin–lattice relaxation rate (Fig. 3) by

$$\frac{1}{T_1} = \frac{B}{\Delta}\int_{-25\text{kOe}}^{+25\text{kOe}} \exp\left(-\frac{H^2}{2\Delta^2}\right)\left[1-\tanh^2\left(0.0806\,\frac{H_0+H}{T}\right)\right]dH; \qquad (4)$$

here H_0 is the external field. It can be seen from Fig. 3 that the quantities Δ are expressed in kiloersteds. It would be hard to expect such strong fields (of explicitly

nondipole origin) in the system of $Cu^{2+}(1)$ ions, which are characterized by dipole fields ~ 400 Oe. These fields give a completely satisfactory explanation of the width of the copper ESR line observed at liquid-helium temperature.[18] In contrast, strong local fields are characteristic of a pair of CuO_2 planes, and the presence of such fields has been revealed by rare-earth probe ions.[14,19] Whatever the case, the set of facts and numerical estimates indicates that the paramagnetic copper centers responsible for the spin–lattice relaxation of thulium in the superconducting samples at low temperatures localize at interfaces between the superconducting and nonsuperconducting (oxygen-deficient) microdomains. At the same time, we know[12] that the $Cu^{2+}(1)$ moments are coupled with the $Cu^{2+}(2)$ moments in adjacent planes by a ferromagnetic interaction. In oxygen-deficient materials ($0.2 < x < 0.4$), the latter interaction leads to the formation of a type-II magnetic structure with a doubled lattice constant, $2c$. In a regular type-II structure, the directions of the $Cu^{2+}(1)$ spins, like those of the $Cu^{2+}(2)$ spins, freeze at liquid-helium temperature. The average magnitude of the Cu(1) moment is far smaller than that ($0.65\,\mu_B$) of the Cu(2) moment. In our case, on the other hand, there may be a motion of end $Cu^{2+}(1)$ spins combined in pairs along the c axis, as in a flip–flop process in paramagnetic systems—a motion which does not freeze even at ultralow temperatures. If this is the case, then this motion may involve a reorientation of Cu(2) spins coupled with Cu(1) spins and also low-frequency ($\sim 10^8\ s^{-1}$) fluctuations of strong local fields at rare-earth ions due to Cu(2) ions. In any case, it appears that the $Cu^{2+}(2)$ centers coupled with end $Cu^{2+}(1)$ ions by a ferromagnetic interaction should nevertheless be regarded as the actual acceptors of the energy acquired by the Tm nuclei at the resonance.

The time T_1 of the Tm nuclei measured at low temperatures is very sensitive to the state of the sample. At the end of a 5-month series of experiments, the value of T_1 in a sample with $x = 1.0$ fell nearly to half its original value (Fig. 2a), while the diamagnetic susceptibility ($-4\pi\chi$) measured at liquid-helium temperature decreased only 2% over this time (from 0.69 to 0.67). These changes are definite evidence that the overdoped 1–2–3–7 state is unstable.

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