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Theory of nuclear spin–lattice relaxation in La_2CuO_4 at high temperatures

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The nuclear spin–lattice relaxation in La_2CuO_4 is reexamined in connection with the recent measurements of the NQR relaxation rate for temperatures up to 900 K [T. Imai, C.P. Slichter, K. Yoshimura, and K. Kosuge, Phys. Rev. Lett. **70**, 1002 (1993)]. We use an approach based on the exact diagonalization for the Heisenberg model to calculate the short-wavelength contribution to the relaxation rate in the high-temperature region, $T \gtrsim J/2$. It is shown that the spin diffusion accounts for approximately 10% of the total relaxation rate at 900 K and would become dominant for $T > J$. The calculated $1/T_1$ is in good agreement with the experiment both in terms of the absolute value and temperature dependence.

The fact that the spin dynamics of the parent insulating compound La_2CuO_4 is described by the $S = 1/2$ Heisenberg model with $J \simeq 1500$ K is now very well established (for reviews, see Refs. 1 and 2). Recently, Imai *et al.*[3] have measured the copper nuclear-spin–lattice relaxation rate, $1/T_1$ in the undoped and Sr-doped La_2CuO_4 for temperatures up to 900 K. They found a plateau in $1/T_1$ as a function of temperature for $700 < T < 900$ K. In this temperature region, the relaxation rate is insensitive to doping, a result which suggests that at high temperatures the dominant relaxation mechanism is the same in both metallic and insulating samples.[3]

As is known, for localized spins, the relaxation rate is determined by the so-called "exchange narrowing" mechanism.[4] The "exchange narrowing" here refers to the relaxation process governed by the spin-spin exchange interaction. An approach based on the Gaussian approximation for the dynamic structure factor has been developed in Ref. 4 in order to calculate the relaxation rate for $T \gg J$. In Refs. 5 and 6, this approach has been combined with a high-temperature expansion method and thus extended to finite temperatures of the order of J. For temperatures larger than J, $1/T_1$ has been shown to increase as the temperature increases. On the other hand, in the low-temperature limit the dominant contribution to the copper relaxation rate is due to critical fluctuations around $q = (\pi/a, \pi/a)$, and it increases exponentially as the temperature decreases, $1/T_1 \propto T^{3/2} \exp(2\pi\rho_s/T)$.[7] For $T \ll J$, the spin stiffness is $\rho_s \simeq 0.18J$. The interpolation from low to high temperatures shows that $1/T_1$ as a function of temperature has a minimum. In Ref. 7, its position has been predicted at $T \simeq 700$ K, a result which seems to be in contradiction with the experimental data of Ref. 3.

Therefore, the purpose of this work is to understand whether or not this experimental result can be *quantitatively* understood in the framework of the nearest-neighbor Heisenberg model. The analysis of the NMR data in $La_{2-x}Sr_xCuO_4$ has led to the conclusion that the hyperfine constants in this material approximately coincide with those of $YBa_2Cu_3O_x$.[3] We take advantage of this and use the values of the hyperfine couplings obtained in Ref. 8 for the yttrium-based compounds. Along with the use of $J \simeq 1500$ K for the exchange constant, this eliminates all adjustable parameters in our calculation.

The copper spin-lattice relaxation rate measured in the NQR experiment is

$$\frac{1}{T_1} = \frac{2T}{g^2\mu_B^2} \lim_{\omega\to 0} \frac{\chi''_{\rm hf}(\omega)}{\omega}, \tag{1}$$

where

$$\chi''_{\rm hf}(\omega) = \int \frac{d^2\mathbf{q}}{(2\pi/a)^2} A^2(\mathbf{q})\, \chi''(\mathbf{q},\omega) \tag{2}$$

(for simplicity, we use the units where $k_B = \hbar = 1$). In the NQR experiment, the hyperfine form factor $A(\mathbf{q})$ is given by[9]

$$A(\mathbf{q}) = A_{xy} + 2B\cos(q_x a) + 2B\cos(q_y a), \tag{3}$$

where A_{xy} and B are the in-plane local and isotropic transferred hyperfine couplings, respectively. In what follows, we use $A_{xy}/B = 0.84$, $B = 40.8\,\mathrm{kOe}/\mu_B$.[8]

The relaxation rate of the Heisenberg antiferromagnet has been discussed in several publications. However, the low-temperature calculation based on the dynamical scaling theory[7] is not valid for $T \sim J/2 = 750$ K, where also the contribution from wave vectors other than $q = (\pi/a, \pi/a)$ becomes important. On the other hand, it has been mentioned in Ref. 5 that the high-temperature expansion results based on the Gaussian approximation do not show the low-temperature increase of $1/T_1$, apparently because of the particular functional form assumed in this calculation for the dynamical structure factor. As it has been shown in Ref. 10 using the scaling considerations, $1/T_1$ is nearly temperature independent for $T \sim J/2$. Unlike our calculation, the $1/N$ approach employed in this paper to calculate the prefactor does not start from the $S = 1/2$ lattice model and so the absolute value of $1/T_1$ is evaluated in Ref. 10 using the low-temperature fit of the *same* data and not the hyperfine couplings A_{xy}, B.

For $T \ll J$, the spin diffusion ($q \to 0$) contribution to the relaxation rate, $(1/T_1)_{\mathrm{diff}}$, is negligible because the spin diffusion constant, D, is exponentially large.[7,11] However, D rapidly decreases as the temperature increases, that is, the $q \to 0$ component may be important for higher temperatures. In a pure two-dimensional (2D) model, the conservation of spin leads to the divergence of $(1/T_1)_{\mathrm{diff}}$; that is, the relaxation would be faster than exponential. However, in a real system $(1/T_1)_{\mathrm{diff}}$ remains finite and its magnitude is determined by the length scale L_s, set either by spin-nonconserving forces or three-dimensional effects. Since in any cluster calculation (exact diagonalization or Monte Carlo) the cutoff is set by the lattice size, we have taken into account the $q \to 0$ contribution separately.

Our approach for the calculation of the short-wavelength contribution to the relaxation rate is based on the exact diagonalization of the Hamiltonian for the 4×4 cluster. Since the nuclear spin-lattice relaxation rate is determined by short-range spin correlations, our results are relevant to the real system as long as the correlation length is not large compared to the cluster size. The spectral representation for χ''_{hf} can be written in terms of the Hamiltonian eigensystem as follows:

$$\frac{\chi''_{\mathrm{hf}}(\omega)}{g^2\mu_B^2} = \frac{\pi}{Z}\sum_{ab}\left[\exp(-E_a/T) - \exp(-E_b/T)\right] \times \delta(E_a - E_b + \omega)\,\frac{1}{N} \times \sum_{q \neq 0} A^2(\mathbf{q})\,|\langle a|S_q^z|b\rangle|^2, \qquad (4)$$

where $E_{a,b}$ are the eigenvalues of the Hamiltonian and $Z = \sum_a \exp(-E_a/T)$ is the partition function. In the thermodynamic limit ($N \to \infty$), χ''_{hf} is a continuous function of frequency, while for finite size it is a superposition of δ functions.

For a finite cluster, the limit $\omega \to 0$ in Eq. (1) is not defined, but we argue that the thermodynamic $\chi''_{\mathrm{hf}}(\omega)$ can be calculated using the following procedure. Consider the auxiliary function $I_N(\omega)$ given, for a cluster of size N, by

$$g^2\mu_B^2 I_N(\omega) = \frac{1}{2}\int_{-\omega}^{\omega} d\epsilon\,\frac{\chi''_{\mathrm{hf}}(\epsilon)}{\epsilon}. \qquad (5)$$

From this equation, $\chi''_{\mathrm{hf}}(\omega)/\omega = g^2\mu_B^2(dI_N/d\omega)$. For a finite cluster, $I_N(\omega)$ can easily be calculated from the eigenstates of the Hamiltonian:

$$I_N(\omega) = \sum_{ab} I_{ab}\left[\theta(E_a - E_b + \omega) - \theta(E_a - E_b - \omega)\right], \qquad (6)$$

where $\theta(x)$ is the Heaviside function and

$$I_{ab} = \frac{\pi}{2Z}\,\frac{\exp(-E_a/T) - \exp(-E_b/T)}{E_b - E_a} \times \frac{1}{N}\sum_{q \neq 0} A^2(\mathbf{q})|\langle a|S_q^z|b\rangle|^2 \qquad (7)$$

(for $a = b$ we take the limit $E_a \to E_b$). The auxiliary function $I_N(\omega)$ is quite smooth as long as the temperature is not much smaller than the gap between the ground state and the rest of the spectrum, which for the 16-site cluster is of order $J/2$. For temperatures $T > 1.5 - 2\,J$, we find no appreciable size dependence: $I_{10} \simeq I_{16}$. In the study of static properties of the Heisenberg model,[12] no discrepancy was found between the 4×4 cluster and Monte Carlo results for larger systems at $T > J$. Both the discrepancy and the error bars in the fitting of I_{16} by a smooth function increase up to approximately 10% for $T \simeq J/2$. Thus, we will assume that our calculation of the short-wavelength contribution to $1/T_1$ has 10% accuracy.

Now we turn to the calculation of the $q \to 0$ contribution to $1/T_1$. For $L_s^{-1} < q < \max(\xi, a)^{-1}$ and $\omega\tau \ll 1$, the dynamical spin susceptibility $\chi(\mathbf{q}, \omega)$ has the following form:

$$\chi(\mathbf{q}, \omega) = \chi(\mathbf{q})\,\frac{Dq^2}{Dq^2 - i\omega}, \qquad (8)$$

where D is the diffusion constant and τ a characteristic relaxation time. Substituting this expression into Eq. (1), we obtain

$$\left(\frac{1}{T_1}\right)_{\mathrm{diff}} = \frac{T\chi_0 a^2 A^2(q=0)}{\pi g^2\mu_B^2 D}\,\log\frac{L_s}{L_{\mathrm{f.s.}}}, \qquad (9)$$

where we take $L_{\mathrm{f.s.}} > \xi$ to be equal to the size of our cluster. For $T \gg J$, the diffusion constant is $D \simeq 0.43Ja^2$,[13] so that $(1/T_1)_{\mathrm{diff}} \sim 7400 \times \log(L_s/L_{\mathrm{f.s.}})\ \mathrm{sec}^{-1}$ is at least several times larger than the measured rate at the maximal accessible temperature 900 K.[3] This contribution is larger than the calculated short wavelength contribution at the same temperature. Therefore, the relaxation rate of the 2D Heisenberg model for $T > J$ is a *poorly defined quantity*, since it strongly depends on the way the cutoff is taken into account. In this temperature region, an accurate calculation of $1/T_1$ would have to involve the actual mechanism destroying the diffusion. However, since temperatures larger than the exchange constant are not experimentally accessible in La_2CuO_4, we will examine now whether or not the spin diffusion substantially contributes to the relaxation rate at 600 − 900 K.

In order to address this issue, we have to determine both the diffusion constant D and the length scale L_s for $T \simeq J/2$. The diffusion constant is estimated as[14,15]

$$D = \gamma \lim_{q\to 0} q^{-2} \langle\omega_\chi^2\rangle_q^{3/2} \langle\omega_\chi^4\rangle_q^{-1/2}, \tag{10}$$

where $\langle\omega_\chi^{2n}\rangle_q$ are the frequency moments of the dynamical response function,

$$\langle\omega_\chi^{2n}\rangle_q = \frac{\int \omega^{2n-1}\chi''(\mathbf{q},\omega)\,d\omega}{\int \omega^{-1}\chi''(\mathbf{q},\omega)\,d\omega}, \tag{11}$$

and γ is a numerical factor which depends on the assumed short-time relaxational behavior.[16] Taking $\gamma = \sqrt{\pi/2} \approx 1.25$ (Ref. 15) yields $D_{T=\infty} = 0.40Ja^2$, which is quite close to the value $0.43Ja^2$ (Ref. 13) obtained through an evaluation of the memory function. In Ref. 17, general expressions for the series in $\beta = J/T$ for $\langle\omega_\chi^{2n}\rangle_q$ have been derived. Using these results, we calculate first two terms of the high-temperature expansion for the diffusion constant:

$$\frac{D}{Ja^2} = \frac{\sqrt{\pi}}{2\sqrt{5}} + \frac{21\sqrt{\pi}\beta}{40\sqrt{5}} + O(\beta^2) \approx 0.40 + 0.42\beta + O(\beta^2). \tag{12}$$

Two leading terms in the high-temperature expansion series are not sufficient for the accurate estimate of D at $T \sim J/2$. However, we know that the diffusion constant should scale approximately as $D \propto \xi$ in the quantum critical region, $\rho_s < T < J$. Using Monte Carlo data of Ref. 18 for the correlation length, $\xi(T)$, we estimate $D \sim 3Ja^2$ at $T = 900$ K, which when substituted into Eq. (9) gives $(1/T_1)_{\rm diff} \sim (200-300) \times \log(L_s/L_{\rm f.s.})$ sec^{-1}.

Now we turn to the evaluation of the logarithm in Eq. (9). Since the hyperfine splitting $\sim 1.5 \times 10^{-7}$ eV is very small and above the tetragonal-to-orthorhombic transition temperature, $T_{T-O} \simeq 525$ K, the Dzyaloshinskii-Moriya interaction vanishes, the cutoff is determined either by the three-dimensional effects or by the nonconservation of spin. Consider first the cutoff due to the three-dimensional effects, $L_s^{\rm 3D}$, which is set by the interplanar diffusion constant, $D_\perp$. For estimation purposes, we express D in terms of the characteristic damping of spin waves for small wave vectors, $\bar{\gamma}$.[19] With omission of all factors of the order of unity, we get $D_\perp/D_\parallel \sim J'/J$, which yields $L_s^{\rm 3D} \sim 300a$, a quite large value.

Given the size of $L_s^{\rm 3D}$, we consider an alternative physical origin for the cutoff, the presence of disorder in CuO$_2$ planes. For temperatures above 700 K, the oxygen content changes after the heating cycle by approximately 0.004 per unit cell;[3] that is, the average distance between nonstoichiometric oxygen atoms, which we identify with L_s, is $10-20a$. The oxygen defects limit spin diffusion by introducing strong local perturbation. Although the value of L_s cannot be determined quite accurately, the $q \to 0$ contribution to $1/T_1$ depends on L_s only weakly. In what follows, we plot the results for $L_s = 10a$ and $L_s = 20a$. Substituting the above values of L_s into Eq. (9), one obtains that the spin diffusion contribution accounts for approximately 10% of the total spin lattice relaxation rate for $T = 900$ K, but rapidly decreases as the temperature decreases. This explains why the tetragonal-to-orthorhombic transition at $T_{T-O} = 525$ K does not have any observable effect on the spin-lattice relaxation although it affects L_s.

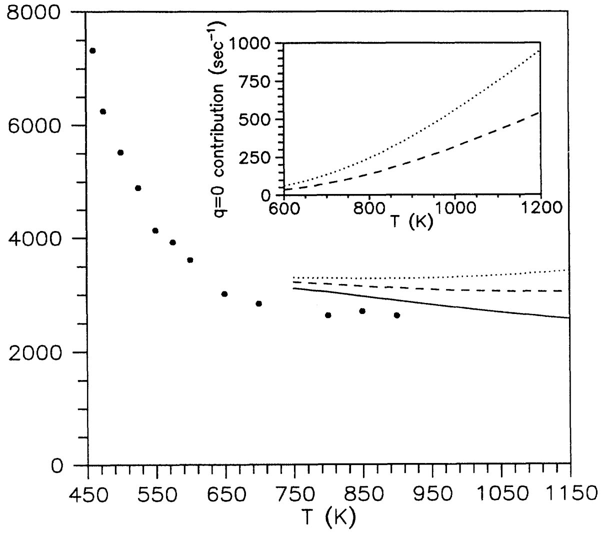

FIG. 1. The calculated $1/T_1$ as a function of temperature without (solid line) and with the spin diffusion contribution for $L_s = 10$ (dashed line), and for $L_s = 20$ (dotted line). Dots are the experimental result of Ref. 3. The error bars due to the calculation inaccuracy (less than 10%, not shown) are smaller than the ambiguity in the definition of $1/T_1$ related to the $q \to 0$ cutoff. Inset: the spin diffusion ($q \to 0$) contribution to the relaxation rate.

The total relaxation rate for $L_s = 10$ and $L_s = 20$ and the short-wavelength contribution alone are plotted in Fig. 1 together with the experimental result of Ref. 3. The theoretical result is in 15% agreement with the experiment (for $L_s = 10$). The agreement can be improved by either taking smaller L_s, or changing the hyperfine

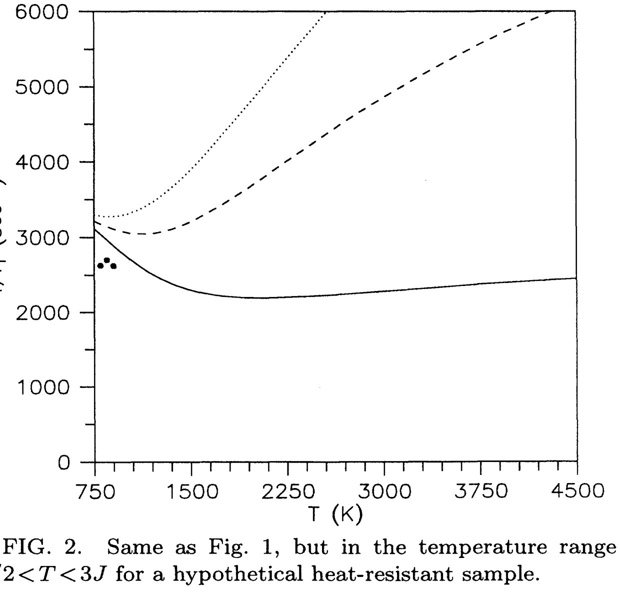

FIG. 2. Same as Fig. 1, but in the temperature range $J/2 < T < 3J$ for a hypothetical heat-resistant sample.

constants by 7% (actually, A_{xy}, B are known only with 5–10% accuracy[8]). It is important to emphasize, however, that the ambiguity in the definition of $1/T_1$ as a function of the cutoff L_s exceeds our estimate of the systematic error of the finite cluster calculation; moreover, the cutoff itself cannot be determined quite accurately. The spin diffusion ($q \to 0$) contribution rapidly increases as the temperature increases (Fig. 1, inset) and becomes dominant for $T > 1.5J$, as is shown on Fig. 2. Although this temperature range is beyond the limit of chemical stability for La_2CuO_4, it may be of interest for other materials described by the Heisenberg model but with smaller J, such as $Cu(HCO_2)_2 \cdot 4H_2O$ and $Cu(pyrazine)_2(ClO_4)_2$.[20]

To summarize, we have calculated the copper spin-lattice relaxation rate for La_2CuO_4 without introducing any adjustable parameters. The spin diffusion ($q \to 0$) contribution is shown to account for 10% of the relaxation for the maximal temperature achieved in the experiment, 900 K, although it would become dominant for larger temperatures, thereby explaining the discrepancy between different calculations of the relaxation rate at high temperatures. The measured $1/T_1$ (Ref. 3) turned out to be quantitatively consistent with the nearest-neighbor Heisenberg model description of the spin dynamics in La_2CuO_4.

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