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Spin fluctuations in $S=\frac{1}{2}$ double-linear-chain γ-LiV_2O_5 studied by ^{7}Li NMR

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The nuclear spin-lattice relaxation rate $(1/T_1)$ of ^{7}Li nuclei has been measured in a spin $S=\frac{1}{2}$ double-linear-chain system with exchange interaction $J=308$ K, γ-LiV_2O_5, in the temperature range from 280 K down to 0.5 K. We observed that $1/T_1$ shows the minimum at about 0.1 J. The increase of $1/T_1$ below and above 0.1 J are well explained by considering the contribution from the staggered-spin fluctuation and the uniform-spin fluctuation, respectively. Especially, the increase of $1/T_1$ below 0.1 J suggests the appearance of the logarithmic correction effect which has been recently predicted by theoretical works in an isotropic Heisenberg linear chain. [S0163-1829(97)52118-7]

Recent experimental studies of low-dimensional magnetic systems in cuprates[1] have advanced precise comparison with field theoretical or numerical works. Eggart, Affleck, and Takahashi[2] have analytically shown that the temperature dependence of the susceptibility $\chi(T)$ in spin $S=\frac{1}{2}$ Heisenberg chains deviates from the Bonner-Fisher curve[3] at low temperatures and obeys the relation $J\pi^2\chi(T)=1+1/\{2[\ln(T_0/T)]\}$ where J is the exchange interaction and T_0 is about 7.7 J. The logarithmic temperature dependence originates from SU(2) and translational symmetries. The recent susceptibility data on Sr_2CuO_3 show good agreement with the theory.[4] On the other hand, Sachdev[5] and Sandvik[6] have investigated dynamic susceptibility $S(q,\omega)$ by an analytic method and quantum Monte Carlo (QMC) calculation, respectively. They both obtained that the temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ behaves as $1/T_1 \sim \ln^{1/2}(J/T)$ at low temperatures. The origin of the logarithmic temperature dependence is the same as that of the static susceptibility. Experimentally, $1/T_1$ has been measurede in Sr_2CuO_3 by Takigawa *et al.*[7] The steep increase of $1/T_1$ has been observed at low temperatures and the possibility for the logarithmic term has been discussed.

Another topic in $S=\frac{1}{2}$ one-dimensional (1D) chains is the competition between the nearest-neighbor exchange interaction J_1 and the next-nearest-neighbor exchange interaction J_2. The phase diagram for J_1 and J_2 is investigated using the renormalization group method[8,9] and the numerical work.[10] The boundary between the spontaneous dimer state and the spin fluid state is investigated in these works and the critical value J_2/J_1 is obtained as $\frac{1}{6}$,[8] $\frac{1}{3}$,[9] and 0.24.[10] Such states may be realized in real zigzag chain materials.

In the present work we have investigated the spin dynamics of a Heisenberg chain system γ-LiV_2O_5 by measuring the temperature dependence of $1/T_1$ of ^{7}Li nuclei from 280 K down to 0.5 K. The exchange interaction J obtained from the susceptibility[11] is about 308 K, then our measurement covers the wide temperature region in the reduced temperature scale with J compared to the studies in cuprates where a typical value of the exchange coupling is about 1000–2000 K.

There exist 4+ and 5+ oxidation states, V^{4+} and V^{5+}, for vanadium ions in γ-LiV_2O_5. Magnetic ions with $S=\frac{1}{2}$ in V^{4+} state and nonmagnetic ions in V^{5+} state are surrounded by pyramids of oxygen and two kinds of ions form the zigzag chains separately as is shown in Fig. 1(a). Lithium ions locate between the layers of the zigzag chains as is shown in Fig. 1(b).[13] The susceptibility $\chi(T)$ shows broad maximum around 200 K. The temperature dependence of $\chi(T)$ fits well the calculation for $S=\frac{1}{2}$ isotropic Heisenberg model with $J=308$ K and $g=1.8$.[11] Two main couplings should be considered magnetically, i.e., one is the nearest-neighbor coupling J_1 between V^{4+} ions in edge shared pyramids, and the other is the next-nearest-neighbor coupling J_2 between those in corner shared pyramids. It is unlikely that J_1 and J_2 are comparable, as there appears no feature in the susceptibility of Majumdar-Ghosh spontaneous dimerization which would

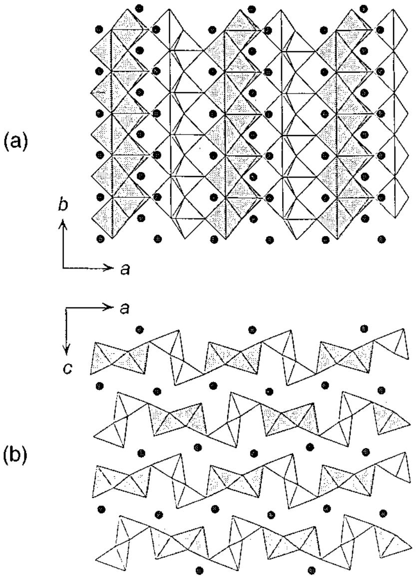

FIG. 1. Crystal structure of γ-LiV_2O_5. The shaded and white square pyramids show $V^{4+}O_5$ and $V^{5+}O_5$, respectively. The black circles represent Li ions.

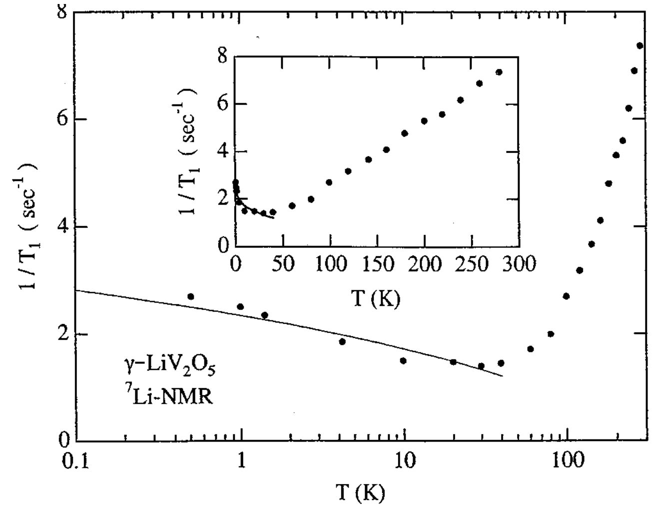

FIG. 2. Temperature dependence of $1/T_1$ measured at the field 1.2 T. The inset shows the same data plotted by linear scale. The solid curves represent Eq. (4).

be expected in this case from theoretical works as is mentioned above. Therefore, the cases $J_1 \gg J_2$ and $J_1 \ll J_2$ are possible. In the case $J_1 \gg J_2$, the system can be treated as Heisenberg zigzag chains, and in the reverse case as Heisenberg double-linear chains. The treatment as the double-linear chain seems rather possible by considering the fact that α-NaV$_2$O$_5$ where 1D chains are constructed only with the corner shared coupling has larger coupling (560 K) (Ref. 12) compared with that of CsV$_2$O$_5$ (Ref. 11) (140 K) where dimers are constructed only with the edge shared coupling.

The nuclear magnetic resonance (NMR) at the field (H) 1.2 T was performed for ^{7}Li nuclei by using powder samples. The susceptibility data have been cited in Ref. 11. The ^{7}Li-NMR spectra observed at $H=1.2$ T shows a powder pattern broadened about 100 Oe due to the electric quadrupole effect. The linewidth of the central line is about 20 Oe. The value of the shift was the same within the experimental accuracy (100 ppm). No drastic broadening was observed even at 0.5 K. This fact implies that there appears no 3D long-range order even at 0.5 K. Detailed analysis of the powder pattern has already been investigated by Hirshinger *et al.*[14] by using the magic angle spinning NMR method at room temperatures. Our ^{7}Li-NMR spectra are consistent with their results.

We have measured $1/T_1$ for ^{7}Li nuclei by the saturation recovery method. The recovery curves fit a single exponential function for nearly two orders of magnitude except for a very short time after the comb pulses. The temperature dependence of $1/T_1$ is shown in Fig. 2. The temperature dependence of $1/T_1$ in a linear scale is shown in the inset. As is seen from the figure, there appears a minimum of about 30–40 K which corresponds to 0.1 J–0.15 J. It should be noted that the temperature dependence of $1/T_1$ shows no gap like behavior. We first analyze the results in view of the double-linear-chain system.

The rate $1/T_1$ for ^{7}Li nuclei originates from the fluctuation of the electron spins through dipole interaction. The rate $1/T_1$ is expressed as

$$1/T_1=\tfrac{1}{2}\gamma_N^2\sum_\alpha \int A^\alpha(q)^2 S^{\alpha\alpha}(q,\omega_N)dq/2\pi$$

$$(\alpha=a,\ b,\ \text{and}\ c), \tag{1}$$

where $S^{\alpha\alpha}(q,\omega_N)$, ω_N, and γ_N represent the dynamic structure factor, the nuclear Larmor frequency, and the gyromagnetic ratio of ^{7}Li nuclei, respectively. The subscripts α represent the directions of the crystal axes and the q is the wave number along the chain direction. The chain direction is the crystallographic b axis. The q dependence of the hyperfine coupling $A^\alpha(q)$ $(\alpha=a,b,c)$ is calculated from the general formula[15] where the arbitrary field direction has been treated with respect to an electron coordinate system. We are able to calculate $A^\alpha(q)$ for an arbitrary field direction by using the positions of vanadium and lithium sites identified by x-ray analysis.[16] The difference among the values of $A^\alpha(q)$ calculated for the arbitrary field direction is almost less than two. Then, $A^\alpha(q)$ for the powder sample is obtained by averaging all chain directions with respect to the field as

$$A^\alpha(q)^2=\sum_{ij}\{[2(1-3\alpha_i^2-3\alpha_j^2)/3 + 6\alpha_1\alpha_j(\alpha_i\alpha_j+\beta_1\beta_j+\gamma_1\gamma_j)]/r_i^3r_j^3\}e^{i\mathbf{q}(\mathbf{r}_i-\mathbf{r}_j)}, \tag{2}$$

where α_i, β_i, γ_i and r_i are the direction cosines and the distance of i-electron spins from a Lithium nucleus, respectively. The other couplings $A^b(q)^2$ and $A^c(q)^2$ are obtained in a similar way. $S^{\alpha\alpha}(q,\omega_N)$ can be regarded as isotropic, i.e., $S^{\alpha\alpha}(q,\omega_N)=S(q,\omega_N)$, in the case where the damping rate of the spin-correlation function is larger than the electron Larmor frequency ω_e. Then, $1/T_1$ is given as $\frac{1}{2}\gamma_N^2\int A(q)^2S(q,\omega_N)dq/2\pi$ where $A(q)^2=\Sigma_\alpha A^\alpha(q)^2$. This assumption may be valid in the case where the overdamped spin wave contributes to $1/T_1$. Then, $A(q)^2$ is given as

$$A(q)^2=\sum_{ij}\{[-2+6(\alpha_i\alpha_j+\beta_i\beta_j+\gamma_i\gamma_j)^2]/r_i^3r_j^3\}e^{i\mathbf{q}(\mathbf{r}_i-\mathbf{r}_j)}. \tag{3}$$

The results of the calculation for $|A(q)|$ are shown by the solid line in Fig. 3. As is seen from the figure, $|A(q)|$ is almost constant.

It is shown by recent theories[5,6] that the contributions from $q=0$ and $q=\pi$ give a different temperature dependence for $1/T_1$, therefore the temperature dependence of $1/T_1$ qualitatively varies depending on the q dependence of the hyperfine coupling. The temperature dependence of $1/T_1$ has been calculated by the QMC method[6] for the hyperfine coupling, $A_h(q)j=A+2B\cos q$ where A and B represent on-site hyperfine and nearest-neighbor transferred hyperfine interactions, respectively. It is shown that $1/T_1$ at high temperatures upturns with increasing temperature due to the contribution from uniform $(q=0)$ spin fluctuation for the case $|A_h(0)|\geqslant|A_h(\pi)|$, while for $|A_h(0)|<|A_h(\pi)|$, $1/T_1$ is almost constant since the contribution from staggered $(q=\pi)$ spin fluctuation dominates even at relatively high temperatures. Our result of $1/T_1$ corresponds to the former, while Sr$_2$CuO$_3$ (Ref. 7) or Ca$_2$CuO $_3$ (Ref. 17) corresponds to

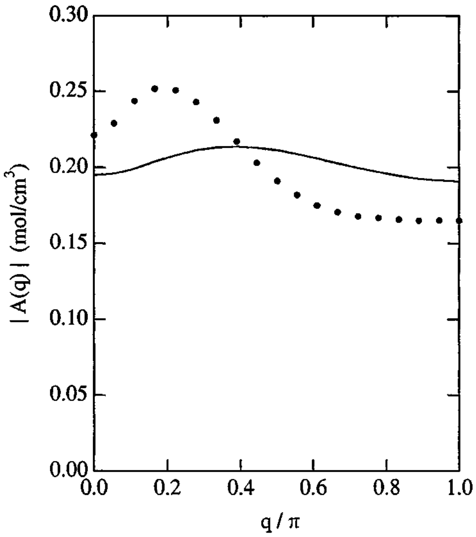

FIG. 3. q dependence of the dipole coupling between the electron systems and a ^{7}Li nucleus. The solid line and dots represent calculated values for the double-linear chain and the zigzag chain, respectively.

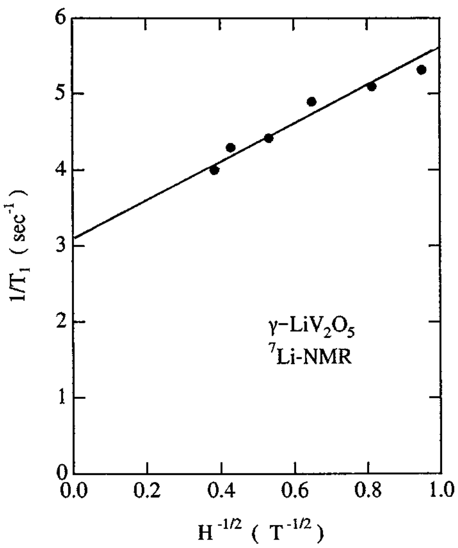

FIG. 4. Field dependence of $1/T_1$ measured at 200 K.

the latter. The $1/T_1$ of Cu nuclei in these cuprates is almost constant at high temperatures. The weight of $q=\pi$ in $|A_h(q)|$ becomes larger than $q=0$ due to the existence of the transferred hyperfine interaction on Cu sites, which yields qualitative differences from our results. On the other hand, at low temperatures the staggered spin fluctuation becomes important for both cases $|A_h(0)|\geqslant|A_h(\pi)|$ and $|A_h(0)| <|A_h(\pi)|$. The upturn of $1/T_1$ towards low temperatures is expected to appear by the logarithmic correction effect, $\ln^{1/2}(J/T)$ (Refs. 5 and 6) for both cases. Then, the crossover of the dominant contribution between $q=0$ and π is expected to appear at 0.2 $J\sim0.3$ J for the case $|A_h(0)| \geqslant|A_h(\pi)|$.[6] Our experimental results also show logarithmic increase at low temperatures and the minimum of $1/T_1$ occurs at 0.1 J which is lower than the theoretical value. The results at low temperatures suggest the appearance of the logarithmic correction effect.

The contribution from $q=\pi$ is dominant at low temperatures below $T<0.1$ J and that from $q=0$ can be neglected, then $1/T_1$ is expressed as[5,6]

$$1/T_1=(\hbar\gamma_e\gamma_N N)^2A(\pi)^2(\hbar D/Jk_B)\ln^{1/2}(J/T), \qquad (4)$$

where D represents a constant originating from the asymptotic equal-time spin-correlation function. The value of $|A(\pi)|$ is calculated as 0.191 mol/cm ^{3}. The solid curves in Fig. 2 represent Eq. (4) where the value of D is chosen as 0.046. As is seen from the figure, the curve fits the experimental results well.

The contribution from $q=0$ is dominant at high temperatures above $T>0.1$ J. The effect of the spin diffusion appears through the damping rate [$\sim D_sq^2$ (Ref. 18) where D_s is the diffusion coefficient] of the transverse spin-correlation function with respect to the field direction. The dynamic structure factors become anisotropic for the field direction and the perpendicular directions due to this effect, unlike the case of the overdamped spin wave. Then, $1/T_1$ is given by neglecting the q dependences of $A^\alpha(q)$ and $\chi_q(T)$ and substituting the value of $q=0$ for all q as

$$1/T_1\sim\tfrac{1}{2}\gamma_N^2k_BT\chi(T)[A_z(0)^2/\Gamma_z+A_\perp(0)^2/\Gamma_\perp], \qquad (5)$$

where Γ_z and $\Gamma_\perp$ are damping rates of the longitudinal and transverse spin-correlation functions with respect to the field, respectively. The $\Gamma_\perp$ is obtained as $2\pi\sqrt{(2\gamma_eD_sH)}$.[19] The coupling for the field direction $|A_z(0)|$ and that for the perpendicular directions $|A_\perp(0)|$ are calculated as 0.11 and 0.16 mol/cm ^{3}, respectively. The field dependence of $1/T_1$ at 200 K is shown in Fig. 4. We have estimated the values of Γ_z and $\Gamma_\perp$ from the experimental results as 2.1×10^{12} and $6.9\times10^{12}\sqrt{H}$ sec^{-1}, respectively. The value of D_s is estimated as 3.4×10^{12} sec $^{-1}$. The value is close to that obtained from the classical calculation at high-temperature limit $D_c=J/\hbar\sqrt{2\pi S(S+1)/3}$, 2.5×10^{13} sec^{-1}, and that from the recent renormalization group analysis,[20] 2.8×10^{13} sec^{-1}. It should be noted that the value of D_s estimated in the present experiments is also close to that obtained in a typical $S=5/2$ Heisenberg linear chain, $(CH_3)_4NMnCl_3$ (TMMC). The value has been estimated from the experiments as 1×10^{13} sec^{-1}.[19] The field dependence of $1/T_1$ and the adequateness of the value for D_s in our experiments also support that the uniform spin fluctuation is dominant at high temperatures. The field dependence of $1/T_1$ has been measured in Sr_2CuO_3,[7] however, it is negligibly small since the $q=\pi$ fluctuation is quite large even at room temperatures. The diffusion constant is estimated as a large value (1×10^{16}–4×10^{17} sec^{-1}) from the $1/\sqrt{H}$ dependence of $1/T_1$. However, the $1/\sqrt{H}$ dependence is derived under the condition that the $q=0$ fluctuation is dominant.[18] In the case that the $q=\pi$ fluctuation is dominant, more sophisticated analysis may be needed to estimate the diffusion constant.

It should be noted that in the present case we have analyzed our results in the viewpoint of the double-linear chain. In the viewpoint of the zigzag chain, the wight of $q=0$ in $|A(q)|$ becomes larger than $q=\pi$ as is shown by the dots in Fig. 3. Our experimental results can also be explained in this viewpoint since $|A(0)| \geqslant |A(\pi)|$ also holds for this case.

In the present work, we have observed that the minimum of $1/T_1$ appears around 0.1 J and explained the fact as a crossover of the dominant contributions from the uniform $(q=0)$ and the staggered $(q=\pi)$ spin fluctuations by considering the q dependence of the hyperfine coupling. The temperature dependence of $1/T_1$ at low temperatures suggests the appearance of the logarithmic correction effect. These results are experimental evidence for the recent theoretical predictions for the $S=\frac{1}{2}$ quantum Heisenberg chain.

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