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Contributions of Spin–Lattice Relaxation to the Echo Decay of Planar Cu in High-Temperature Superconductors

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Measurement of T_{2G}, the Gaussian component of the spin-echo envelope of planar Cu nuclei in high-temperature superconductors, gives important information about the real part of the Cu electron spin susceptibility. In the traditional picture of the planar Cu echo decay, the internuclear coupling is assumed to remain static with respect to spin–lattice relaxation and mutual exchange fluctuations. In some circumstances, however, this assumption breaks down. We calculate the internuclear corrections arising from spin–lattice relaxation to the conventional theory of T_{2G} and show that T_{2G} can be easily corrected for these effects. We argue that mutual exchanges due to the perpendicular indirect couplings are suppressed in these materials. For $YBa_2Cu_4O_8$, we find a correction on the order of 10% in T_{2G} and using the corrected values we find that the isotope ratio $^{63}T_{2G}/^{65}T_{2G}$ agrees with theory. © 1998 Academic Press

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INTRODUCTION

One of the most important magnetic resonance measurements of high-temperature superconductors is the Gaussian time constant for the spin-echo decay of planar Cu, T_{2G}. In these materials planar Cu nuclei are coupled indirectly to one another via electron spins. By measuring T_{2G} one can obtain information about the real part of the complex Cu electron spin susceptibility. Since electron spin susceptibility describes the correlations of the electrons, T_{2G} reveals important information about the electronic system. Indeed, evidence for d-wave superconductivity, the normal state pseudogap, magnetic scaling, and crossovers to mean field behavior of the electronic system at high temperatures has been observed through measurements of T_{2G} (*1–3*). In the majority of such experiments, however, comparisons with theoretical models are based on the static model for echo decay in which spin–lattice fluctuations of other nuclei and mutual exchanges between pairs of nuclei are assumed negligible. If such fluctuations are not negligible at all temperatures, one might wonder whether one should change the interpretation of certain experiments. The spin–lattice fluctuations, or T_1 corrections, are largest at high temperatures, where T_{2G} increases with T and T_1 remains constant or decreases. Mutual exchanges, on the other hand, are probably suppressed considerably in many of the high-temperature superconductors. The determining factor for suppressing mutual exchanges is the anisotropy ratio of the hyperfine couplings: the greater this ratio, the more suppressed are the mutual exchanges. In this paper we discuss these two potential corrections to the conventional theory of T_{2G}.

THE STATIC MODEL OF ECHO DECAY

In 1989, Pennington *et al.* (*4*) showed that in high-temperature superconductors the coupling between planar Cu nuclei is an order of magnitude greater than what one would expect for direct nuclear dipolar coupling. They discovered that Cu nuclei are coupled indirectly through Cu electron spins. The indirect nuclear coupling is described by the Hamiltonian

$$H = \sum_{\mathbf{r},\mathbf{r}_1 \neq 0} \hbar a_z(\mathbf{r}) I_z(\mathbf{r}) I_z(\mathbf{r}+\mathbf{r}_1) + \frac{\hbar a_\perp(\mathbf{r})}{2} \times [I_+(\mathbf{r}) I_-(\mathbf{r}+\mathbf{r}_1) + I_-(\mathbf{r}) I_+(\mathbf{r}+\mathbf{r}_1)], \quad [1]$$

where a_z and $a_\perp$ are the indirect coupling constants parallel and perpendicular to the c axis of the crystal. There is no general solution for the echo decay for the above Hamiltonian. In 1991, Pennington and Slichter (*5*) (PS) showed, however, that often $a_z \gg a_\perp$ in high-temperature superconductors. If one neglects the $a_\perp$ term in [1] (which gives rise to mutual exchanges) and neglects spin–lattice relaxation effects of the coupling to other nuclei, the echo decay takes on a simple form when the static field is parallel to the c axis. PS showed that the echo signal $M(t)$ at time t for the central transition in high-field NMR is a product of a Gaussian and an exponential,

$$M(t) = M(0) e^{-t^2/2T_{2G}^2} e^{-t/T_{2R}}, \quad [2]$$

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where T_{2R} (R for Redfield) represents transitions induced by the spin–lattice relaxation of the nucleus under observation. T_{2R} can be computed if one knows the spin–lattice relaxation rates when the static field is parallel and perpendicular to the c axis (*6*). The Gaussian decay constant T_{2G} is given by

$$\left(\frac{1}{{}^{\eta}T_{2G}^{2}}\right)_{\mathrm{NMR}} = \frac{{}^{\eta}P}{8}\sum_{\mathbf{r}\neq 0} a_z^2(\mathbf{r}). \quad [3]$$

Here ${}^{\eta}P$ is the natural abundance of the observed nucleus (i.e., $\eta = 63, 65$ for $^{63,65}Cu$). Furthermore, PS gave the theory of $a_z(\mathbf{r})$ in terms of the electron spin susceptibility and the hyperfine couplings,

$$a_z(\mathbf{r}) = -\frac{1}{N}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} F_{\perp,\mathrm{eff}}^{2}(\mathbf{q})\chi'(\mathbf{q}), \quad [4]$$

where N is the number of lattice sites, and $\chi'(\mathbf{q})$ is the real part of the static electronic spin susceptibility at wavevector $\mathbf{q}$. $F_{\perp,\mathrm{eff}}(\mathbf{q})$ is a form factor for electron spin fluctuations of wave vector $\mathbf{q}$ (introduced to analyze spin–lattice relaxation when the static field is perpendicular to the crystal field axis). It involves the Fourier transform of the hyperfine couplings between the Cu nuclei and the Cu electron spins for the magnetic field oriented parallel to the c axis (*7*):

$$F_{\perp,\mathrm{eff}}(\mathbf{q}) = (A_{\parallel} + 2B[\cos(q_x a) + \cos(q_y a)])^2. \quad [5]$$

$A_{\parallel}$ is the parallel on-site hyperfine coupling and B is the hyperfine coupling to the next neighbor Cu. Using these relationships, they calculated the spatial dependence of the coupling for $YBa_2Cu_3O_{7-\delta}$ (94 K), and its temperature dependence using the expression for electron susceptibility given below. Later, Thelen and Pines (*8*) and Takigawa (*9*) independently simplified the theoretical expression for T_{2G}. Substituting Eq. [4] into Eq. [3], one can replace the sum over $\mathbf{r}$ with a sum over $\mathbf{q}$, obtaining a particularly useful expression:

$$\left(\frac{1}{{}^{\eta}T_{2G}^{2}}\right) = \frac{{}^{\eta}P}{8}\left[\frac{1}{N}\sum_{\mathbf{q}} {}^{\eta}F_{\perp,\mathrm{eff}}^{4}(\mathbf{q})\chi'(\mathbf{q})^2 - \left(\frac{1}{N}\sum_{\mathbf{q}} {}^{\eta}F_{\perp,\mathrm{eff}}^{2}(\mathbf{q})\chi'(\mathbf{q})\right)^2\right]. \quad [6]$$

A widely accepted model for susceptibility in high-temperature superconductors is that given by Millis, Monien, and Pines (MMP) (*10*),

$$\chi(\mathbf{q}, \omega) = \frac{\alpha\xi^2}{1 + (\mathbf{q} - \mathbf{Q})^2\xi^2 - i\omega/\omega_{\mathrm{sf}}}, \quad [7]$$

where ξ is the antiferromagnetic correlation length, ω_{sf} is a damping term, α is a parameter, a is the lattice constant, and $\mathbf{Q} = (\frac{\pi}{a}, \frac{\pi}{a})$ is the antiferromagnetic wavevector. Using this model one can show that in the limit of long correlation length $T_{2G} \sim 1/\alpha\xi$. MMP assume that α is independent of temperature; thus the quantity T_{2G} gives one a measure of the degree of spatial correlation of the electron spins.

For many cases, T_1 is on the order of 1–2 ms whereas T_{2G} is on the order of 100 μs, so $T_1 \gg T_{2G}$ and the assumption of static internuclear coupling remains valid. But at high temperatures when T_1 decreases and T_{2G} increases, the static model can break down and cast doubt on the validity of conclusions about the behavior of the electronic system based upon measurements of T_{2G}. Recent numerical simulations by Walstedt and Cheong (*11*) showed evidence that the echo decay of $^{63,65}Cu$ in $La_{1.85}Sr_{0.15}CuO_4$ has contributions due to T_1 fluctuations. Also, Keren *et al.* (*12*) have shown evidence that the echo decay of ^{17}O in $YBa_2Cu_3O_7$ is determined by antiferromagnetic spin fluctuations of the planar Cu. Furthermore, Recchia *et al.* (*13*) demonstrated that the echo decay for ^{89}Y in the superconducting state of $YBa_2Cu_3O_7$ is dominated by the spin–lattice fluctuations of the nuclear spins of the planar Cu. They derive the form of the Y echo decay based on the Gaussian-approximation formalism, and they fit their data with no adjustable parameters by including only the T_1 of the planar Cu as the source of the Cu nuclear spin fluctuations. We have analyzed the effects of T_1 fluctuations of the internuclear coupling of the planar Cu nuclei on the planar Cu echo decay by adopting the approach of Recchia *et al.* and generalizing their model for a spin-3/2 nucleus.

THE GAUSSIAN-APPROXIMATION FORMALISM

Recchia *et al.* calculated the echo decay of the Y echo magnetization, $M(2\tau)$, produced by the T_1 fluctuations of Cu nuclear spins. They used the so-called Gaussian approximation, in which the magnetization at time 2τ is given by

$$M(2\tau) = M_0 e^{-\langle\phi^2\rangle/2}, \quad [8]$$

where $\langle\phi^2\rangle$ is the mean squared phase accumulated by the Y spins in the rotating frame produced by Cu nuclear spins fluctuations. We consider the decay of the Cu echo arising from coupling to other Cu nuclear spins. We assume that $a_{\perp} = 0$, and we denote the gyromagnetic ratio of the nucleus under observation by γ and the I_z quantum number of the neighboring nucleus at position $\mathbf{r}$ by m. The local field seen by the observed nucleus arising from the neighbors is given in units of magnetic field by

$$h_z(t) = \frac{-1}{\gamma}\sum_{m,\mathbf{r}} a_z(\mathbf{r})\, m\, p_{m,\mathbf{r}}(t). \quad [9]$$

The function $p_{m,\mathbf{r}}(t)$ is defined such that it is unity if the mth state of the nucleus at $\mathbf{r}$ is occupied at time t and zero otherwise.

In the rotating frame the observed nucleus precesses in the field given by [8] accumulating a phase ϕ over the time interval zero to t given by

$$\phi(t) = \gamma \int_0^t h_z(t')dt'. \qquad [10]$$

The spin-echo decay is obtained by measuring the size of the echo as a function of the pulse spacing τ in the pulse sequence $\frac{\pi}{2}-\tau-\pi-\tau$. The π pulse at time τ does two things. First it acts as though it changes the direction of phase accumulation. This simply changes the sign of [9] for $t > \tau$:

$$\phi(2\tau) = \gamma \int_0^\tau h_z(t')dt' - \gamma \int_\tau^{2\tau} h_z(t')dt'. \qquad [11]$$

Second, the π pulse can affect the populations $p_{m,\mathbf{r}}(t)$ of a neighboring spin depending on whether it is a like or unlike nucleus. If it is an unlike nucleus, the populations $p_{m,\mathbf{r}}(t)$ are unaffected. If it is a like nucleus, the populations $p_{m,\mathbf{r}}(t)$ are changed. For the case of high-field NMR in which the central transition is observed, and defining τ^- and τ^+ as the times just before and just after the π pulse, we have

$$p_{m,\mathbf{r}}(\tau^+) = \sum_j Z_{mj} p_{j,\mathbf{r}}(\tau^-), \qquad [12]$$

where the matrix $\mathbf{Z}$ for like nuclei in NMR is given by

$$\mathbf{Z} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \qquad [13]$$

For zero-field NQR the matrix $\mathbf{Z}$ is given by

$$\mathbf{Z} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}. \qquad [14]$$

To calculate the mean square phase $\langle \phi^2 \rangle$ one must square Eq. [11] and take an ensemble average:

$$\langle \phi^2 \rangle = \Big\langle \Big(\int_0^\tau \int_0^\tau - \int_\tau^{2\tau} \int_0^\tau - \int_0^\tau \int_\tau^{2\tau} + \int_\tau^{2\tau} \int_\tau^{2\tau} \Big) \times \sum_{m,m',\mathbf{r},\mathbf{r}'} a_z(\mathbf{r}) a_z(\mathbf{r}') m m' p_{m\mathbf{r}}(t) p_{m'\mathbf{r}'}(t') dt dt' \Big\rangle. \qquad [15]$$

In order to evaluate the above expression, it is necessary to compute the quantity

$$\langle p_{m\mathbf{r}}(t) p_{m'\mathbf{r}'}(t') \rangle. \qquad [16]$$

To do so, we must remember that we are calculating the mean squared phase angle, not the mean phase angle squared. Therefore, we must follow individual histories in which the quantities $p_{m,\mathbf{r}}(t)$ are treated as zero or one. Eventually we perform an average over all possible histories. We assume that the nuclear spins fluctuate independently at each site so that [16] vanishes for $\mathbf{r} \neq \mathbf{r}'$. Furthermore, [16] depends on whether or not t and or t' occur before or after the π pulse at time τ. We define $P_{m',m}(t)$ as the probability that a nucleus in state m at time $t = 0$ will be in state m' at time t. Consider then the case (a) $t, t' < \tau$. We assume that the system is initially in a state i, and that at time t finds itself in state m. We then calculate $P_{m'm}(|t' - t|)$, the probability that the system goes from state m to state m' in the time interval $|t' - t|$, and multiply this by the probability $P_{mi}(t)$ that the system, starting in state i, finds itself in state m at time t. We then average over the four possible initial states:

$$\langle p_{m\mathbf{r}}(t) p_{m'\mathbf{r}'}(t') \rangle = \frac{1}{4} \sum_i P_{mi}(t) P_{m'm}(|t' - t|) \delta_{\mathbf{r}\mathbf{r}'}. \qquad [17]$$

For case (b) $t < \tau$, $t' > \tau$ and case (c) $t > \tau$, $t' < \tau$, one must account for the probability for the population in a particular state j being affected by the π pulse:

$$\langle p_{m\mathbf{r}}(t) p_{m'\mathbf{r}'}(t') \rangle = \frac{1}{4} \sum_{i,j,k} P_{mi}(t) P_{jm}(|\tau^- - t|) \times Z_{km} P_{m'k}(|t - \tau^+|) \delta_{\mathbf{r}\mathbf{r}'}. \qquad [18]$$

Finally for case (d) $t, t' > \tau$,

$$\langle p_{m\mathbf{r}}(t) p_{m'\mathbf{r}'}(t') \rangle = \frac{1}{4} \sum_{i,j,k} P_{ji}(\tau^-) Z_{kj} P_{mk}(|t' - \tau^+|) \times P_{m'm}(|t' - t|) \delta_{\mathbf{r}\mathbf{r}'}. \qquad [19]$$

The probabilities $P_{mm'}(t)$ are determined by the spin–lattice relaxation rate $W_1 = 3/(2T_1)$ and the equation

$$\frac{d\varrho_{n,\mathbf{r}}(t)}{dt} = \sum_m W_{nm} \varrho_{m,\mathbf{r}}(t), \qquad [20]$$

where $\varrho_{n,\mathbf{r}}(t)$ is the average population of state n at time t, and the W_{nm} values are given in the matrix

$$\mathbf{W} = \begin{pmatrix} -W_1 & W_1 & 0 & 0 \\ W_1 & -W_1 - W_2 & W_2 & 0 \\ 0 & W_2 & -W_1 - W_2 & W_1 \\ 0 & 0 & W_1 & -W_1 \end{pmatrix}. \quad [21]$$

Then, $P_{m'm}(|t' - t|)$ is given by solving these equations for $\varrho_{m'}(t)$ for the initial condition $\varrho_k(0) = \delta_{mk}$. The ratio of W_1 to W_2 is given by the ratio of the matrix elements:

$$\frac{W_1}{W_2} = \frac{|\langle +\frac{3}{2}|I_+|+\frac{1}{2}\rangle|^2}{|\langle +\frac{1}{2}|I_+|-\frac{1}{2}\rangle|^2} = \frac{3}{4}. \quad [22]$$

It is straightforward to generalize Eq. [20] to include fluctuations from other sources, such as mutual exchanges, although we will not do so here.

To calculate $\varrho_{m'}(t)$, one must solve for the normal modes of [20] by transforming to a basis $\mathbf{q} = \mathbf{R}^{-1}\varrho$, where $\mathbf{R}$, given below, is a matrix of the normalized eigenvectors of $\mathbf{W}$:

$$\mathbf{R} = \begin{pmatrix} \frac{1}{2} & \frac{3}{2\sqrt{5}} & \frac{1}{2} & \frac{1}{2\sqrt{5}} \\ \frac{1}{2} & \frac{1}{2\sqrt{5}} & \frac{-1}{2} & \frac{-3}{2\sqrt{5}} \\ \frac{1}{2} & \frac{-1}{2\sqrt{5}} & \frac{-1}{2} & \frac{3}{2\sqrt{5}} \\ \frac{1}{2} & \frac{-3}{2\sqrt{5}} & \frac{1}{2} & \frac{-1}{2\sqrt{5}} \end{pmatrix}. \quad [23]$$

Note that $\mathbf{R}$ is a unitary matrix, so $R_{ij}^{-1} = R_{ji}$.

If the nucleus is initially in state m at $t = 0$, then $q_i^{(m)}(t) = R_{im}^{-1}e^{\lambda_i t}$, where λ_i is the ith eigenvalue of $\mathbf{W}$ ($\lambda_1 = 0$, $\lambda_2 = -2W_1/3$, $\lambda_3 = -2W_1$, $\lambda_4 = -4W_1$). $\varrho_{m'}(t)$ is then given by $\varrho_{m'}(t) = \sum_i R_{m'i}q_i^{(m)}(t)$, so

$$P_{m'm}(t) = \sum_i R_{m'i}e^{\lambda_i t}R_{im}^{-1}. \quad [24]$$

These transition probabilities are shown in Fig. 1.

Utilizing Eqs. [13], [14], [17]–[19], and [24] one can simplify Eq. [15], obtaining

$$\langle\phi^2\rangle = \sum_{\mathbf{r}} a_z^2(\mathbf{r}) \left(\int_0^\tau \int_0^\tau g_1(|t'-t|)dtdt' - \int_\tau^{2\tau}\int_0^\tau g_2(|t'-t|)dtdt' - \int_0^\tau\int_\tau^{2\tau} g_3(|t'-t|)dtdt' + \int_\tau^{2\tau}\int_\tau^{2\tau} g_4(|t'-t|)dtdt' \right), \quad [25]$$

where the correlation functions $g_i(t)$ are given by

$$g_1(t) = g_4(t) = \tfrac{5}{4}e^{-2W_1t/3}, \quad [26]$$

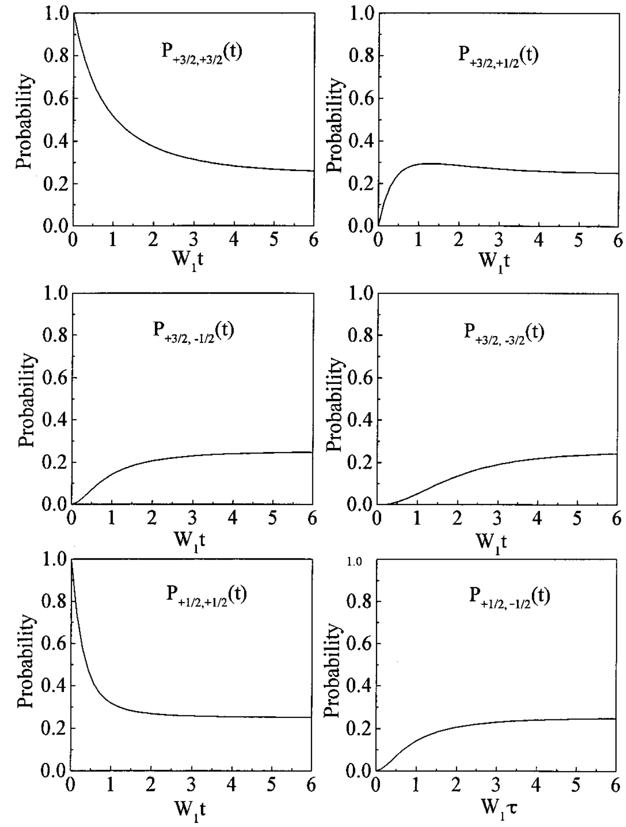

FIG. 1. The spin–lattice relaxation transition probabilities $P_{m,m'}(t)$ as a function of W_1t. The six distinct possible transitions are shown.

and

$$g_2(t) = g_3(t) = Ne^{-2W_1t/3}, \quad [27]$$

where N is 5/4 for unlike nuclei, 1 for like nuclei in NMR, and 3/4 for like nuclei in NQR. Here we have utilized the relations

$$\sum_i P_{mi}(t) = \sum_{i,j} R_{mj}e^{\lambda_j t}R_{ji}^{-1} = \sum_j R_{mj}e^{\lambda_j t}(2\delta_{j1}) = 2R_{m1} = 1, \quad [28]$$

and

$$\sum_m mR_{mj} = \sqrt{5}\delta_{j2}, \quad [29]$$

where we take $m = (3/2, 1/2, -1/2, -3/2)$. Performing the integrals in [25], taking care with the integral limits, and utilizing Eq. [3] one obtains the following for like nuclei in NMR (Eq. [30]), like nuclei in NQR (Eq. [31]), and unlike nuclei in both NMR and NQR (Eq. [32]):

$$\langle\phi^2\rangle_{\mathrm{NMR}} = \frac{2^{\eta}P^{-1}}{W_1^2T_{2G}^2}[30W_1\tau + 81e^{-2W_1\tau/3} - 18e^{-4W_1\tau/3} - 63] \quad [30]$$

$$\langle\phi^2\rangle_{\mathrm{NQR}} = \frac{2^{\eta}P^{-1}}{W_1^2T_{2G}^2}\left[30W_1\tau + 72e^{-2W_1\tau/3} - \frac{27}{2}e^{-4W_1\tau/3} - \frac{117}{2}\right] \quad [31]$$

$$\langle\phi^2\rangle_{\mathrm{unlike}} = \frac{2^{\eta}P^{-1}}{W_1^2T_{2G}^2}\left[30W_1\tau + 90e^{-2W_1\tau/3} - \frac{45}{2}e^{-4W_1\tau/3} - \frac{135}{2}\right]. \quad [32]$$

For $W_1\tau \ll 1$, the Taylor series expansions of these quantities gives

$$\langle\phi^2\rangle_{\mathrm{NMR}} = \frac{2}{^{\eta}P}\frac{(2\tau)^2}{2T_{2G}^2}\left(1 + \frac{7}{9}W_1(2\tau) - \frac{23}{108}W_1^2(2\tau)^2 + \cdots\right) \quad [33]$$

$$\langle\phi^2\rangle_{\mathrm{NQR}} = \frac{4}{^{\eta}P}\frac{(2\tau)^2}{2T_{2G}^2}\left(1 + \frac{2}{9}W_1(2\tau) - \frac{8}{27}W_1^2(2\tau)^2 + \cdots\right) \quad [34]$$

$$\langle\phi^2\rangle_{\mathrm{unlike}} = \frac{2}{^{\eta}P}\frac{(2\tau)^2}{2T_{2G}^2}\left(0 + \frac{10}{9}W_1(2\tau) - \frac{5}{18}W_1^2(2\tau)^2 + \cdots\right). \quad [35]$$

Note that for $W_1 = 0$, there is no contribution to echo decay from unlike spins, and the echo decay from the like spins is simply the traditional Gaussian T_{2G} decay. The factor of 2 between the NMR and NQR like echo decays arises from the fact that in NQR there are twice as many like nuclei as in the NMR case. Usually this factor is absorbed into the definition of the NQR T_{2G}. We adopt this convention below. Also, for NQR we have assumed an aligned powder. For an unaligned powder, there is another factor of 1.03 (*1*), which has not been included here.

The relative sizes of the W_1 correction term (the τ^3 term) are of interest. The correction is greatest for unlike nuclei and least for NQR of like nuclei. In Figs. 2 and 3 we compare the phase accumulated with and without spin–lattice relaxation for a spin-3/2 nucleus coupled to an unlike nucleus, a like nucleus in NMR, and a like nucleus in NQR. Figure 2 shows the phase accumulated by the observed nucleus when the coupling nucleus is in each one of the four possible spin states. Figure 3 shows the root mean square (rms) value of the phase assuming that there is equal probability of finding the neighboring nucleus in any of the four possible spin states. The T_1 fluctuations of unlike nuclei affect the rms phase more than the fluctuations of the like nuclei, but only after the π pulse at time τ. In Fig. 2, note that for a spin state that is not affected by the π pulse (i.e., all states of the unlike nucleus), the T_1 fluctuations prevent perfect refocusing and result in a large phase difference at time 2τ. For a spin state which is affected by the π pulse, the T_1 fluctuations prevent the observed nucleus from accumulating as much phase as it would in the absence of T_1 fluctuations. Thus for levels that are affected by the π pulse, the T_1 correction is negative, whereas for levels that are not affected by the π pulse, the T_1 correction is positive. Consequently, for the NMR case, where the central states are flipped by the π pulse and the outer states are unaffected, there is a positive and a negative correction to the phase, and the overall correction to the rms phase is less than the case for an unlike nucleus. For the NQR case, in which there are twice as many levels which are affected by the π pulse, the T_1 correction is even smaller.

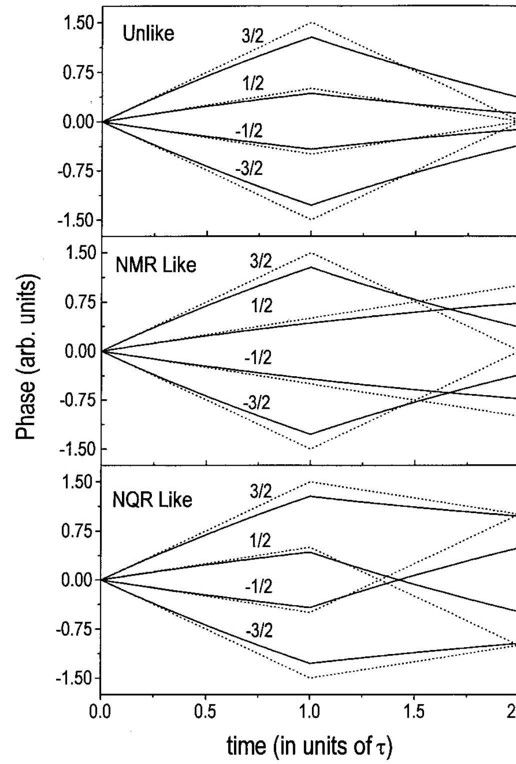

FIG. 2. The phase accumulated by a nucleus coupled to an unlike neighbor, a like neighbor in NMR, and a like neighbor in NQR, in which the coupling nucleus is in each one of the four possible spin states. The phase is plotted as a function of τ, the spacing between the $\pi/2$ pulse and the π pulse. The dotted lines are for no spin–lattice relaxation and the solid lines are calculated for $W_1 = 1/2\tau$.

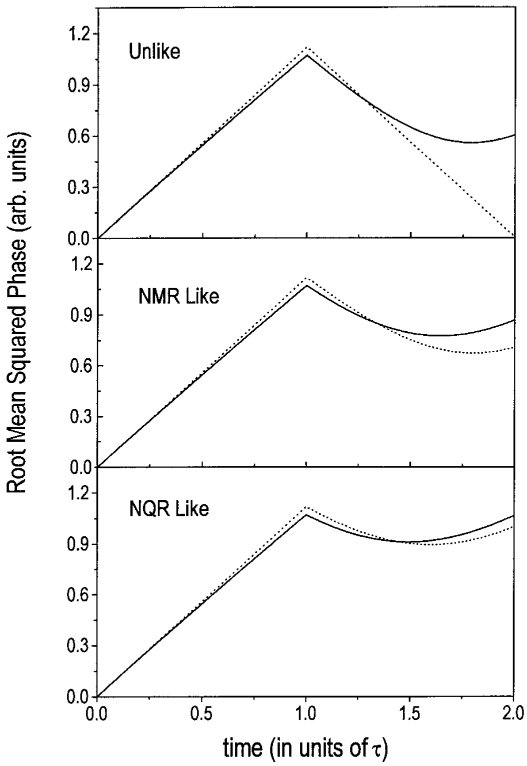

FIG. 3. The root mean squared phase accumulated by a nucleus coupled to an unlike neighbor, a like neighbor in NMR, and a like neighbor in NQR. The phase is plotted as a function of τ, the spacing between the $\pi/2$ pulse and the π pulse. The dotted lines are for no spin–lattice relaxation and the solid lines are calculated for $W_1 = 1/2\tau$.

Also of interest in Fig. 3 is the phase accumulated after the π pulse. Note that the phase distribution for like spins actually reaches a minimum before the refocusing time $t = 2\tau$. This result contrasts with that for a spin-1/2 nucleus in which the system continues to accumulate phase monotonically after the π pulse. The reason for the difference is that we consider the case in which only the central transition (in NMR) of the spin-3/2 nucleus is inverted by the π pulse (or only the two outer transitions in NQR). The nuclei in states other than those affected by the π pulse behave as unlike spins, and thus tend to partially cancel out the phase, resulting in a minimum in the phase. Furthermore, it is of interest to note that the phase at $t = 2\tau$ is twice as large for NQR as for NMR. This difference arises because in NQR, there are twice as many like nuclei, so a greater fraction of the nuclei do not refocus as unlike nuclei. This difference between the NMR and NQR phases is the reason for the factor of $\sqrt{2}$ between their T_{2G}'s.

In high-temperature superconductors, there is in reality a mixture of like and unlike nuclei in the plane because there is a mixture of ^{63}Cu and ^{65}Cu. We assume that at each site the probability of finding a particular isotope is given by its natural abundance, $^{\eta}P$, where $\eta = 63$ or 65, and we will denote η' as the isotope other than that observed, i.e., an unlike nucleus. Since these two isotopes fluctuate independently with rates $^{63}W_1$ and $^{65}W_1$, they contribute independently to $\langle \phi^2 \rangle$. Their relaxation rates are related by

$$^{65}W_1 = \frac{^{65}\gamma^2}{^{63}\gamma^2}\, {}^{63}W_1. \qquad [36]$$

Incorporating Eqs. [30]–[32] and Eq. [8], the echo decay for NMR is

$$\log\left(\frac{^{\eta}M}{M_0}\right) = \frac{-1}{(^{\eta}W_1 {}^{\eta}T_{2G})^2}\,[30\,{}^{\eta}W_1\tau + 81e^{-2\,{}^{\eta}W_1\tau/3} - 18e^{-4\,{}^{\eta}W_1\tau/3} - 63] + \frac{-1}{(^{\eta'}W_1 {}^{\eta}T_{2G})^2}\left(\frac{^{\eta'}P}{^{\eta}P}\right)\left(\frac{^{\eta'}\gamma}{^{\eta}\gamma}\right)^2 \times \left[30\,{}^{\eta'}W_1\tau + 90e^{-2\,{}^{\eta'}W_1\tau/3} - \frac{45}{2}e^{-4\,{}^{\eta'}W_1\tau/3} - \frac{135}{2}\right] \qquad [37]$$

and that for NQR is

$$\log\left(\frac{^{\eta}M}{M_0}\right) = \frac{-1}{(^{\eta}W_1 {}^{\eta}T_{2G})^2}\left[15\,{}^{\eta}W_1\tau + 36e^{-2\,{}^{\eta}W_1\tau/3} - \frac{27}{4}e^{-4\,{}^{\eta}W_1\tau/3} - \frac{117}{4}\right] + \frac{-1}{2(^{\eta'}W_1 {}^{\eta}T_{2G})^2}\left(\frac{^{\eta'}P}{^{\eta}P}\right)\left(\frac{^{\eta'}\gamma}{^{\eta}\gamma}\right)^2 \times \left[30\,{}^{\eta'}W_1\tau + 90e^{-2\,{}^{\eta'}W_1\tau/3} - \frac{45}{2}e^{-4\,{}^{\eta'}W_1\tau/3} - \frac{135}{2}\right]. \qquad [38]$$

We are assuming here that the data have already been corrected for the Redfield contribution to the echo decay. The factor of 1/2 in the unlike spin contribution to the NQR echo decay arises from the factor of $\sqrt{2}$ between the definitions of the NMR T_{2G} and the NQR T_{2G}.

Expanding the right-hand side of these expressions for small $W_1\tau$, one obtains expressions of the form $e^{-(2\tau)^2/2T_{2G}^2} f(2\tau)$, where

$$f(2\tau) = \exp\left[-{}^{\eta}C_1 \frac{W_1(2\tau)^3}{T_{2G}^2} - {}^{\eta}C_2 \frac{W_1^2(2\tau)^4}{T_{2G}^2} + \cdots\right]. \qquad [39]$$

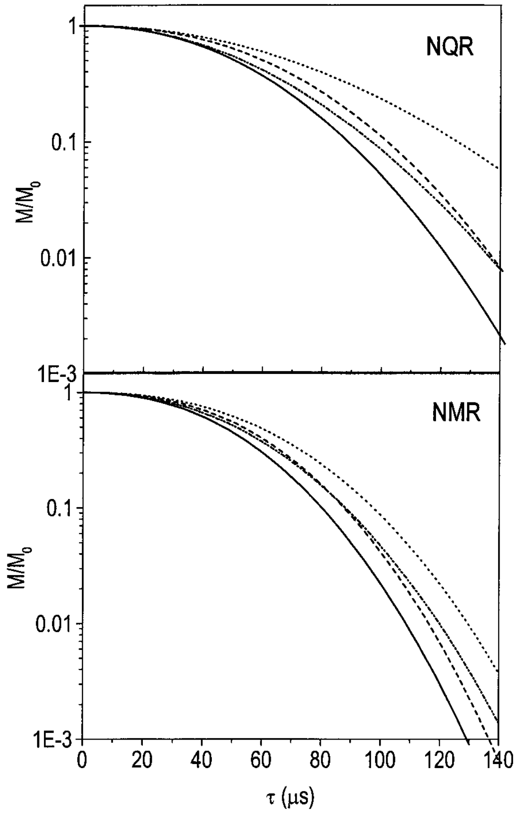

FIG. 4. Echo decays for ^{63}Cu and ^{65}Cu in NMR and NQR with and without the T_1 correction. The solid line is the echo decay for the ^{63}Cu for a finite T_1, the dash-dot-dot line is the echo decay for the ^{63}Cu for infinite T_1, the dashed line is the echo for the ^{65}Cu for a finite T_1, and the dotted line is the echo decay for the ^{65}Cu for infinite T_1. These plots show Eqs. [37] and [38] in the text for $^{63}T_{2G} = 90\ \mu s$ and $^{63}W_1 = 2.16\ \text{ms}^{-1}$.

The expansion coefficients are functions of the natural abundances and the gyromagnetic ratios, which are known constants. For example, for NMR, the lowest order coefficients are

$$^{63}C_1 = 0.7177, \quad ^{63}C_2 = -0.2008$$
$$^{65}C_1 = 1.3276, \quad ^{65}C_2 = -0.3109 \qquad [40]$$

and those for NQR are

$$^{63}C_1 = 0.2755, \quad ^{63}C_2 = -0.0830$$
$$^{65}C_1 = 0.5804, \quad ^{65}C_2 = -0.1393. \qquad [41]$$

In Fig. 4 we show the effects of T_1 fluctuations on the echo decay for typical values for W_1 and T_{2G}. Note that the T_1 fluctuations affect the NQR ^{63}Cu case minimally. Since all of the parameters in these expressions are known and W_1 can be measured separately, one can fit the echo decay data by including the function $f(2\tau)$ as a correction factor. We

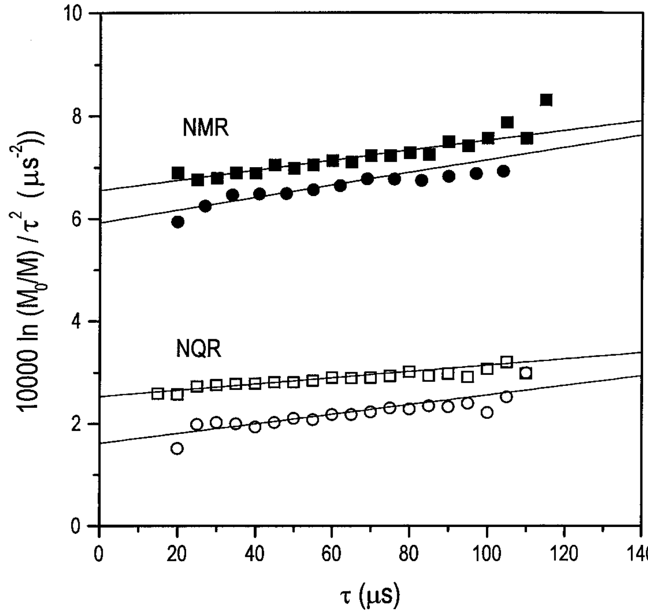

FIG. 5. The experimental NMR and NQR echo decays for ^{63}Cu and ^{65}Cu in $YBa_2Cu_4O_8$. The quantity $-\log(M/M_0)/\tau^2$ is plotted as a function of τ, the time between the $\pi/2$ and the π pulse. The Redfield term has been divided out. The squares are for ^{63}Cu and the circles are for ^{65}Cu. The solid symbols are the NMR data points and the open symbols are for NQR. The NMR echo decays have been displaced upward for clarity. The solid lines are linear functions using parameters obtained from a fit using Eq. [39]. The only variable parameters involved are M_0 and T_{2G}.

have fit the echo decay data at room temperature of the planar Cu in these four cases for $YBa_2Cu_4O_8$, and we show the data in Fig. 5. We have chosen to plot the quantity $-\log(M/M_0)/\tau^2$ versus τ, which to first order in W_1 should be a straight line. Plotted in this manner, the slope of the data indicates the size of the T_1 correction. The solid lines in Fig. 5 are linear plots based on parameters from fits to the M versus τ data using Eq. [39]. The NQR measurements were made on an unaligned powder as described in (*2*), and the NMR measurements were made on an aligned powder. The room temperature corrections to T_{2G} are about 7% for ^{63}Cu NQR, 19% for ^{65}Cu NQR, 19% for ^{63}Cu NMR, and 37% for ^{65}Cu NMR. The data are summarized in Table 1. It is useful to compute the ratio of the T_{2G}'s from the various experiments. The theoretical values of these ratios are known (*14, 15*), and one can compare the ratios obtained with and without the T_1 correction. Table 2 summarizes the results.

TABLE 1

Measurement	T_{2G} (μs) (uncorrected)	T_{2G} (μs) (corrected)
NQR ^{63}Cu	83.21 ± 0.10	88.88 ± 0.11
NQR ^{65}Cu	93.75 ± 1.89	111.17 ± 2.29
NMR ^{63}Cu	95.48 ± 0.95	113.37 ± 0.52
NMR ^{65}Cu	107.18 ± 1.11	147.19 ± 1.88

TABLE 2

Quantity	Theory	Experiment (uncorrected)	Experiment (corrected for T_1)
NMR isotope ratio	$({}^{65}\gamma/{}^{63}\gamma)^2\sqrt{({}^{63}P/{}^{65}P)} = 1.30$	1.12 ± 0.02	1.30 ± 0.02
NQR isotope ratio	$({}^{65}\gamma/{}^{63}\gamma)^2\sqrt{({}^{63}P/{}^{65}P)} = 1.30$	1.13 ± 0.03	1.25 ± 0.03
^{63}Cu NMR/NQR ratio	$\sqrt{2}/1.03 = 1.37$	1.15 ± 0.01	1.28 ± 0.01
^{65}Cu NMR/NQR ratio	$\sqrt{2}/1.03 = 1.37$	1.14 ± 0.03	1.32 ± 0.03

EXCHANGE FLUCTUATIONS

It has been argued that the $a_\perp$ term in Eq. [1], which gives rise to mutual exchanges, is important in $La_{1.85}Sr_{0.15}CuO_4$ (*11*). We argue that these processes are suppressed for the Cu in $YBa_2Cu_4O_8$. First we give the theoretical reason, and then we cite evidence to support this theory. We will discuss the case for NMR of the $+1/2$ to $-1/2$ transition.

In order for two nuclei to undergo a mutual spin flip, they must be able to conserve energy. The two nuclei must be like nuclei, and the local fields at two nuclei must also be similar. Consider then mutual spin flips between nearest neighbor nuclei which we designate as I and II. Each has three other nearest neighbors, each of which can be in one of four nuclear levels. Thus, there is very little chance that nuclei I and II have the same local fields. In fact, if one assumes that I and II are in the $\pm 1/2$ levels and are each coupled to the three next nearest neighbors, the probability that I and II will have identical local fields is only $\sim$14%.

Mutual spin flips are further suppressed due to the relative size of a_z and $a_\perp$. The transverse coupling $a_\perp$ is given by

$$a_\perp(\mathbf{r}) = -\frac{1}{N}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} F^2_{\parallel,\mathrm{eff}}(\mathbf{q})\chi'(\mathbf{q}), \qquad [42]$$

where $F_{\parallel,\mathrm{eff}}(\mathbf{q})$ is the form factor for the field oriented perpendicular to the c axis, given by (*16*)

$$F_{\parallel,\mathrm{eff}}(\mathbf{q}) = (A_\perp + 2B[\cos(q_x a) + \cos(q_y a)])^2. \qquad [43]$$

$A_\perp$ is the perpendicular on-site hyperfine coupling. As described above, PS (*5*) showed that typically $a_\perp/a_z \ll 1$ in $YBa_2Cu_3O_7$ and hence $a_\perp$ can be neglected. One might argue that this condition is not met in all of the HTSCs. One can approximate the ratio $a_\perp/a_z \ll 1$ for large correlation length (in which case $\chi(\mathbf{q})$ is peaked at $\mathbf{Q} = (\pi/a, \pi/a)$) as

$$\frac{a_\perp}{a_z} \approx \frac{F^2_{\parallel,\mathrm{eff}}(\mathbf{Q})}{F^2_{\perp,\mathrm{eff}}(\mathbf{Q})} \approx \frac{1}{2}\left(\frac{W_{1ab}}{W_{1c}} - \frac{1}{2}\right)^{-2}, \qquad [44]$$

where W_{1ab}/W_{1c} is the T_1 anisotropy ratio. This formula provides one with a method for estimating how strongly mutual spin flips are suppressed. We believe that this calculation reveals the reason that in (*4*) Pennington *et al.* found that for the chain Cu, which have isotropic T_1's, the T_{2G} did not obey the isotope ratio law.

The experimental evidence for the suppression of mutual spin flips in $YBa_2Cu_3O_7$ (and we suppose in $YBa_2Cu_4O_8$) is the following. If one has mutual spin flips, this process should happen randomly and have a correlation time associated with it. Recchia *et al.* studied the echo decay for the Y in $YBa_2Cu_3O_7$. We expect the ratio $a_z/a_\perp$ to be large for this material (somewhat larger than for $YBa_2Cu_4O_8$). They show that the Y echo decay results from flips of the Cu nuclei. They found that they could fit their data exactly using only the spin–lattice fluctuations of the planar Cu to limit its lifetime in a state. One would expect that if mutual spin flips between the planar Cu were indeed important then the Y echo decay would have an extra component associated with the correlation time for spin flips.

CONCLUSIONS

In high-temperature superconductors, spin–lattice relaxation fluctuations can contribute to the echo decay of the planar Cu when T_1 becomes of the order of the echo decay time. The echo decay takes on a simple form in which the T_1 fluctuations can be treated in an exact manner as a correction to the T_{2G}. The correction is minimized for the case of NQR of ^{63}Cu. Mutual exchange processes arising from the $a_\perp$ term in the Hamiltonian are suppressed in these materials due to the small probability that neighboring nuclei see the same local field. The degree to which exchange processes are suppressed is determined also by the ratio $a_z/a_\perp$. In the limit of large correlation length this quantity is determined by the T_1 anisotropy ratio.

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16. Here we simply take the expression in Eq. [5] and replace the on-site hyperfine coupling for the parallel direction with the perpendicular on-site coupling.