^{63}Cu nuclear relaxation in the spin-Peierls compound $CuGeO_3$

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(Received 22 July 1996)

We have measured the temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ and the nuclear spin-spin relaxation rate $1/T_{2G}$ due to indirect nuclear coupling for ^{63}Cu NQR in the spin-Peierls (SP) compound $CuGeO_3$, which undergoes the SP transition at $T_{SP}\sim 14$ K, using a single crystal. We perform a combined analysis of $1/T_1$ and $1/T_{2G}$ on the basis of theoretical results recently obtained for the $S=1/2$ one-dimensional Heisenberg antiferromagnet (1DHAF) model to clarify the spin dynamics. Consequently we find that the spin dynamics above T_{SP} in $CuGeO_3$ is not described by the pure $S=1/2$ 1DHAF model. [S0163-1829(96)52138-7]

Nuclear relaxation measurements[1–4] in high-T_c superconducting copper oxides and related compounds have been shown to be powerful techniques in studying the low-energy spin dynamics of a two-dimensional quantum magnet. In particular, the nuclear spin-lattice relaxation rate $1/T_1$ and the nuclear spin-spin relaxation rate $1/T_{2G}$ due to the indirect coupling enable us to study the wave-vector q dependence of the dynamical susceptibility $\chi(q,\omega)$. Recently, Sachdev[5] analytically derived in the low-temperature region of $T\ll J$ (intrachain exchange interaction) the temperature T dependence of $1/T_1$ and $1/T_{2G}$ for a one-dimensional Heisenberg antiferromagnet (1DHAF) with a half-integer spin, using the analytical expression of $\chi(q,\omega)$ at $q\sim\pi$ obtained by Schulz.[6] Subsequently, Sandvik calculated the T dependence of $1/T_1$ and $1/T_{2G}$ up to $T\sim J$ for the $S=1/2$ 1DHAF model using quantum Monte Carlo (QMC) and maximum-entropy analytic continuation.[7] He showed the low-T behavior predicted by Sachdev persists up to a high temperature $T\sim 0.5J$, if the nuclear hyperfine form factor $A(q)$ is peaked around $q=\pi$. On the other hand, the $q=0$ contribution becomes important even at low temperatures, if $A(q)$ has significant weight for $q\sim 0$. Experimentally, the nuclear relaxation measurements were recently reported for a typical $S=1/2$ 1DHAF Sr_2CuO_3 with a large J of $\sim$2200 K,[8] and the experimental results were well reproduced by the analytical study[5] for $T\leqslant J$.

Hase, Terasaki, and Uchinokura recently found a new inorganic spin-Peierls (SP) compound $CuGeO_3$ which undergoes the SP transition at $T_{SP}\sim 14$ K.[9] There are in a unit cell two elongated CuO_6 octahedra which form linear chains along the c axis. This compound above T_{SP} can be treated as a pseudo-1DHAF of $S=1/2$. The intrachain exchange constant J along the c axis in the form of $\Sigma_{ij}JS_iS_j$ was reported to be 160 K (Ref. 10) and 150 K (Ref. 11) by theoretical analyses of the magnetic susceptibility, 120 K by the inelastic neutron-scattering measurement,[12] and 183 K by the magnetization study in ultra-high magnetic fields.[13] Previously, it was pointed out that the overall-T dependence of $1/T_1$ measured above T_{SP} up to 80 K for ^{63}Cu nuclear quadrupole resonance (NQR) in $CuGeO_3$ may be understood by the 1DHAF model.[14,15] However, this has not been confirmed up to now. In the present study, we have measured the T dependence of $1/T_{2G}$ for ^{63}Cu NQR to further clarify the spin dynamics in $CuGeO_3$, using a single crystal. Also we have measured the T dependence of $1/T_1$ up to 300 K. We will perform the combined analysis of $1/T_1$ and $1/T_{2G}$ based on the theoretical results for 1DHAF of $S=1/2$ by Sachdev and Sandvik, and discuss the spin dynamics in $CuGeO_3$.

A single crystal of $CuGeO_3$ was prepared by the floating zone method. The sample was confirmed to be a single phase by x-ray analysis. The $1/T_1$ and $1/T_{2G}$ measurements were performed for ^{63}Cu NQR by using a coherent pulsed spectrometer. The rate $1/T_1$ was measured by the saturation recovery method, whereas $1/T_{2G}$ was measured by changing the interval between focusing and refocusing rf pulses. A typical width of a π pulse was 1.5 μsec, that is, the strength of the rf pulse H_1 is 295 kHz which is comparable to the full width at half maximum of the ^{63}Cu NQR spectrum 300$\pm$20 kHz, at 4.2 K. Therefore, the obtained $1/T_{2G}$ value may provide a slight underestimating of the indirect coupling.

In general, the spin-echo amplitude $M(2\tau)$ as a function of the time interval τ between focusing and refocusing rf pulses is expressed as

$$M(2\tau)=M_0\exp\left[-\frac{2\tau}{T_{2R}}-\frac{1}{2}\left(\frac{2\tau}{T_{2G}}\right)^2\right], \tag{1}$$

where M_0 is a value at $\tau=0$ of $M(2\tau)$ and $1/T_{2R}$ is the spin-echo decay rate due to the nuclear spin-lattice relaxation process. The value of $1/T_{2R}$ can be estimated from the $1/T_1$ data using the relation $1/T_{2R}=(2+r)(1/T_1)$ for NQR by the Redfield theory.[3] In $CuGeO_3$, the anisotropy of $1/T_1$, r, was estimated to be $\sim$1/37 from the anisotropy of the hyperfine coupling constant as will be discussed later. Based on the T_1 data for ^{63}Cu NQR in $CuGeO_3$ which will be presented below, the T_{2R} process is concluded to have a negligible contribution to the spin-echo decay in $CuGeO_3$.

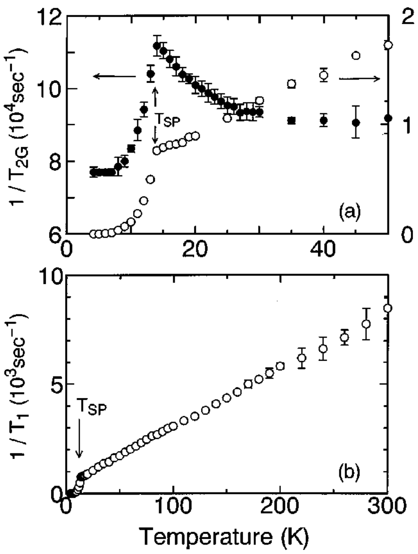

FIG. 1. Temperature dependence of (a) the Gaussian rate of the nuclear spin-spin relaxation $1/T_{2G}$ and the nuclear spin-lattice relaxation rate $1/T_1$ below 50 K, and (b) $1/T_1$ up to 300 K measured for ^{63}Cu NQR in $CuGeO_3$.

We measured $M(2\tau)$ for ^{63}Cu NQR in the T range of 4.2–50 K. We clearly observed the Gaussian decay above $\sim$12 K, whereas below $\sim$12 K the deviation from the Gaussian decay, which may be due to the modulation effect,[1] appeared in the long-time range. Therefore T_{2G} was determined by the least-squares fitting of the data to Eq. (1) without including the T_{2R} term. Particularly below 12 K the fitting was done only for the initial decay. Thus we found the T dependence of $1/T_{2G}$ as is presented in Fig. 1(a). The rate $1/T_{2G}$ gradually increases with decreasing T, and after a peak at $T_{\rm SP}$ decreases with further decreasing T. On the other hand, $1/T_1$ above $T_{\rm SP}$ increases with increasing T up to 300 K as is seen in Fig. 1(b). Below $T_{\rm SP}$, $1/T_1$ rapidly decreases due to the opening of the gap in the magnetic excitation spectrum, and the T dependence of $1/T_1$ is well traced by $T^{5.73\pm0.3}$ s^{-1} as the same as the previous report.[14]

The contribution of the nuclear dipole-dipole interaction to $1/T_{2G}$ in $CuGeO_3$ is smaller than $\sim 1.3\times10^3$ s^{-1}, which is evaluated by assuming that all Cu sites are equivalent. Therefore $1/T_{2G}$ in $CuGeO_3$ is predominantly ascribed to the indirect nuclear spin-spin coupling. In this case, $(1/T_{2G})^2$ is expressed for NQR as

$$(1/T_{2G})^2=\frac{p}{4\hbar^2(g\mu_B)^4}\sum_q \{|A_z(q)|^4\chi^2(q) -[|A_z(q)|^2\chi(q)]^2\}, \quad (2)$$

where p (=0.69 for ^{63}Cu) is the natural abundance of the nuclear spin, $\hbar$ is the Planck's constant, g is the electron g value, μ_B is the Bohr magneton, and $\chi(q)$ is the static susceptibility.[1,16] In a 1DHAF, the form factor of the hyperfine interaction is expressed as $A_\alpha(q)=A_\alpha^{(0)}+2A^{(1)}\cos(q)$ ($\alpha=x$, y, and z) where $A_\alpha^{(0)}$ and $A^{(1)}$ are anisotropic on-site and isotropic nearest-neighbor coupling constants, respectively. On the other hand, $1/T_1$ is expressed as

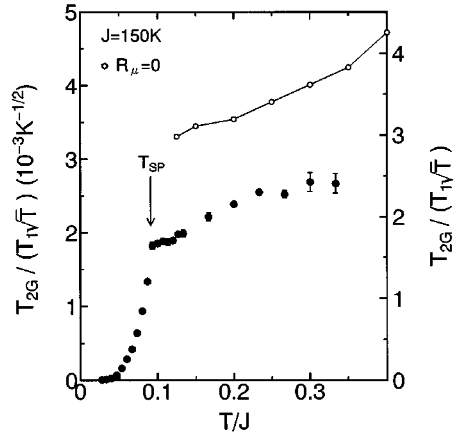

FIG. 2. Temperature dependence of $T_{2G}/(T_1\sqrt{T})$ measured for ^{63}Cu NQR in $CuGeO_3$. The solid curve with open circles represents the QMC result of the hyperfine ratio $R_\mu=0$ for the $S=1/2$ 1DHAF model (after Ref. 7).

$$\frac{1}{T_1}=\frac{2k_BT}{(\hbar g\mu_B)^2}\sum_q A_\perp^2(q)\frac{{\rm Im}\chi(q,\omega_n)}{\omega_n}, \quad (3)$$

where $A_\perp^2(q)=[A_x^2(q)+A_y^2(q)]/2$, and ω_n is the nuclear Larmor frequency.[17]

We will discuss $1/T_1$ and $1/T_{2G}$ above $T_{\rm SP}$ in $CuGeO_3$ based on the $S=1/2$ 1DHAF model. In half-integer spin chains, both $q=0$ and π components of $\chi(q,\omega)$ contribute to the nuclear relaxation. However, the $q=\pi$ contribution is predominant for $T\ll J$. In this case, Sachdev derived the following expressions for $1/T_1$ and $1/T_{2G}$ by neglecting the $q=0$ component:

$$\frac{1}{T_1}=A_\perp^2(\pi)\frac{\pi D}{\hbar c} \quad (4)$$

and

$$\frac{1}{T_{2G}}=A_\parallel^2(\pi)\frac{DI}{4\hbar}\sqrt{\frac{p}{ck_BT}}, \quad (5)$$

where $A_\parallel(\pi)=A_z(\pi)$, D is an unknown parameter, $I=8.4425\ldots$, and c ($=\pi J/2$) is the spinon velocity at $T=0$ K.[5,8] If the ratio of $1/T_1$ to $\sqrt{T}/T_{2G}$ is taken, the parameter D is canceled out as

$$\frac{T_{2G}}{T_1\sqrt{T}}=\frac{A_\perp^2(\pi)}{A_\parallel^2(\pi)}\frac{4\pi}{I}\sqrt{\frac{k_B}{pc}}. \quad (6)$$

Thus the ratio $T_{2G}/(T_1\sqrt{T})$ is independent of T at low temperatures. Figure 2 shows the T dependence of $T_{2G}/(T_1\sqrt{T})$ in $CuGeO_3$. If the SP transition is removed down to $T=0$ K, a finite value of $\sim1.7\times10^{-3}$ K$^{-1/2}$ is extrapolated at $T=0$ K and should be compared with a value calculated from Eq. (6). For this calculation, we must know a value of $A_\perp^2(\pi)/A_\parallel^2(\pi)$. As was previously discussed from the analysis of the hyperfine interaction,[16,17] $A^{(1)}$ is very small in $CuGeO_3$. Thus reasonably assuming $A^{(1)}=0$, we

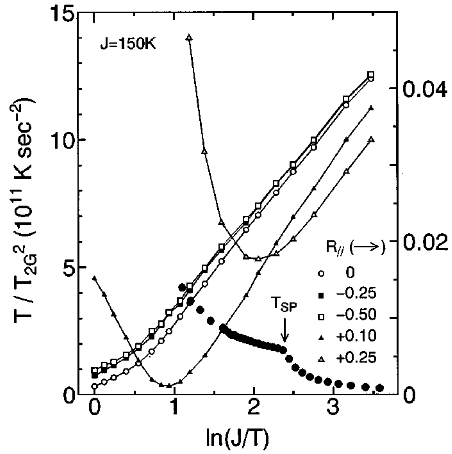

FIG. 3. T/T_{2G}^2 vs ln(*J*/*T*) plot for the Gaussian nuclear spin-spin relaxation rate $1/T_{2G}$ measured for ^{63}Cu NQR in $CuGeO_3$. The solid curves with several kinds of symbols represent QMC results of various values of the hyperfine ratio $R_\parallel$ for the $S=1/2$ 1DHAF model (after Ref. 7). The right vertical axis can be referred for the experimental data (solid circles), if $A^{(1)}=0$.

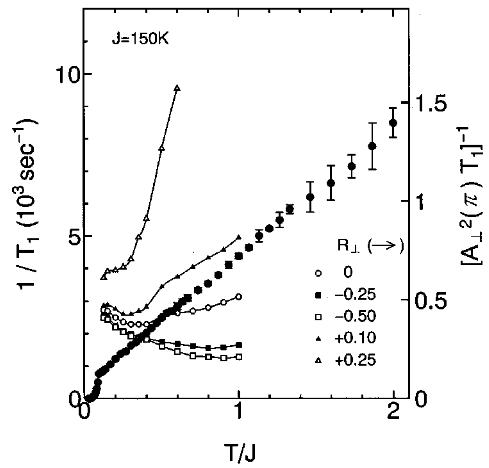

FIG. 4. $1/T_1$ vs T/J plot for the nuclear spin-lattice relaxation rate $1/T_1$ taken for ^{63}Cu NQR in $CuGeO_3$. The solid curves with several kinds of symbols represent QMC results of various values of the hyperfine ratio $R_\perp$ for the $S=1/2$ 1DHAF model (after Ref. 7). The right vertical axis can be referred for the experimental data (solid circles), if $A^{(1)}=0$.

obtain $A_\perp(\pi)/(2\gamma_n\hbar)=A_\perp(0)/(2\gamma_n\hbar)=-24.4$ kOe/μ_B and $A_\parallel(\pi)/(2\gamma_n\hbar)=A_\parallel(0)/(2\gamma_n\hbar)=-209$ kOe/μ_B (Refs. 18 and 19), where γ_n is the nuclear gyromagnetic ratio, $2\pi\times1.1285\times10^3$ Hz/Oe for ^{63}Cu. Using $J=150$ K for $CuGeO_3$, $T_{2G}/(T_1\sqrt{T})$ is evaluated to be 1.6×10^{-3} K$^{-1/2}$, which agrees with the extrapolated value at $T=0$ K. In the finite T region above T_{SP}, the QMC results[7] are available to compare the experimental data of $T_{2G}/(T_1\sqrt{T})$ with theoretical results for the $S=1/2$ 1DHAF model. The solid curve with the open circles represents the QMC result of $R_\mu=A^{(1)}/A_\mu^{(0)}=0$ ($\mu=\parallel$ and $\perp$) after correction for p, NQR, hyperfine coupling constants, and a normalization factor. It should be noted that the QMC results for $p=1$, NMR, and isotropic $A^{(0)}$ are presented in Ref. 7. The T dependence of the ratio in the QMC simulation seems to reproduce the experimental results, because the QMC result provides a larger value than the Sachdev's prediction of Eq. (6) as was pointed out in Ref. 7. However, only from these discussions of $T_{2G}/(T_1\sqrt{T})$ we cannot conclude that the spin dynamics in $CuGeO_3$ is described by the $S=1/2$ 1DHAF model.

Next, we will discuss each T dependence of $1/T_1$ and $1/T_{2G}$ above T_{SP}. By considering the marginally irrelevant operator, Sachdev[5] predicted the correction of a multiplicative prefactor $\ln^{1/2}(\Lambda/J)$, where Λ ($\sim J$) is an ultraviolet cutoff, for both Eq. (4) of $1/T_1$ and Eq. (5) of $1/T_{2G}$. Thus T/T_{2G}^2 is expected to be a linear function of ln(*J*/*T*) at low temperatures. Figure 3 shows the T/T_{2G}^2 vs ln(*J*/*T*) plot with QMC results[7] of various $R_\parallel$ values for comparison. The right vertical axis can be referred for the experimental data, if $A^{(1)}=0$ which corresponds to $R_\parallel=0$. The data above T_{SP} show the T dependence different from the QMC result of $R_\parallel=0$ and qualitatively similar to that of a positive $R_\parallel$ value. However, if $A^{(1)}$ is present, the $R_\parallel$ value seems not to be positive, because $A^{(1)}$ should be positive in the supertransferred mechanism through the hybridization between $Cu(3d_{x^2-y^2})-O(2p)$ and Cu(4*s*).[20] Even if $R_\parallel$ is positive, we cannot at the same time explain the following $1/T_1$ data by the QMC result with $A^{(1)}$ which may qualitatively reproduce the $1/T_{2G}$ data. Figure 4 shows the $1/T_1$ vs T/J plot with QMC results[7] with various $R_\perp$ values for comparison. The QMC result of $R_\perp=0$ cannot reproduce the experimental data of $1/T_1$. Also the T dependence due to the prefactor $\ln^{1/2}(\Lambda/J)$ which is seen in the QMC results below $T/J\sim0.4$ conflicts with the experimental data. Thus we cannot obtain R_μ values which reproduce the experimental data of both $1/T_1$ and $1/T_{2G}$. This fact indicates that other relaxation mechanisms are present in the ^{63}Cu nuclear relaxation of $CuGeO_3$ and modify the pure $S=1/2$ 1DHAF dynamics. One of them seems to come from a second nearest-neighbor exchange interaction J_2 in the chain introduced independently by Riera and Dobry[10] ($J_2\sim0.36J$, $J\sim160$ K) and by Castilla *et al.*[11] ($J_2\lesssim0.24J$, $J\sim150$ K) to explain the magnetic susceptibility. Other origins may be interchain exchange interactions which were estimated to be $J_b\sim0.1J$ and $J_a\sim-0.01J$ by the inelastic neutron-scattering study.[12] A theoretical study including such effects on the nuclear relaxation of the $S=1/2$ 1DHAF is desired to understand the nuclear magnetic relaxation in the uniform phase of $CuGeO_3$.

Below T_{SP} we have no available theories to describe $1/T_{2G}$ in the dimerized phase of SP compounds. Also $1/T_1$, which shows the characteristic T dependence of $T^{5.73\pm0.03}$ just below T_{SP}, cannot be explained at present, although there is a theoretical study of the T_1 mechanism including three pseudofermion excitations in the dimerized phase by Ehrenfreund and Smith.[21] Further theories are desired to understand the present $1/T_{2G}$ result with the $1/T_1$ data in the dimerized phase of $CuGeO_3$.

In summary, we measured the T dependence of $1/T_1$ and $1/T_{2G}$ to understand the spin dynamics in the spin-Peierls compound $CuGeO_3$. Based on recent theoretical results for the $S=1/2$ 1DHAF model by Sachdev and Sandvik, we have performed the combined analysis of $1/T_1$ and $1/T_{2G}$ above T_{SP}. We have found that the spin dynamics in $CuGeO_3$ is not described by the pure $S=1/2$ 1DHAF model. It has been pointed out that the second-nearest and/or the interchain exchange interactions may provide contributions to the nuclear relaxation in $CuGeO_3$.

We would like to thank Dr. M. Takigawa and Dr. Y. Itoh for fruitful discussions. This study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

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