

Oxygen diffusion in $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ at room temperature

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The NMR of thulium-169 has been used to study the oxygen ordering dynamics in nonequilibrium $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ samples at room temperature. The average time for the diffusive hop $\text{O}(5) \rightarrow \text{O}(1)$ of an oxygen atom at room temperature has been found to be $\tau_{\text{RT}} \sim 1$ h. This result corresponds to a diffusion coefficient $D_{\text{RT}} \sim 0.5 \times 10^{-19} \text{ cm}^2/\text{s}$.

The process by which oxygen atoms become ordered in the nonequilibrium 1–2–3 compounds can be thought of as consisting of three steps: an ordering within fragments of CuO chains, an ordering of these chains in a 2D periodic structure (e.g., the Ortho II type), and, finally, an ordering of CuO_x planes in a 3D periodic structure.¹ The first step should be the fastest, since it requires only a single diffusive hop of an oxygen atom from an O(5) site to a chain O(1) site. We can estimate the average hopping time $\tau \sim r_{51}^2/4D$ [here $r_{51} = a_0/\sqrt{2}$ is the O(5)–O(1) distance, and $a_0 = 3.85 \text{ \AA}$ is the lattice constant] if we know the diffusion coefficient $D = D_0 \exp(-E_a/kT)$. Taking the activation energy E_a to be 1.0 eV [this is an average of the values 0.97 eV (Ref. 2), 0.96 eV (Ref. 3), 0.99 eV (Ref. 4), 1.03 (Ref. 5), and 1.07 (Ref. 6)], and using the diffusion coefficients measured at 300°C [$4 \times 10^{-13} \text{ cm}^2/\text{s}$ (Ref. 2) and $1 \times 10^{-12} \text{ cm}^2/\text{s}$ (Ref. 7)], we find D_0 to lie between 2.5×10^{-4} and $6.2 \times 10^{-4} \text{ cm}^2/\text{s}$. We also find that the average hopping time at room temperature (300 K), i.e., $\tau_{\text{RT}} = a_0^2/8D_{\text{RT}}$, lies between 5 and 13 h. It would be natural to expect the occupancies of the O(1) and O(5) sites to change drastically during this first step. However, neutron-diffraction experiments on a quenched $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ powder⁸ have detected no substantial changes in $n_{\text{O}(1)}$ or $n_{\text{O}(5)}$. It was noted that, during an “annealing” at room temperature, other structural parameters (a_0, b_0, c_0 , the extent to which the structure is orthorhombic, and the interatomic distances) change in the same way as the transition temperature, i.e., in accordance with

$$T_c(t) = T_c(\infty) - [T_c(\infty) - T_c(0)] \exp(-\sqrt{t/\tau}), \quad (1)$$

with a time scale⁸ $\tau_{\text{RT}} = 386$ min. Later experiments³ with a $\text{YBa}_2\text{Cu}_3\text{O}_{6.45}$ sample yielded $\tau_{\text{RT}} = 572$ min. A shorter duration of the process has been found only in experiments on Raman scattering by quenched $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ single crystals:⁹ It was observed, in particular, that the shape of the spectral line at 490 cm^{-1} “senses” the ordering of oxygen in a CuO_x plane quite well (this is a transition from a tetragonal phase to an orthorhombic one). At room temperature, this process is basically completed in the first 60 min. Since the estimates of the minimum value of τ_{RT} found by different authors are in clear contradiction, an independent experiment was necessary.

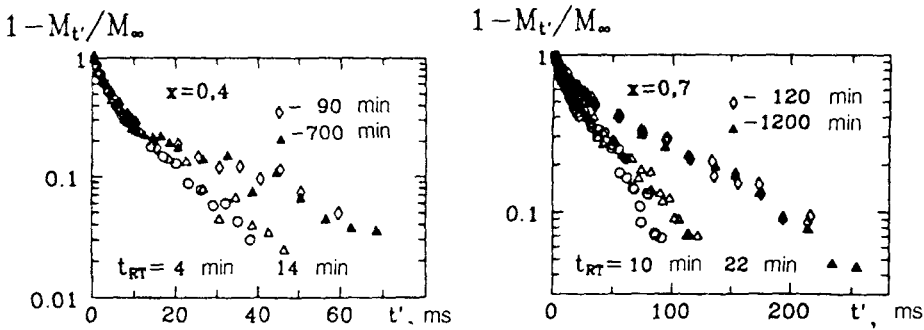


FIG. 1. Restoration of the longitudinal magnetization of thulium nuclei ($1 - M_{t'}/M_{\infty}$) in $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ samples at a time t' after the application of a $\pi/2 - \pi$ pair of pulses. $T = 1.5$ K, $\nu = 48$ MHz, $H = 9.1$ kOe ($H \parallel a$; Ref. 10). Here t_{RT} is the duration of the "aging" of a quenched sample at room temperature.

To estimate the average time for O(5)–O(1) diffusive hopping in the present study, we made use of the NMR of thulium in $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ (the nuclear spin of ^{169}Tm is $I = 1/2$; the natural abundance of this isotope is 100%). It had been shown previously^{10,11} that the rate of nuclear spin–lattice relaxation at liquid-helium temperatures is proportional to the square of the concentration of pairs of Cu^{2+} (1) terminating ions in the CuO chains. Since hops of oxygen atoms from O(5) sites to O(1) chain sites lead to a coalescence of short CuO fragments into long chains, there should be a rapid decrease in the concentration of Cu^{2+} (1) terminating ions and thus a lengthening of the nuclear-relaxation time T_1 .

Nonequilibrium $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ samples were prepared from a compound with $x = 0.95$ (a product of the Monokristallreaktiv Research and Production Association, Kharkov) by annealing in air at 700–750 °C for a day followed by quenching in liquid nitrogen. After a reheating to room temperature in flowing helium and a rapid grinding into a powder, each sample was then divided into two parts, which were quickly placed in two cryostats and cooled to liquid-nitrogen temperature or below. The shortest time spent by the samples at room temperature between the quenching and the first cooling ranged from 4 to 10 min. Independent measurements were carried out in the two separate cryostats. We measured 1) the rate of nuclear spin–relaxation of thulium at 1.5 K at the frequency $\nu = 48$ MHz in a field $H = 2\pi\nu/\gamma_a$, corresponding to the orientation $H \parallel [100]$ (γ_a is the effective gyromagnetic ratio of the thulium nuclei¹⁰). We also measured 2) the diamagnetic susceptibility at temperatures in the range 77–4.2 K at the frequency 1 kHz in the absence of a static field (the measurement field was $H_1 \sim 1$ Oe). We estimate the oxygen content in our samples ($x = 0.4$ and 0.7) from the limiting value of $T_{c,\text{onset}}$ after a prolonged "aging." Here we made use of the known $T_{c,\text{onset}}(x)$ dependence for compounds held for more than 1.5 yr at room temperature.¹¹ In each subsequent aging cycle, the samples were raised into the warm zone of the cryostat and held there for a set time in a helium atmosphere. The samples were then quickly cooled again.

The relaxation measurements clearly show (Fig. 1) that the nuclear spin–lattice relaxation of the thulium slows down appreciably in both samples, primarily during the

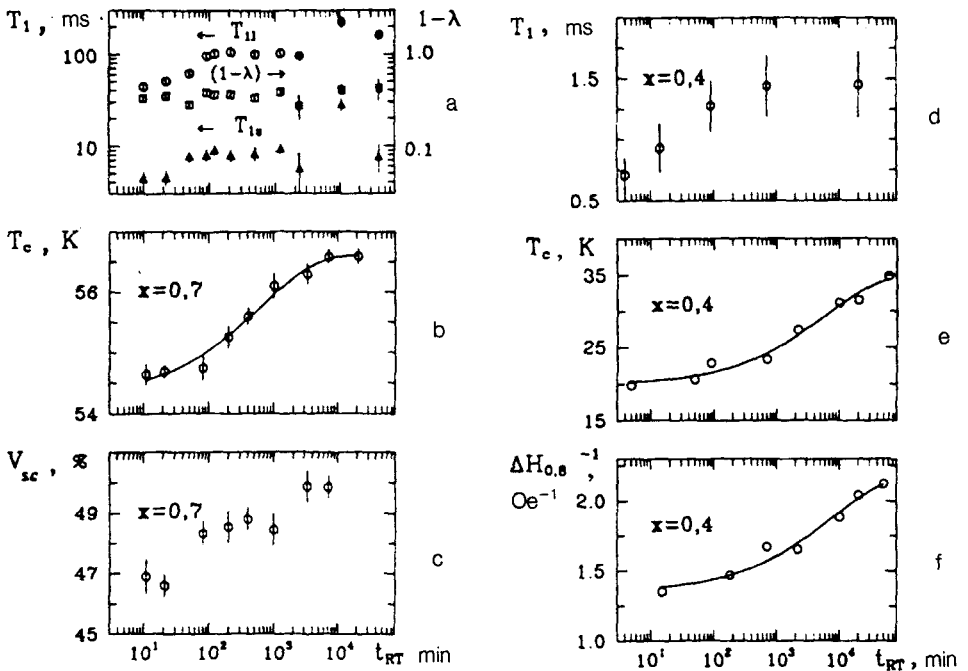


FIG. 2. Properties of the NMR of ^{169}Tm at $T = 1.5$ K and superconducting properties of $\text{TmBa}_2\text{Cu}_3\text{O}_{6+x}$ versus the duration of the aging at room temperature. a: Parameters of the nuclear relaxation, (2). Open points—Aging in a helium atmosphere; filled points—in air. b: Transition temperature (at the transition midpoint). Solid line—Equation (1) with the parameter values $T_c(0) = 54.2$, $T_c(\infty) = 56.6\text{K}$, and $\tau = 610$ min. c: Fraction of the material which is superconducting. d: Nuclear relaxation time (at the transition onset). Solid line—Equation (1) with the parameter values $T_c(0) = 19.8$ K, $T_c(\infty) = 35.1$ K, and $\tau = 6200$ min. f—Reciprocal of the half-width of the thulium NMR spectrum at the 0.8-maximum level (Fig. 3). Solid line— $(1/\Delta H) = (1/\Delta H)_\infty - [(1/\Delta H)_\infty - (1/\Delta H)_0] \exp(-\sqrt{t}/\tau)$, $1/(\Delta H)_0 = 1.35$ kOe^{-1} , $1/(\Delta H)_\infty = 2.18$ kOe^{-1} , $\tau = 7500$ min.

first hour of aging. The shape of the curve of the recovery of the longitudinal nuclear magnetization of thulium ($1 - M_{l'}/M_x$) after the application of rf pulses to the spin system will be discussed in detail in a separate paper.¹² Here we simply note that, after a $\pi/2 - \pi$ pair of pulses in a sample with $x = 0.4$ we have $1 - M_{l'}/M_x = \exp[-3\sqrt{t'/T_{1l}}]$, while in a sample with $x = 0.7$ [with a lower concentration of Cu^{2+} (1) paramagnetic centers] a two-exponential law turns out to be the best choice for describing the relaxation in the early stages of the aging:

$$1 - M_{l'}/M_x = (1 - \lambda) \exp(-t'/T_{1s}) + \lambda \exp(-t'/T_{1l}). \quad (2)$$

We should stress that, with increasing aging time t_{RT} at room temperature, the relaxation parameters [T_{1s} , T_{1l} , and λ in the sample with $x = 0.7$ (Fig. 2a); T_1 in the sample with $x = 0.4$ (Fig. 2d)] initially change sharply. After ~ 1 h, they remain approximately constant as long as the sample is in the helium atmosphere. On the other hand, the behavior of the transition temperature as a function of the annealing time at room temperature (Fig.

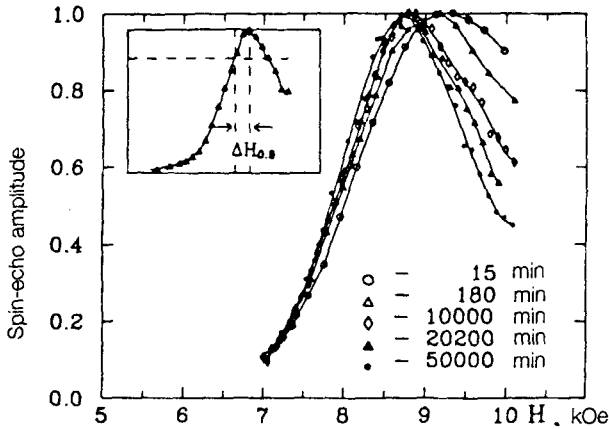


FIG. 3. Spectra of the pulsed NMR of thulium in $\text{TmBa}_2\text{Cu}_3\text{O}_{6.4}$ samples of various ages t_{RT} . $T = 1.5$ K, $\nu = 46.7$ MHz, $\pi/2$ pulse $3 \mu\text{s}$ in length. The inset is a plot used in determining the inhomogeneous half-width of the spectrum, $\Delta H_{0.8}$.

2, b and e) is described by law (1), as in Refs. 3 and 8. In the sample with $x = 0.7$ the time τ_{RT} is $\tau = 610$ min. The superconducting volume fraction V_{SC} increases in approximately the same way as $T_c(t)$ during the aging of this sample (Fig. 2c). In the sample of $x = 0.4$, the oxygen ordering process is clearly slower: $\tau_{\text{RT}} = 6200\text{--}7500$ min (Fig. 2, e and f). The experiments thus make it possible to distinguish two characteristic parameters: the time $\tau_1 \approx 60$ min, which is apparently independent of the oxygen concentration, and the time τ_2 , which is at least an order of magnitude greater than τ_1 and which clearly increases with increasing oxygen deficiency. Since a diffusion along the $[001]$ crystallographic direction should be exceedingly slow [$D_c/D_{ab} \sim 10^{-4}$ even at 400°C (Ref. 13)], we cannot associate the parameter τ_2 with the process by which the 3D Ortho-II structure forms. We are forced to associate it with a 2D ordering of “complete” (Cu–O–Cu) and “empty” (Cu–V–Cu) chains (V is an oxygen vacancy). In this case, however, τ_1 can play no role other than that of the time scale for an $\text{O}(5) \rightarrow \text{O}(1)$ hop. Our measurements show that this rapid process increases the nuclear relaxation time T_1 sharply. In other words, it reduces the concentration of paramagnetic centers (acceptors) (Fig. 2, a and d), while having essentially no effect on the superconducting parameters (Fig. 2, b and e). Individual $\text{O}(5) \rightarrow \text{O}(1)$ hops are of course also incapable of causing any great reduction of the inhomogeneous broadening of the resonant spectrum of thulium (Fig. 3), which stems from local distortions of the crystal electric field at Tm^{3+} ions due to structural defects of the crystal.¹⁴ It can be seen from Figs. 2f and 3 that the “homogeneity” of the spectrum (as a measure of which we adopt the reciprocal half-width $\Delta H_{0.8}^{-1}$) increases during the low-temperature annealing of the sample, as does $T_c(t_{\text{RT}})$, with a time scale of τ_2 .

Knowing the time τ_1 , we can estimate the oxygen diffusion coefficient at room temperature: $D \approx a_0^2/8\tau_1 = 0.5 \times 10^{-19} \text{ cm}^2/\text{s}$. This value is about an order of magnitude greater than expected, suggesting that current carriers (holes) may be having an effect on

the oxygen diffusion.¹⁵ Our experiments essentially confirm the results of a simulation of the ordering of a planar oxygen 1–2–3 sublattice¹⁶ and yield the times scales for the formation of the primary tweed Ortho-I structure (τ_1) and that for the secondary tweed Ortho-II structure (τ_2). It would be interesting to estimate the parameter τ_3 —the time scale for the formation of the bulk Ortho-II structure—but our data do not support such a calculation. If we identify τ_3 with the time ~ 500 h which has been observed previously¹⁷ at a temperature of 51°C, and if we extrapolate it to room temperature, assuming $E_a = 1.0$ eV as before, we find $\tau_3 = 1$ yr. This result is consistent with our observations of the long-term drift of the rates of nuclear relaxation of thulium in Tm-BCO samples.¹⁰

The slowing of the nuclear spin–lattice relaxation during the first hour of aging at room temperature is also seen clearly in the case of ⁸⁹Y nuclei. Preliminary experiments with a YBa₂Cu₃O_{6.5} sample, carried out using a Bruker MSL-400 spectrometer at a frequency of 19.6 MHz and a temperature of 195 K, yielded the following results: After a 10-min annealing at room temperature, the nuclear spin–lattice relaxation time ⁸⁹ τ_1 turned out to be 25 s. After a 50-min annealing, it turned out to be about twice as long. The relaxation was characterized by an ordinary exponential function $\exp(-t'/^{89}T_1)$. These results, combined with the data on the nuclear spin–lattice relaxation of thulium, mean that, in analyzing the nuclear spin–lattice relaxation of yttrium and, in general, all nuclei in the oxygen-deficient 1–2–3 samples,¹⁸ we need to allow for the possibility of a nuclear relaxation through local paramagnetic centers of copper or copper–oxygen complexes.^{10,11}

After this study was completed, we learned of the results¹⁹ of direct measurements of diffusion in YBCO. Those results agree well with our estimate of D .

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