NMR Study of ^{17}O Transverse Relaxation in $YBa_2Cu_3(^{16}O_{1-c}{}^{17}O_c)_7$

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NMR transverse relaxation (TR) measurements of $^{17}O(2,3)$ in $YBa_2Cu_3(^{16}O_{1-c}{}^{17}O_c)_7$ are presented. A Gaussian-like relaxation is found. The origin of this relaxation is investigated by varying c, the temperature, the external field, and by comparing it with the $^{17}O(4)$ site. Our results are consistent with a model in which this relaxation is caused by the dynamical fluctuation of copper nuclei, including both spin-lattice and flip-flop processes. With this model we can also explain the TR of ^{89}Y and $^{63}Cu(1)$. We use our results to reanalyze previous NMR $^{63}Cu(2)$ TR data and find the dynamical exponent $z = 1$. [S0031-9007(97)02758-0]

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Transverse and longitudinal nuclear spin relaxation measurements, carried out by spin echo NMR, have been very successful in determining some of the electronic properties of high-T_c superconductors. The comparison between ^{89}Y, ^{17}O, and $^{63,65}Cu$ longitudinal relaxation in $YBa_2Cu_3O_y$ ($YBCO_y$) gave the first clues to the existence of antiferromagnetic correlations in the normal state [1], and $^{63,65}Cu$ transverse relaxation (TR) provided the temperature dependence of the static part of the staggered susceptibility $\chi(Q_{\rm AF})$ [2–5]. Recently, the interpretation of copper TR has been taken even further and is now used to distinguish between s- and d-wave theories [6], as well as between models of critical behavior in the normal state [7,8]. In contrast, there is very little published data on the TR of ^{17}O in YBCO [9], and the forces which control it are not understood. As we demonstrate here, studying this relaxation provides the clue to understanding the TR of all nuclear species in the structure, other than the plane copper [$^{63,65}Cu(2)$]. In addition, it allows us to clarify some of the assumptions used in $^{63,65}Cu(2)$ TR data analysis, and leads to a reevaluation of the dynamical critical exponent z. We find that $z = 1$, and not 2 as previously thought [8]. Finally, we hope that our findings will accelerate the ongoing efforts to use TR of other nuclei as probes of the CuO_2 electronic system [10].

The TR is measured by a $\pi/2$–π pulse sequence. The pulses are separated by time τ, and an echo appears at time 2τ with an amplitude M_x which decreases with increasing τ. The rate of echo size decay is usually ascribed to two elements: (I) the Lorentzian contribution of the spin lattice relaxation ($1/T_{2L}$), and (II) the nuclear spin-spin relaxation. The latter contribution reflects on the coupling constants in the secular part of the two spin nuclear Hamiltonian $\mathcal{H}_{12} = \hbar[^{i-j}a_z I_{i,z} I_{j,z} + {}^{i-j}a_\perp (I_{i,+} I_{j,-} + I_{i,-} I_{j,+})/4]$, where $a_\perp = a_x + a_y$. When the nuclear spins $\mathbf{I}_i$ and $\mathbf{I}_j$ belong to the same isotope ("like spins"), the perpendicular coupling $a_\perp$ generates the flip-flop transitions ("dynamical" TR) and the longitudinal coupling a_z is responsible for nonrefocusable field fluctuations ("static" TR).

In $YBCO_y$, the echo decay of the plane copper [$^{63}Cu(2)$] has the form $M_x(2\tau) = \exp[-2\tau/T_{2L} - \frac{1}{2}(2\tau/T_{2G})^2]$, where $M_x(0) \equiv 1$. Up to now, the Gaussian part of M_x has been accounted for solely by the pure static case ($a_z \gg a_\perp$) of like-spins coupling [2] where it is given by $(T_{2G}^{\rm sta})^{-2} = \frac{c}{8}\sum_{R\neq 0} |a_z(\mathbf{R})|^2$. The sum is taken over all copper sites at position $\mathbf{R}$, and c is the isotopic concentration. The dynamical contributions of either the like-spins coupling or the unlike-spins coupling are considered to be negligible, or to contribute only to the Lorentzian part of the echo decay.

In this Letter we show, both experimentally and theoretically, that *the Gaussian part of the echo decay can contain unlike-spins dynamical contribution as well.* In particular, the ^{17}O has a Gaussian TR which stems solely from these dynamical modulations. We account for this TR by a model which is based on dipolar field fluctuations at the oxygen site due to copper nuclear spin dynamics; the same model was used by Walstedt and Cheong to explain the echo decay of ^{17}O in $La_{1.85}Sr_{0.15}CuO_4$ at 100 K by means of Monte Carlo simulations [11]. We, in contrast, develop an analytical approach which allows us to obtain the total copper fluctuation rate from the ^{17}O TR while also explaining the TR data of ^{89}Y and the chain copper [$^{63,65}Cu(1)$]. Based on our model we show how to subtract the contribution of unlike-spins coupling to $^{63,65}Cu(2)$ TR. This allows a more accurate determination of $^{63-63}a_z$ [and therefore of $\chi(Q_{\rm AF})$] [2–5].

Our measurements are performed on YBa_2Cu_3 $(^{16}O_{1-c}{}^{17}O_c)_7$ samples in which ^{17}O is exchanged mainly with the planar O(2,3) and apical O(4) sites by the method described in Ref. [12]. We prepared samples in which $c = 0.2$, 0.06, and 0.02. These ratios are verified by intensity measurements of the NMR signal. The samples are also oriented in the method detailed in Ref. [13]. The TR measurements are made on the oxygen central line ($\pm 1/2$ transition) in a field $H \parallel \mathbf{c}$ of 7.5 T. We record the entire echo intensity after 2τ and Fourier transform it to obtain the spectral line. We then integrate only the high frequency half of the spectrum of the O(2,3) line,

thus avoiding contamination from parts of the sample which have oxygen deficiencies. These deficiencies cause a distribution of internal fields and shift the line towards lower frequencies. By using a short repetition time of the pulse sequence (every 0.05 sec) we almost saturate the ^{17}O(4) nuclear spin transition and therefore minimize its contribution to the O(2,3) lines. Using a long repetition time (every 0.5 sec) we can also maximize the signal of the ^{17}O(4). One such spectrum is shown in the inset of Fig. 1. The shaded part represents the portion of the lines used to determine the TR.

The echo decays of the ^{17}O at $T = 100$ and 300 K in the three samples are shown in Fig 1 on a semilog scale, and as a function of $(2\tau)^2$ (the curves are displaced for clarity). Three features are readily apparent in this figure: (I) the relaxation rate increases with increasing temperature; (II) the relaxation curves could be well fitted to a Gaussian down to $\sim$5% of their initial value, with small deviations seen only after $2\tau = 0.8$ msec; (III) for a given temperature, there is hardly any difference in the relaxation rates of samples of different isotope concentration. The last feature allows us to conclude that neither static nor dynamic like-spins coupling could be responsible for this Gaussian TR of the ^{17}O, as it would yield a change of factor 3 in the slope of the lines between the different samples [2,14].

Therefore, in order to extract physical parameters from our experimental results, we must use an unlike-spins coupling model which produces a Gaussian relaxation. Such a model was first provided by Klauder and Anderson, on the basis of Lorentzian diffusion [15]. In their model, the dipole field at the observed nuclear site (i) fluctuates along the $\hat{\mathbf{z}}$ direction due to dynamical fluctuations of nearby "unlike" nuclei (j). They found that the relaxation is determined by two parameters: the line width $^{i-j}\lambda$ of the instantaneous field distribution, caused by nuclei j at the site of nuclei i, and the fluctuation rate $^{j}\nu$ of nuclei j. The Gaussian dynamical relaxation rate was given by

$$(^{i}T_{2G}^{\mathrm{dyn}})^{-2} \propto {}^{i-j}\lambda\,{}^{j}\nu\,. \tag{1}$$

However, there are two elements in their derivation which prevent us from using it directly: (I) it is restricted to fluctuations of spin $1/2$ nuclei, and (II) their approximation yields a relaxation line shape which is always Gaussian, in contrast to laboratory experience (see below). For those reasons (and for completeness) we present here a different, and more primitive, derivation of a dynamical Gaussian line. Our derivation bypasses the discussion on the dynamical source, but, in turn, allows for the desired line shape variation. We describe the ^{17}O spin as a classical vector and allow the magnetic field to hop with a probability ν per unit time between different values along the $\hat{\mathbf{z}}$ direction. If there are n hops at times $t_1, \ldots, t_n$ before the $\pi/2$ pulse and m hops at times $t_{n+1}, \ldots, t_{m+n}$ between the $\pi/2$ and the π pulses, the phase acquired by the spin in the rotating reference frame (RRF) would be

$$\begin{aligned}\theta_{n,m} = {} & \omega_{n+m+1}(2\tau - t_{n+m}) + \sum_{j=2}^{m} \omega_{j+n}(t_{n+j} - t_{n+j-1}) \\ & - \omega_{n+1}(t_{n+1} - \tau) + \omega_{n+1}(\tau - t_n) \\ & + \sum_{i=1}^{n} \omega_i(t_i - t_{i-1})\,,\end{aligned} \tag{2}$$

where the ω's are the precession frequencies in the different time intervals, and the π pulse reverses the sense of precession at time τ. This definition of the π pulse is equivalent to the experimental one. The probability of finding such $n + m$ hops is $\exp(-\nu 2\tau)\prod_{i=1}^{n}\nu dt_i \times \prod_{j=1}^{m}\nu dt_{n+j}$. We employ the strong collision approximation, namely, that after each hop the system can assume any frequency from its equilibrium distribution in the RRF which we take here to be the Lorentzian $\rho(\omega) = \lambda/[\pi(\omega^2 + \lambda^2)]$. The transverse magnetization is a sum over different numbers of hops, at different times, with all possible frequencies after each hop, taking into account their appropriate probability, and is given by

$$\begin{aligned}M_x(2\tau) = {} & \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \nu^{n+m}\exp(-\nu 2\tau)\int\cdots\int \cos(\theta_{n,m}) \\ & \times \prod_{l=1}^{n+m+1}\rho(\omega_l)d\omega_l \prod_{i=1}^{n} dt_i \prod_{j=1}^{m} dt_{n+j}\,.\end{aligned} \tag{3}$$

In the integrations, causality ($t_i > t_{i-1}$) must be respected. The evaluation of this series [16] gives

$$M_x(2\tau) = \frac{\nu\exp(-2\lambda\tau) - \lambda\exp(-2\nu\tau)}{\nu - \lambda}\,. \tag{4}$$

When the fluctuation rate is large, namely, $\nu \gg \lambda$, the relaxation has the familiar exponential shape. On the other hand, when $\nu \simeq \lambda$, the line shape at early time could be approximated using the expansion

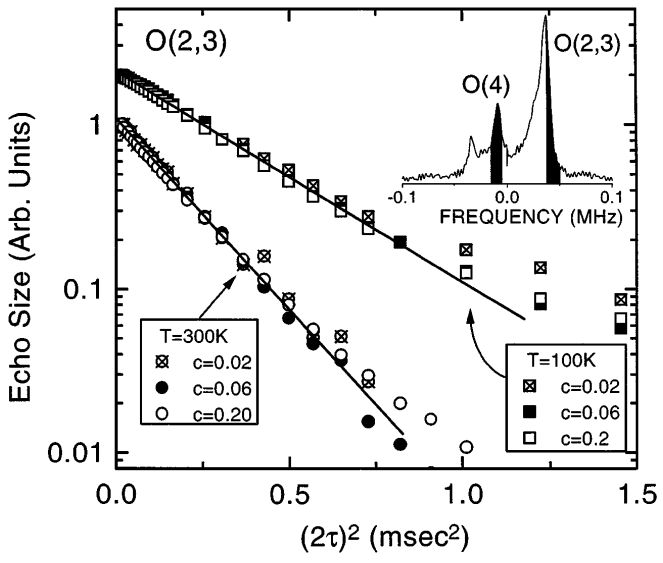

FIG. 1. The spin echo decay of ^{17}O at the O(2,3) site in three samples of $YBa_2Cu_3(^{16}O_{1-c}{}^{17}O_c)_7$. The curves are displaced for clarity. The inset shows the ^{17}O central ($\pm 1/2$) line shape at a slow repetition time of 0.5 sec. The shaded areas are used to determine the echo decay.

$$M_x(2\tau) \cong 1 - \frac{1}{2}\lambda\nu(2\tau)^2 + \ldots \cong e^{-\frac{1}{2}(2\tau/T_{2G}^{\rm dyn})^2}, \quad (5)$$

defining $1/T_{2G}^{\rm dyn}$ in our model. Since the strongest coupling of the ^{17}O is to the neighboring copper nuclei, and since these nuclei have the fastest fluctuations, we conclude that $1/^{17}T_{2G}$ probes the total Cu fluctuation rate, including spin-lattice and flip-flop rates ($\nu^{\rm ff}$). Indeed, if we approximate $^{17-63}\lambda \sim 6.2$ rad/msec from the unlike-spins second moment of the near neighbors copper nuclear dipolar field, and $^{63}\nu \sim 10$ msec^{-1} from $^{63}T_{2G}$ data, we find that $\lambda \sim \nu$ and a Gaussian relaxation is expected.

We can check the model by comparing T_{2G} of ^{17}O on the O(4) site ($^{\rm O(4)}T_{2G}$) and on the O(2,3) site ($^{\rm O(2,3)}T_{2G}$). At a temperature of 300 K and slow repetition time, the O(4) and O(2,3) lines are well separated, as shown in the inset of Fig 1, and we can determine their TR separately. In Fig. 2 we depict the TR of ^{17}O on both sites. It is clear from the solid lines which are parallel that no difference between the relaxation rates in the two sites is observed within experimental accuracy. Using $(^{\rm O(4)}T_{2G}/^{\rm O(2,3)}T_{2G})^2 = {}^{\rm O(2,3)-Cu(2)}\lambda/{}^{\rm O(4)-Cu(2)}\lambda$ [see Eq. (1)], we estimate that $1/^{\rm O(4)}T_{2G}$ should be only 0.92 times smaller than $1/^{\rm O(2,3)}T_{2G}$, which is in agreement with our measurement. In contrast, if there would have been any transferred interaction between copper and oxygen, we would expect ${}^{\rm O(2,3)-Cu(2)}\lambda$ to be much larger than ${}^{\rm O(4)-Cu(2)}\lambda$. Therefore, our results indicate that the Cu-O coupling is dipolar. We also check that the data taken in two different fields (with two different spectrometers) are indistinguishable, as they should be in our model (see Fig. 2).

Another test for the model is provided by the ^{89}Y data. Here we find ${}^{\rm Y\text{-}Cu(2)}\lambda = 0.12$ rad/msec (considering the dipolar second moment of near neighbors only) which is much smaller than the Cu fluctuation rate ν. In that case we expect [from Eq. (4)] the TR to have the exponential shape $\exp(-t/T_2)$ with a temperature independent $1/T_2 = 2\lambda$. Indeed, Markert *et al.* found that above T_c the ^{89}Y has a temperature-independent exponential TR, with $1/T_2 = 0.2$ msec^{-1}% [17]. Our model thus explains the relaxation shape, the lack of temperature dependence, and the order of magnitude of T_2 for the yttrium in the normal state of YBCO.

We now turn to discuss the temperature dependence of the ^{17}O TR. Since the oxygen spin lattice relaxation rate $^{17}T_1(\sim 10$ msec) is very slow on the time scale of the TR, we can safely ignore $1/T_{2L}$ and fit the echo decay curves using only a Gaussian, and the first $2\tau = 1$ msec of our data. The results are presented in Fig. 3(a), where it is seen that $1/^{17}T_{2G}$ is monotonically increasing with increasing temperature. We can try to account for this temperature dependence using Eq. (1) with $\nu = 1/(2^{63}T_1) + {}^{63}\nu^{\rm ff}$, where $1/^{63}T_1$ and $^{63}\nu^{\rm ff}$ are the spin-lattice and the flip-flop rates of ^{63}Cu, respectively. Since $^{63}\nu^{\rm ff}$ is due to the perpendicular like-spins coupling between ^{63}Cu, it could be expressed as ${}^{63}\nu^{\rm ff} = \alpha|{}^{63-63}a_\perp^{\rm tra} + {}^{63-63}a_\perp^0|$, where α is a proportionality constant of the order of unity, $^{63-63}a_\perp^{\rm tra}$ is the temperature dependent transferred interaction governed by the electronic susceptibility, and $^{63-63}a_\perp^0$ is temperature independent background interaction. We expect ${}^{63-63}a_\perp^0 = -1.0$ rad/msec if it were solely determined by dipolar coupling. In order to evaluate $^{63-63}a_\perp^{\rm tra}$ we use the calculated ratio of longitudinal to perpendicular transferred couplings ${}^{63-63}a_x^{\rm tra} = {}^{63-63}a_z^{\rm tra}/10.2$, and

$$^{63-63}a_z^{\rm tra} = 1.7/^{63}T_{2G}^{\rm sta}, \quad (6)$$

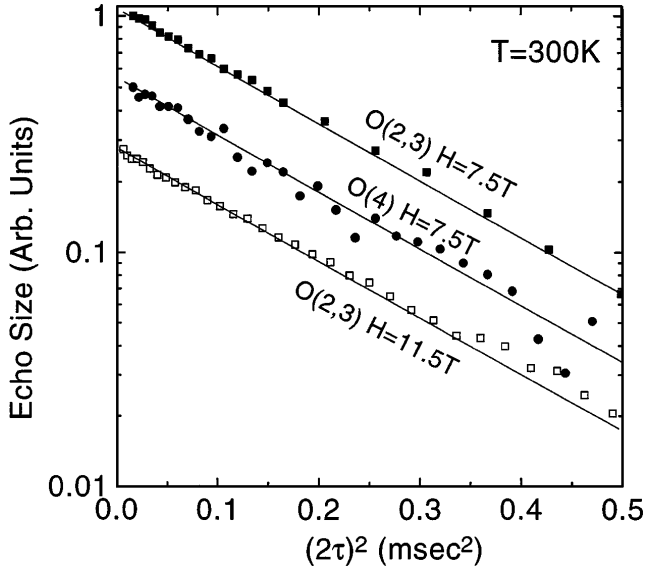

FIG. 2. The spin echo decay of ^{17}O at the O(2,3) and O(4) sites and at external fields of 7.5 and 11.5 T in $YBa_2Cu_3(^{16}O_{0.94}{}^{17}O_{0.06})_7$. The curves are displaced for clarity. The solid lines are parallel.

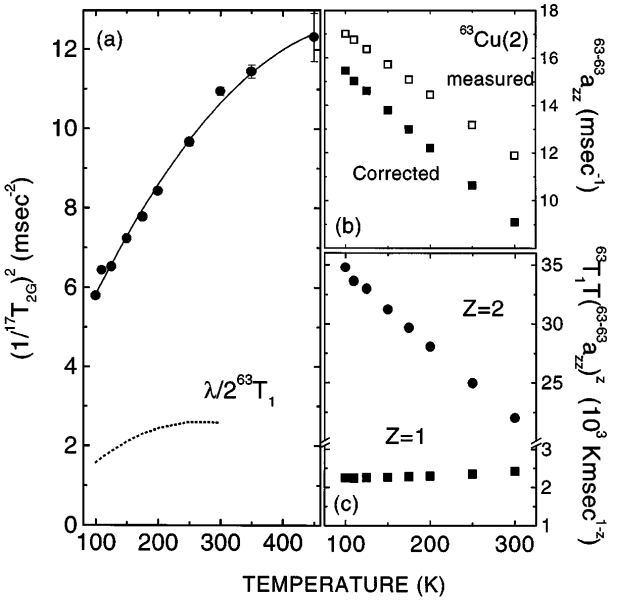

FIG. 3. (a) The temperature dependence of $(^{17}T_{2G})^{-2}$. The solid line is a fit to Eq. (7) as described in the text. Also plotted is $\lambda/2^{63}T_1$ with $\lambda = 4.6$ rad/msec (with T_1 from Ref. [18]). (b) Measured and corrected $^{63-63}a_{zz}(T)$ deduced for T_{2G} measurements as described in the text. (c) Corrected plot of $T_1T(^{63-63}a_z^{\rm tra})^z$ vs T for $z = 1$ and $z = 2$.

both taken from Pennington *et al.* [2]. Thus, the temperature dependence of $^{63-63}a_{\perp}^{\mathrm{tra}}$ could be determined from the data for $^{63}T_{2G}$. Finally, the fitting function is

$$(^{17}T_{2G}^{\mathrm{dyn}})^{-2} = \lambda\left(\frac{1}{2^{63}T_1} + \alpha\left|\frac{0.33}{^{63}T_{2G}} + a_{\perp}^{0}\right|\right). \quad (7)$$

Since there are only small variations in $1/^{63}T_{2G}$ between samples of different doping, we use the $1/^{63}T_{2G}$ data of Imai *et al.* [4], which were purposely taken in a low applied field in $YBCO_{6.9}$. The experimental values of $1/^{63}T_1$ are taken from Hammel *et al.* [18]. Both data have been linearly extrapolated up to $T = 450$ K. The best fit to Eq. (7) is obtained with $\lambda = 4.6(7)$ rad/msec, $\alpha = 0.8(1)$, and $a_{\perp}^{0} = -4.4(1)$ rad/msec, and is presented in Fig. 3(a) by the solid line. Although $a_{\perp}^{0}$ is about 4 times larger than expected from pure dipolar coupling, the fact that λ and α have reasonable values further emphasizes that the ^{17}O transverse relaxation is caused by copper nuclear spin fluctuations. Finally, in order to demonstrate the contribution of spin lattice relaxation processes to the total copper nuclear dynamics we depict $\lambda/2^{63}T_1$ in Fig. 3(a). Clearly this contribution is small at all temperatures compared to $(1/^{17}T_{2G}^{\mathrm{dyn}})^2$.

Having demonstrated through the ^{17}O data that a Gaussian TR could stem from unlike-spins coupling, we obviously must question whether such a contribution occurs for copper nuclear TR. For example, Pennington *et al.* found that T_{2G} of Cu(1) ($^{\mathrm{Cu}(1)}T_{2G}$) in YBCO is not due to like-spins coupling. Using the same method applied for the O(4), but considering first and second near neighbors, we estimate that $1/^{\mathrm{Cu}(1)}T_{2G} = 2.3\ \mathrm{msec}^{-1}$. This is only 20% less than the measured value and our model can explain the magnitude of the Cu(1) TR quite naturally. Thus the unlike-spins dynamical contribution to the copper $1/T_{2G}$ is quite sizable in the published results on $YBCO_7$, and should be accounted for. In the case of ^{63}Cu(2), the most important unlike spins would be the ^{65}Cu(2) [11]. Therefore, we write

$$(^{63}T_{2G}^{\mathrm{exp}})^{-2} = (^{63}T_{2G}^{\mathrm{sta}})^{-2} + \frac{^{63-65}\lambda}{^{17-65}\lambda}(^{17}T_{2G})^{-2}, \quad (8)$$

where the second term on the right-hand side is $(^{63}T_{2G}^{\mathrm{dyn}})^{-2}$, and the superscript "exp" stands for experimental. Using $^{i-j}\lambda \propto {}^{i-j}a_{zz}\sqrt{^{j}I(^{j}I+1)} \times {}^{j}c$, a dipolar expression for $^{17-65}\lambda$, and $^{65}\gamma/^{63}\gamma \simeq 1$, we expect $^{63-65}\lambda/^{17-65}\lambda = 0.2^{63-63}a_z^{\mathrm{tra}}$. Combining this result with Eq. (6) leads to a quadratic equation for $^{63-63}a_z^{\mathrm{tra}}$ which we solve separately at each temperature using our ^{17}O results and the data of Ref. [4] for $^{63}T_{2G}^{\mathrm{exp}}$. In Fig. 3(b) we plot $^{63-63}a_z^{\mathrm{tra}}$ after correcting for the dynamic contribution with Eq. (8), and, for comparison, we show $^{63-63}a_z^{\mathrm{tra}}$ as obtained usually. It is clear from this plot that the dynamic contribution is quite large at high temperatures. Therefore, one should reanalyze the equation $T_1T(^{63-63}a_z^{\mathrm{tra}})^z = \mathrm{const}$, where z is the critical exponent in the scaling relations $\tau \propto \xi^z$ of the correlation time τ with length ξ [8]. In Fig. 3(c), we clearly show that z is much closer to 1 than to 2 (in agreement with the numerical work presented in Ref. [19]). It is also seen in Fig. 3(a) that the dynamical correction is getting smaller as the temperatures approach T_c. We therefore claim that the data analysis of $^{63}T_{2G}$ performed in the superconducting state, and possibly the conclusions drawn from it (e.g., d-wave symmetry [6]) are valid.

In conclusion, the ^{17}O Gaussian transverse relaxation in $YBCO_7$ is due to dipolar field fluctuations emerging from copper nuclear spin dynamics which is dominated by flip-flop processes. We develop a general method which allows us to perform the necessary correction to the copper T_{2G} on the basis of ^{17}O data.

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