

Singlet-ground-state paramagnetic centers in CuO_2 layers as seen from ^{169}Tm NMR in $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ superconductors

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The ^{169}Tm nuclear spin-lattice relaxation in oxygen-deficient $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ compounds, as quenched and room-temperature annealed, has been measured at low temperatures. The results are consistent with the existence of paramagnetic centers in the CuO_2 double layer, which have a nonmagnetic (singlet) ground state separated from an excited magnetic state by an energy gap of the order of 1 K.

Recent experiments on thulium-“enhanced” NMR in $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ compounds exposed to rather long room-temperature annealing (RTA) have shown^{1,2} that the ^{169}Tm (spin $I = \frac{1}{2}$, 100% abundance) nuclear spin-lattice relaxation (NSLR) at temperatures below 4.2 K is governed by paramagnetic centers (PC’s) distributed in CuO_2 planes at boundaries between superconducting and nonsuperconducting mesoscopic platelike domains of ortho-I or ortho-II structure. From the Tm NSLR data taken at temperatures down to 0.04 K the mean size of superconducting domains in the b direction was estimated to vary from 23 to 50 Å for $0.5 \leq x \leq 0.8$. The NSLR kinetics obey the so-called “Förster’s law,” $(1 - M_t/M_\infty) \propto \exp[-(t/T_1)^{1/2}]$, with M_t the magnetization at time t , and the T_1 the NSLR time. This relation is known to be valid in the absence of the nuclear spin diffusion. Based on the $^{169}\text{Tm}^{3+}$ NMR, Gd^{3+} EPR (see Ref. 3), and diamagnetic susceptibility measurements,⁴ a model for the oxygen-deficient 1-2-3 superconductor has been proposed² consisting of alternating superconducting (nonmagnetic) and nonsuperconducting (magnetic) CuO_2 bilayers or superconductor-insulator-superconductor (SIS) nanosandwiches. The experiments on dc and ac Josephson effects in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ single crystals with current flow in the c -axis direction also point to the existence of stacks of SIS Josephson junctions,⁵ the junction thickness in the Bi compound being of the order of 15 Å. These junctions are also suggested as an explanation for the so-called “Wohllleben effect” (or paramagnetic Meissner effect⁶⁻⁸) recently observed by the Karlsruhe group in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ single crystals.⁹

As concluded from specific-heat measurements,¹⁰ at small enough concentrations n_2 of the Cu^{2+} localized PC’s in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ compounds the superconducting volume fraction f_s reduces according to the approximate relation $f_s = 1 - n_2/0.012$, where n_2 is given in (mole Cu^{2+} /mole $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$). In fact, the f_s vs n_2 data deduced from the Tm NSLR and diamagnetic susceptibility measurements^{1,2} nicely confirm the data by Phillips *et al.*¹⁰ Therefore, the important role played by nanoscale magnetic properties in the superconductivity of oxygen-deficient 1-2-3 compounds becomes more and more evident and is being studied by a variety of techniques.^{1-3,11,12}

The present work continues the investigation of the Tm NSLR at temperatures below 4.2 K.^{1,2} Since PC’s in CuO_2 planes are, most likely, induced by the crystal lattice defects, such as oxygen vacancies, we studied the NSLR evolution as a function of RTA time. The procedure was similar to that described earlier.^{13,14} The principal goal of our experiments was to clarify the origin of those PC’s which might well explain both the NSLR effects, and the low-temperature specific heat of the 1-2-3 compounds.^{10,15,16}

Three nonequilibrium samples with $x \approx 0.5$ (A), 0.5(B), and 0.6(C) were prepared from the starting material with $x = 0.95$ (Cryos Ltd., Khar’kov) by annealing in air at 750 °C for 24 h (sample A), 5 h (sample B), and at 700 °C for 1 h (sample C) followed by fast quenching. Since the oxygen diffusion coefficient at temperatures above 700 °C exceeds¹⁷ $10^{-9} \text{ cm}^2 \text{ s}^{-1}$, the diffusion length $2(D_{t_0})^{1/2}$ for $t_0 > 1$ h was much greater than the maximum grain size of the starting material ($\approx 10 \mu\text{m}$), resulting in a homogeneous distribution of oxygen in the samples. After high-temperature annealing all samples were rapidly (< 1 s) quenched in liquid nitrogen. The diamagnetic susceptibility of each sample vs RTA time was studied using either an ac 1 kHz bridge (for sample A) or a superconducting quantum interference device magnetometer (for samples B and C), the critical temperatures T_c of the aged compounds (middle points of 32 K, 35 K, and 57 K, respectively, after two week RTA) being used for an estimation of x (Ref. 2). Sample A was measured as a “dry powder,” being aged for several progressively increasing RTA time intervals, whereas only two kinds of B and C samples mixed with teflon oil were studied by NMR, i.e., an “as quenched” one [RTA time ($t_{\text{RTA}} \approx 30$ min)] and an “aged” one ($t_{\text{RTA}} = 2$ weeks). Homebuilt pulsed NMR spectrometers were used to study the Tm NMR at frequencies ν of 48 MHz (sample A) and 90 MHz (samples B and C). The NMR spectra of ^{169}Tm nuclei in the samples annealed for the time $t_{\text{RTA}} > 1.5$ year are very sensitive to the structure of the crystal lattice (see Ref. 1 and references therein). They are described by the Hamiltonian $\mathcal{H} = -\hbar \sum \gamma_i H_i I_i$. The parameters $|\gamma_b/2\pi|$ and $|\gamma_c/2\pi|$ at $T \leq 4.2$ K have the following values 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)

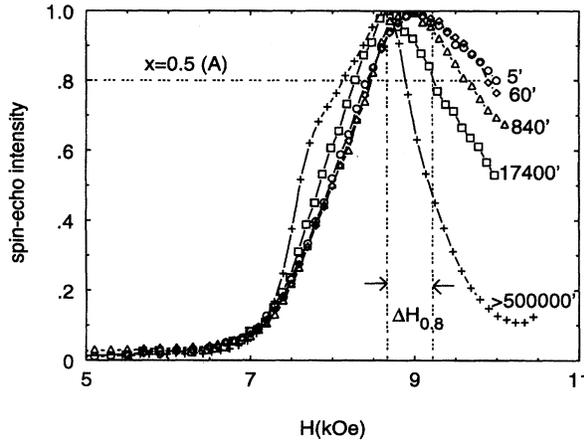


FIG. 1. ^{169}Tm NMR spectra in sample A annealed for $t_{\text{RTA}} = 5$ min (\circ), 60 min (\diamond), 840 min (\triangle), and 17 400 min (\square); $T = 1.5$ K, $\nu = 46.6$ MHz, 3-22-6 μs -pulse sequence, the magnetic field of $2\pi\nu/\gamma_a = 9.1$ kOe corresponds to the condition $\mathbf{H}_a \parallel \mathbf{a}$; the fit to the line with $t > 500\,000$ min ($+$) showed orthorhombic symmetry, see text.

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 relaxation measurements described below the strength of the field was always $H/\nu = 2\pi/\gamma_a = 0.189$ Oe/kHz. Here the resonant effect of the rf field of 100 Oe is felt mainly by those particles whose \mathbf{a} axes are nearly parallel to \mathbf{H} (Ref. 1). The temperatures from 1.2 K down to 0.7 K were obtained in a ^3He cryostat.

The RTA procedure of sample A results in the evolution of the Tm NMR spectrum from tetragonal to orthorhombic symmetry (Fig. 1), a decrease of the inhomogeneous half-width $\Delta H_{0,8}$ of the spectrum [Fig. 2(a)], and an increase of the critical temperature T_c [Fig. 2(b)], all these changes developing in a time scale of approximately 30 h. This characteristic time appears to be considerably longer than those found earlier for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ samples, i.e., ≈ 6 h for $x=0.41$ (Ref. 14) and ≈ 10 h for $x=0.45$ (Ref. 13). Such a discrepancy could be partially due to a difference in “room temperatures.” In every consequent “aging” cycle of our experiment sample A was lifted into a warm zone of the cryostat, where it was kept in a helium atmosphere for a certain time interval, and then rapidly cooled again. Therefore, the temperature of the sample inside the cryostat was slightly ($\approx 5^\circ\text{C}$) lower than the real room temperature. With an activation energy for oxygen diffusion of about 0.97 eV,^{13,17} the oxygen ordering rate would decrease by a factor of 3 if the temperature is 287 K instead of 296 K. Another reason for the discrepancy in τ values might be associated with the particular mesoscopic structure of the sample, which is known to be strongly dependent on the cooling (quenching) rate.¹⁸ The most peculiar features were found in the Tm NSLR at low temperatures:

(a) The Tm NSLR kinetics of the $\exp[-(t/T_1)^{1/2}]$ type observed for sample A at $t_{\text{RTA}} > 1000$ min [corresponding T_1 's are shown by filled circles in Fig. 2(c)] and found pre-

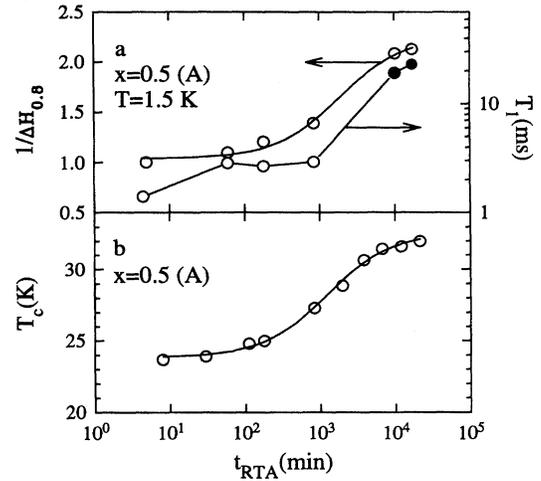


FIG. 2. The inverse half-width and relaxation time (a), and transition temperature (b) of sample A vs RTA time. The time evolution in (a) and (b) can be described with a $\tau/(\tau+t)$ dependence (Ref. 14), where τ is of the order of a day. For the difference between closed and open circles in the T_1 data, see text.

viously for well annealed TmBCO samples,^{1,2} transform into an $\exp[-(t/T_1)^{1/3}]$ type at short RTA times [empty circles in Fig. 2(c)].

(b) The $\exp[-(t/T_1)^{1/3}]$ -type NSLR kinetics are found for both the “as quenched” and the “aged” sample B at temperatures above ≈ 2 K [Fig. 3(b)], however the “ $\frac{1}{3}$ ” power in the “aged” sample B transforms into the “ $\frac{1}{2}$ ” power at $T < 1$ K [dashed line in Fig. 3(a)].

(c) The experiments with sample C [Fig. 3(c)] confirm the $\exp[-(t/T_1)^{1/2}]$ -type kinetics^{1,2} in the whole temperature range from 0.7 to 4.2 K.

(d) The temperature dependence of the NSLR rate of samples B and C (Fig. 4) obeys the law $T_1^{-1} \approx (1 - \tanh^2 \delta/2kT)$ characteristic for the NSLR via paramagnetic impurities.^{1,2}

Keeping in mind that the “ $\frac{1}{2}$ ” and “ $\frac{1}{3}$ ” powers in the $\exp[-(t/T_1)^n]$ -type recoveries are characteristic¹⁹ for three-dimensional (3D) and 2D distributions of PC acceptors, respectively, we explain the features mentioned above as follows. Depending on the average distance R between neighboring PC's, two regimes for NSLR can be distinguished: the 2D or high-concentration regime with $R < R_c$ and the 3D or low-concentration regime with $R > R_c$. R_c is a critical distance coupled in some way to the interlayer distance and the lattice parameter c_0 . Since the PC's are located at the boundaries of SC microdomains,^{1,2} one can assume the average distance R to be approximately equal to the mean length L of CuO chain fragments. In the equilibrium $x=0.5$ sample the value of L has been found to be approximately $6a_0$ or $2c_0$ (Refs. 1 and 2), so, in the A and B samples it can be reasonably assumed to be even smaller than $2c_0$. Thus, the critical value of $R_c \approx L$, separating 2D and 3D regimes of the NSLR kinetics from one another, indeed appears to be close to the lattice parameter c_0 .

The formula $T_1^{-1} \propto (1 - \tanh^2 \delta/2kT)$ holds usually for a two-level system with the Zeeman splitting $\delta = g\mu_B H$. However, the analysis of the experimental results show that the

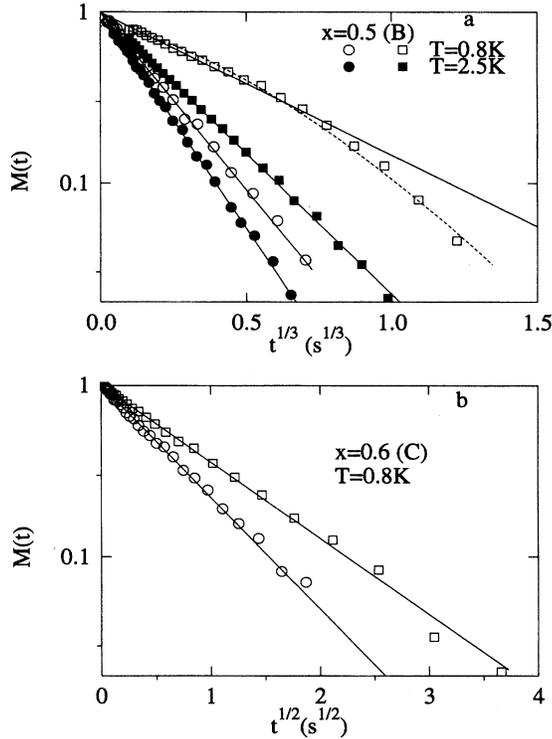


FIG. 3. The recovery of ^{169}Tm nuclear magnetization ($1 - M_t/M_\infty$) in $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ as quenched (circles) and aged (squares) for samples B and C, $\nu = 90$ MHz, $\mathbf{H}_a \parallel a$, $H = 17$ kOe. For discussion, see text.

PC acceptors cannot be described by a simple $S = \frac{1}{2}$ model for several reasons. (1) The g value of 3.1(1) for sample B is not consistent with plausible g values of Cu^{2+} localized PC's (2.05–2.4). (2) The g value appears to be field dependent: the NMR measurements at frequency of 125 MHz ($H = 23.6$ kOe) give $g = 2.6(2)$. (3) One can see that the transition from the 2D regime to the 3D regime can be driven by the decrease of the PC concentration, i.e., either by an oxygenation of the sample [cf. Figs. 3(b) and 3(c)] or by the RTA procedure for a long enough time [Fig. 2(c)]. The most interesting fact is, however, that this transition in the “aged” sample B can be driven also by the temperature lowering from 2.5 K down to 0.8 K [cf. Figs. 3(a) and 3(b)]. The latter fact means that the concentration of PC acceptors starts to decrease at low temperatures. Such an effect of a thermal depopulation cannot take place in simple two-level systems. However, it is well consistent with a model of a singlet-doublet (or singlet-triplet) system. Indeed, the effect of the thermal depopulation must occur in the system where the paramagnetic centers (or copper-oxygen complexes) in the CuO_2 planes have a nonmagnetic (singlet) ground state, separated from an excited magnetic state by an energy gap of the order of 1 K. A similar assumption has been discussed earlier^{15,16} in connection with an excess contribution to the specific heat of Y-Ba-Cu-O compounds at low temperatures.

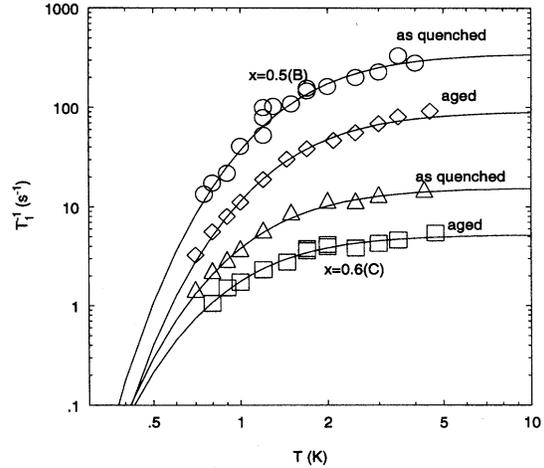


FIG. 4. ^{169}Tm NSLR rate in the samples B (\circ and \diamond) and C (\triangle and \square): $\nu = 90$ MHz, $H = 17$ kOe; the solid line represents the law $T_1^{-1} \sim (1 - \tanh^2 \delta/2kT)$ with $\delta = 3.6$ K (\circ), $\delta = 3.4$ K (\diamond), $\delta = 2.7$ K (\triangle), and $\delta = 2.3$ K (\square).

Pairs of PC's with weak antiferromagnetic interactions can be *a priori* expected to appear naturally in oxygen-deficient 1-2-3 systems, as we illustrate with the following example. Since $(1-x)$ oxygen vacancies exist in a unit cell of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ -like compounds, $2(1-x)^2$ pair O vacancies (n_2) appear in the neighboring CuO chains. Each O-pair vacancy attracts four O(4) apical atoms and four Cu(2) atoms from both below and above,²⁰ so that four copper spin dimples appear in both lower and upper CuO_2 layers, which may happen to be the traps for oxygen holes. Such a four copper spin cluster with a trapped oxygen hole has a spin $S = \frac{3}{2}$ in a ground state,²¹ and two clusters coupled by an antiferromagnetic exchange interaction $J_{\perp 2} = 0.04(1)$ meV (Ref. 22) may form the singlet pair state with the appropriate properties. The PC concentration in the $\text{TmBa}_2\text{Cu}_3\text{O}_7$ sample was estimated to be $n_2 = 0.0042$ mole PC/mole $\text{TmBa}_2\text{Cu}_3\text{O}_7$ (Ref. 1), in which case the real oxygen content $x = 1 - \sqrt{n_2/2}$ appears to be $x = 0.95$, i.e., very close to $x = 1.0$ (see also Ref. 23). Although in the discussion given above, the PC's were thought to be located in the CuO_2 double layer,^{1,2,21,24} we do not exclude other possibilities.²⁵

In conclusion, Tm NMR clearly shows the presence of paramagnetic centers in low-doped 1-2-3 compounds. The typical excitation energy as seen in the NMR experiments is of the order of a few kelvin. Our findings are consistent with a location of the centers in the CuO_2 double layers, although further experiments are needed for a quantitative description.

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 - ²⁵Indeed, recent studies of photo-induced superconductivity in oxygen-deficient YBa₂Cu₃O_{6+x} films [K. Tanabe *et al.*, *Phys. Rev. Lett.* **72**, 1537 (1994)] have revealed the critical hole density for both metallic conduction and superconductivity to be approximately $4 \times 10^{20} \text{ cm}^{-3}$ which is the same as the maximum PC concentration in TmBa₂Cu₃O_{6+x} observed at $x=0.4$, i.e., at the *T-O* phase transition boundary (Refs. 1 and 2). In combination with the facts that the mean length *L* of CuO chain fragments equals 2 and the PC concentration is equal to the concentration of these *L*=2 fragments at $x=0.4$ (Refs. 1 and 2), this may mean that all PC's at the critical oxygen content $x=0.35-0.4$ are localized in hole-doped Cu²⁺ - O²⁻ - Cu²⁺ - O²⁻ - Cu²⁺ chain fragments. After further oxygenation of the chains the mean length grows (*L*>3) resulting in an appearance of holes in CuO₂ planes [G. V. Uimin *et al.*, *Physica C* **192**, 481 (1992)] and a corresponding disappearance of those PC's, which are associated with the short CuO chain fragments. However, the dimensionality change seen in our *T*₁ measurements is easier to understand from the presence of PC's in the CuO₂ planes.