Dynamics in the $S = 1$ One-Dimensional Antiferromagnet $AgVP_2S_6$ via ^{31}P and ^{51}V NMR

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The nuclear spin-lattice relaxation rate $(1/T_1)$ has been measured at ^{31}P and ^{51}V nuclei in the one-dimensional spin-1 antiferromagnet $AgVP_2S_6$ single crystal. In addition to an activated temperature dependence, $1/T_1$ at P sites shows $1/\sqrt{H}$ magnetic field dependence due to spin diffusion above a certain cutoff field at high temperatures. While the diffusion constant shows a modest temperature dependence, the cutoff field increases rapidly on cooling. The spin-diffusion model is incompatible with the data at low temperatures, suggesting a crossover at $T \sim 100$ K.

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Experiments and numerical calculations have established the existence of an excitation gap in spin-1 one-dimensional Heisenberg antiferromagnets first predicted by Haldane [1]. Although the excitation spectrum at $T = 0$ is now fairly well understood, we know relatively less about finite-temperature properties. Recently, theories have been developed [2–5] for static and dynamic properties at low temperatures (T) based on a nonlinear σ model or a free boson (fermion) model, allowing comparison with various experiments. Of these, the nuclear spin-lattice relaxation rate $(1/T_1)$ provides important information on the spin dynamics at small frequencies [6–8]. In this Letter, we report the results of $1/T_1$ at ^{31}P and ^{51}V nuclei in a $AgVP_2P_6$ single crystal, a spin-1 Haldane system. Compared with $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP) and other $S = 1$ chains, this material has the advantages that (1) the large gap (300 K) [9] allows us to measure $1/T_1$ over a wide range of magnetic field (H) without changing the excitation spectrum and (2) the single-ion anisotropy is much smaller than the gap [10]. We observed, in addition to an activated T dependence due to the gap, $1/\sqrt{H}$ magnetic field dependence at P sites for $T \geq 120$ K above a T-dependent cutoff field, indicating diffusive behavior of the long wavelength spin correlation function, in contrast to the field-theoretical prediction. The cutoff field increases rapidly upon cooling and the spin-diffusion model does not describe the data properly below $T \sim 100$ K, indicating a crossover to a different regime.

$AgVP_2S_6$ crystallizes in the monoclinic $P2/a$ structure [11], where V^{3+} ions form a zigzag chain along the a axis. Detailed NMR shift measurements have been done [10] on the crystal used in the present study. The T dependence of the shift at V sites is consistent with the prediction of a free boson model with the gap $\Delta = 320$ K, in good agreement with the neutron result [9] (300 K) on a powder sample. The single-ion anisotropy energy $DS_\zeta^2 - E(S_\xi^2 - S_\eta^2)$ determined from the Van Vleck orbital shift at V sites is nearly axial, $D = 4.5$ K and $|E| \leq 0.1$ K, where ζ is the direction $31° \pm 2°$ away from the c^* axis in the a-c^* plane and η is along the b axis.

The T dependence of $1/T_1$ at P and V sites are shown in Fig. 1. The P data were taken at $H = 5.976$ T along the c^* axis. The V data were obtained at $H = 8.0$ T along the direction 32° away from the b axis in the a-b plane, where the quadrupole splitting vanishes. The recovery of the nuclear magnetization after the inversion π pulse was a single exponential function above 50 K. This was not the case below 50 K, indicating that dilute impurity spins begin to contribute. The magnetic susceptibility of the same crystal [12] showed a Curie term corresponding to 0.3% $S = \frac{1}{2}$ impurity moments. An activated T dependence of $1/T_1$, similar to the results in NENP [6–8], is observed over three decades with the activation energy of 390 K (420 K) at P (V) sites. These values are, however, somewhat larger than the gap determined from neutrons (300 K) and the shift data (320 K). The H dependence of $1/T_1$ shown below indicates that the limiting low-T behavior has not been reached at least for $T > 120$ K.

The nuclear relaxation rate due to the hyperfine interaction between a nuclear spin (I) and

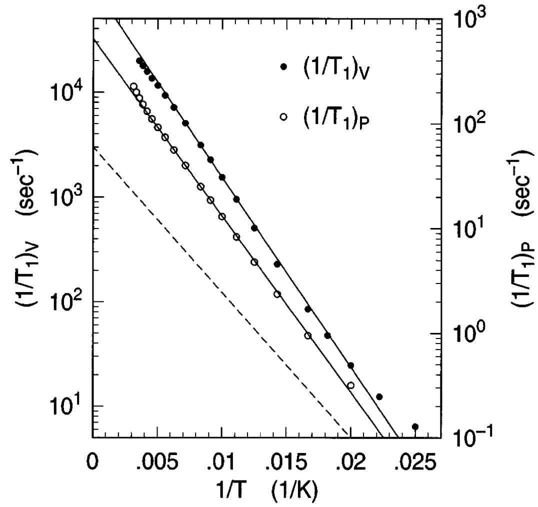

FIG. 1. $1/T_1$ at V (solid circles) and P (open circles) sites plotted against $1/T$. The dashed line indicates the slope for the gap of 320 K estimated from the shift data [11].

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electron spins (S_i), $\mathcal{H}_{\rm hf} = \sum_{i\alpha\beta} I_\alpha A^i_{\alpha\beta} S_{i,\beta}$, is expressed in terms of the spin correlation function $S_{\alpha\beta}(q,\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle\{S_\alpha(q,t), S_\beta(-q,t)\}\rangle$ as

$$1/T_1 = (1/2\hbar^2)(1/N) \sum_{\alpha=x,y} \sum_{\beta=x,y,z} \sum_q A_{\alpha\beta}(q) \times A_{\alpha\gamma}(-q) S_{\beta\gamma}(q,\omega_N), \qquad (1)$$

where $A(q) = \sum_i A^i \exp(iqR_i)$, $S(q) = (1/\sqrt{N}) \sum_i S_i \times \exp(-iqR_i)$, $\omega_N = \gamma_N H$ is the nuclear Larmor frequency (γ_N is the nuclear gyromagnetic ratio), and z is the magnetic field direction [13]. A field-theoretical calculation of $1/T_1$ in Haldane systems has been made based on a free boson model [4,5], which is expected to be valid at low T. If the single-ion anisotropy is neglected, the magnon dispersion is given by $\varepsilon_{k,\sigma} = [v^2(k-\pi)^2 + \Delta^2]^{1/2} + g\mu_B H\sigma$, where σ is the z component of the total spin and takes the value 0 or ± 1. Since ω_N is much smaller than the gap, the nuclear relation is expected to occur dominantly via the two-magnon Raman process [13,14], in which a thermally excited magnon $|k,\sigma\rangle$ is scattering into a state $|k+q,\sigma'\rangle$ by the hyperfine interaction accompanied by nuclear spin flop. Because magnons are excited only near $k=\pi$ and energy conservation requires $\varepsilon_{k,\sigma} - \varepsilon_{k+q,\sigma'} = \pm\omega_N \sim 0$, the main contribution to $1/T_1$ comes from the region $q \sim 0$, despite the strong short range antiferromagnetic correlations at $q = \pi$. Thus $A(q)$ in Eq. (1) can be replaced by $A(0)$, which were determined accurately from the shift data [10]. This situation is in sharp contrast to the case of half-integer spin chains, where the spin fluctuations near $q \sim \pi$ play the dominant role [15]. The two-magnon process leads to [4,5]

$$(1/N) \sum_q S_{\alpha\alpha}(q,\omega_N) = (2\Delta/\pi v^2) K_0(\omega_0/2T) \times \exp(-\Delta/T), \qquad (2)$$

where $\omega_0 = \omega_e = g\mu_B H/\hbar$ (electron Larmor frequency) for $\alpha = x$ or y, $\omega_0 = \omega_N$ for $\alpha = z$, and $K_0(\omega_0/2T) \sim 0.809 - \ln(\omega_0/T)$ is the modified Bessel function [16]. In addition to the activated T dependence, it predicts a logarithmic H dependence arising from the Van Hove singularity of the magnon density of states that can be tested experimentally [17].

We have examined the H dependence of $1/T_1$ at P sites for $H \parallel c^*$ as shown in Fig. 2, where $1/T_1$ is normalized by the value at $H = 5.976$ T. At sufficiently large H ($H > D/g\mu_B = 3.3$ T), we may ignore the single-ion anisotropy. Then from the values of $A_{\alpha\beta}(0)$ given in Ref. [10], Eq. (1) becomes $1/T_1 = (1/2\hbar^2)\{\Gamma_1 \sum_q S_{xx}(q,\omega_N) + \Gamma_2 \sum_q S_{zz}(q,\omega_N)\}$, with $\Gamma_1 = (5.7 \pm 0.14) \times 10^{-6}$ and $\Gamma_2 = (1.4$ or $2.1) \times 10^{-8}$ K^2. Since the second term is negligible ($\Gamma_2/\Gamma_1 \ll 1$), the two-magnon process predicts the H dependence $1/T_1 \propto 0.809 - \ln(g\mu_B H/T)$, which is

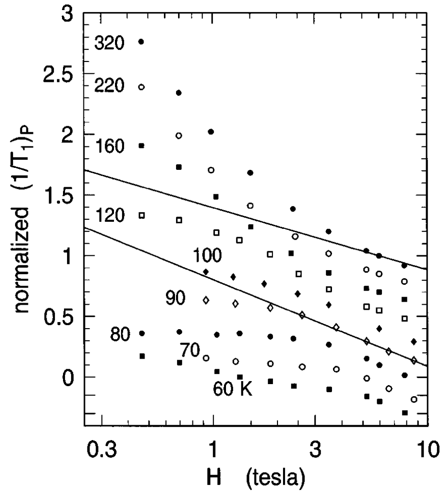

FIG. 2. Magnetic field dependence of $1/T_1$ at P sites normalized by the value at $H = 5.976$ T at each temperature. The field is applied along the c^* axis. The data at different temperatures are vertically displaced for the sake of clarity. The lines indicate the prediction of a free boson model at 90 and 320 K.

shown by the lines in Fig. 2 at 90 and 320 K. At 90 K, the observed H dependence agrees with the two-magnon calculation above 3 T. Below this field, $1/T_1$ starts to saturate. The saturation is expected in the presence of the interchain coupling or anisotropy, which remove the singularity in the product of initial and final magnon density of states, and thus cutoff the $\ln(\omega)$ divergence at small ω. The free boson model is expected to be accurate in the low-T limit. Using the result of numerical simulation [18] $v = 6.06\Delta$ with $\Delta = 300$ K, the value of $1/T_1$ at P sites is calculated to be 0.37 s^{-1} at $T = 60$ K and $H = 8$ T, whereas the measured value is 0.87 s^{-1}. The disagreement is slightly larger at V sites, $(1/T_1)_{\rm calc} = 22.3$ s^{-1} and $(1/T_1)_{\rm exp} = 85$ s^{-1} at 60 K and 8 T. For $T \geq 120$ K, however, the data show much stronger H dependence than the calculation at small H, indicating that *the free boson model is not valid even qualitatively* for $T/\Delta > 0.4$.

It has been known that the spin correlation function in classical Heisenberg magnets shows diffusive behavior $S_{xx}(q,t) \propto \exp(-D_s q^2 t) \exp(-i\omega_e t)$ for small q [19]. In one dimension, such behavior leads to the slow decay of $\sum_q S(q,t) \propto 1/\sqrt{t}$ at large t and the H dependence $1/T_1 \propto 1/\sqrt{\omega_e} \propto 1/\sqrt{H}$. This H dependence has been observed, for example, in $(CH_3)_4NMnCl_3$, an $S = \frac{5}{2}$ Heisenberg chain compound [20,21]. For $S = 1$, we would expect such classical behavior only in the high-T limit, $T \gg \Delta$, which is beyond our range of measurements. Nevertheless, we found the dependence of the form $1/T_1 = P + Q/\sqrt{H}$ at high T as shown in Fig. 3, indicating the diffusive dynamics near $q \sim 0$ as opposed to the dynamics governed by almost freely propagating magnons. To our knowledge, this is the first observation of spin diffusion in Haldane systems. In NENP, for example, a drastic change in the excitation spectrum caused by the applied field should have masked such a moderate field effect [7,8]. Upon cooling, there appears a certain cutoff field, below which $1/T_1$ deviates from this relation and starts to saturate. A remarkable feature is the strong T dependence of the cutoff field.

In classical 1D systems, cutoff to the $1/\sqrt{H}$ divergence of $1/T_1$ arises from such perturbations as dipolar or interchain coupling or single-ion anisotropy, which break the conservation of uniform magnetization along the chain and truncate the slow decay of $\sum_q S(q,t)$ [22]. This cutoff effect can be taken into account phenomenologically by assuming the following form for small q,

$$S_{xx}(q,t) = kT(\chi/g^2\mu_B^2)\exp[(-D_s q^2 - \omega_c)t]\exp(-i\omega_e t)\,, \tag{3}$$

where ω_c is the cutoff frequency and χ is the spin susceptibility. We then obtain

$$\sum_q S_{xx}(q,\omega_N) = \frac{kT}{(g\mu_B)^2}\frac{\chi}{\sqrt{2D_s}}\left(\frac{\omega_c + \sqrt{\omega_e^2 + \omega_c^2}}{\omega_e^2 + \omega_c^2}\right)^{1/2}. \tag{4}$$

The right hand side is proportional to $1/\sqrt{\omega_e}$ when $\omega_e \gg \omega_c$ and become constant when $\omega_e \ll \omega_c$ as expected. Since $\omega_N \ll \omega_c$ as we will see later, $S_{zz}(q,\omega_N)$ does not depend on H. We fit the data in Fig. 3 by the form $1/T_1 = (1/T_1)_0 + (\Gamma_1/2\hbar^2)\sum_q S_{xx}(q,\omega_N)$, with Eq. (4), treating $(1/T_1)_0$, D_s, and ω_c as fitting parameters. We used the value of χ determined from the shift measurements [10]. This expression has been used by Soda *et al.* [23] to analyze the $1/T_1$ data in 1D organic conductors, where the cutoff is determined by interchain electron hopping. The constant term $(1/T_1)_0$ may include the contribution from large-q spin fluctuations which are not described by spin diffusion and the contribution from $S_{zz}(q,\omega)$, although the latter would be very small.

As shown by the lines in Fig. 3, the diffusion model fits the data remarkably well, except the low field region at 60 K where $1/T_1$ becomes field dependent again. This field dependence becomes more significant at lower temperatures where impurity spins contribute to $1/T_1$. Therefore, this is presumably an impurity effect. The cutoff field $\hbar\omega_c/g\mu_B$ marked by the vertical bars in Fig. 3 increases rapidly with decreasing temperature. As shown in Fig. 4, this T dependence can be represented by either an exponential function, $\omega_c \propto \exp(\Gamma/T)$ with $\Gamma = 390$ K, or a power law, $\omega_c \propto T^{-3}$. We do not have reasonable explanation for such T dependence yet.

The T dependence of the diffusion constant D_s is shown in Fig. 5. The value of D_s is of the same order as the classical limit [21] $\sqrt{2\pi/3}\,(J/\hbar)\sqrt{S(S+1)} = 2.14 \times 10^{14}\ \mathrm{s}^{-1}$, where $J = \Delta/0.41$ is the exchange integral. The modest increase of D_s from 320 down to 120 K may be related to the increase of the antiferromagnetic correlation length ξ by the dynamic scaling relation $D_s \propto v\xi$ [24,25]. To our knowledge, such *critical speeding up* of the diffusion constant has not been observed before. At low T, below 100 K, D_s decreases abruptly. In the same T range, however, the constant term $(1/T_1)_0$ also shows sudden decrease and becomes even negative below 80 K, which is clearly unphysical. (See the inset of Fig. 5.) This means that the diffusion model is *not valid* at least below 80 K and strongly suggests a crossover around 100 K from the high-T diffusion regime to a different regime at low T. The apparent abrupt decrease of D_s also signifies the breakdown of the diffusion model. (For

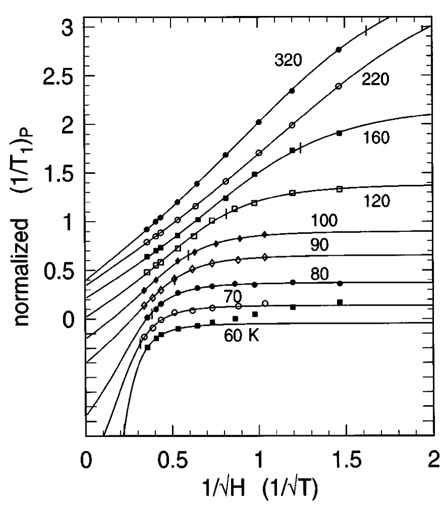

FIG. 3. The same data as Fig. 2 are plotted against $1/\sqrt{H}$. The lines are fits by the diffusion model, described in the text. The cutoff field $H_c = \hbar\omega_c/g\mu_B$ is marked by vertical bars.

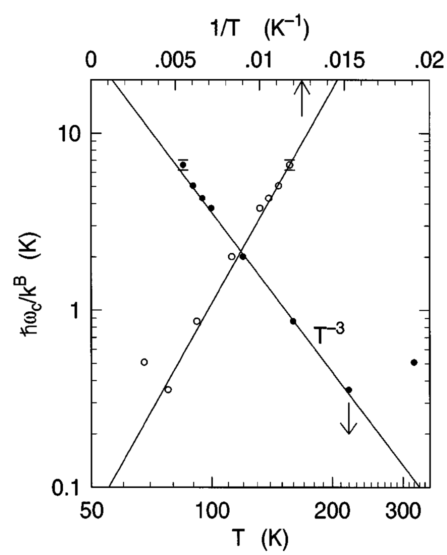

FIG. 4. The cutoff frequency is plotted against T (solid circles, lower scale) and $1/T$ (open circles, upper scale).

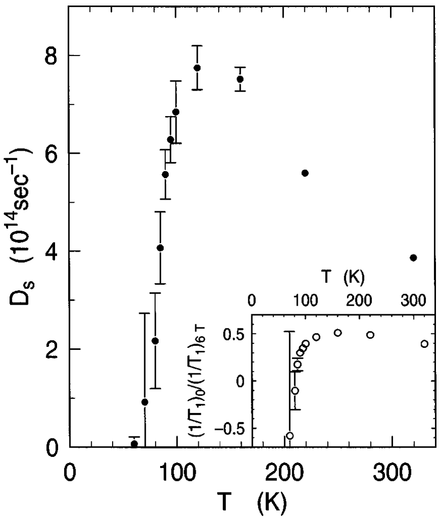

FIG. 5. Temperature dependence of the spin-diffusion constant. The inset shows the constant term $(1/T_1)_0$ normalized by the value of $1/T_1$ at 6 T.

this reason, the value of ω_c in Fig. 4 should be trusted perhaps only for $T > 100$ K.) As we mentioned earlier, the H dependence of $1/T_1$ below 100 K is consistent with the free boson model, although the absolute value of $1/T_1$ does not agree quite well.

An important open question is the cutoff mechanism. Mutka *et al.* [9] estimated the interchain exchange J' as $|J'| \leq J \times 10^{-5} = 8 \times 10^{-3}$ K by assuming that the broadening of the gap observed by neutrons at $T = 5$ K is due to the interchain magnon dispersion and is equal to $8(JJ')^{1/2}$. This value of J' is much smaller than the dipolar coupling (0.06 K) and ω_c. Therefore, it will not be important in the diffusion regime. However, the observed broadening of the gap is 1.4 meV, which is much larger than J', and will be an important cutoff mechanism at low T. The single-ion anisotropy in this material ($D = 4.5$ K) is sufficiently large that it should not be ignored at small H. For the present field direction $H \parallel c^*$, however, the anisotropy will only partially cut off the spin diffusion, since the magnetization along the anisotropy axis is still conserved and the spin fluctuations along this direction contribute to $1/T_1$. Measurements for different field directions will be useful to understand the effect of anisotropy. Preliminary results indicate that ω_c depends on the field direction.

In conclusion, the H dependence of $1/T_1$ at P sites revealed the diffusive spin dynamics near $q \sim 0$ above a certain cutoff frequency in the temperature range $0.4 \leq T/\Delta \leq 1.0$, where $1/T_1$ shows an activated T dependence and one might have expected a free (propagating) boson model to work at least qualitatively [4]. However, the cutoff frequency increases rapidly upon cooling, until the diffusion model becomes invalid in the whole frequency range of measurements below $T \sim 100$ K. Although we expect the dynamics in the low T limit is described by freely propagating magnons, and indeed the H dependence is consistent with the free boson model, there is about a factor of 2 (4) disagreement in the absolute value of $1/T_1$ at P (V) sites at $T/\Delta \sim 0.2$.

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[1] F. Haldane, Phys. Lett. **93A**, 464 (1983).
[2] I. Affleck, Phys. Rev. B **41**, 6697 (1990).
[3] A. M. Tsvelik, Phys. Rev. B **42**, 10 499 (1990).
[4] T. Jolicoeur and O. Golinelli, Phys. Rev. B **50**, 9265 (1994).
[5] J. Sagi and I. Affleck (unpublished).
[6] P. Gaveau *et al.,* Europhys. Lett. **12**, 647 (1990).
[7] N. Fujiwara *et al.,* Phys. Rev. B **45**, 7873 (1992).
[8] N. Fujiwara *et al.,* Phys. Rev. B **47**, 11 860 (1993).
[9] H. Mutka *et al.,* Phys. Rev. Lett. **67**, 497 (1991).
[10] M. Takigawa *et al.,* Phys. Rev. B **52**, R13087 (1995).
[11] S. Lee, P. Colombet, G. Oucrard, and R. Brec, Mater. Res. Bull. **21**, 917 (1986).
[12] T. Asano *et al.,* Solid State Commun. **88**, 795 (1994).
[13] T. Moriya, Prog. Theor. Phys. **16**, 23 (1956).
[14] D. Beeman and P. Pincus, Phys. Rev. **166**, 359 (1968).
[15] S. Sachdev, Phys. Rev. B **50**, 13 006 (1994).
[16] A similar result was obtained for the Heisenberg ladder system having an excitation spectrum identical to the Haldane system. M. Troyer, H. Tsunetsugu, and D. Wurtz, Phys. Rev. B **50**, 13 515 (1994).
[17] Equation (2) does not take the suppression of the gap by magnetic field into account. While this is important in NEMP, it is negligible in our case because the gap is always much larger than the Zeeman energy.
[18] E. Sorensen and I. Affleck, Phys. Rev. Lett. **71**, 1633 (1993).
[19] L. van Hove, Phys. Rev. **95**, 1374 (1954).
[20] F. Borsa and M. Mali, Phys. Rev. B **9**, 2215 (1974).
[21] D. Hone, C. Scherer, and F. Borsa, Phys. Rev. B **9**, 965 (1974).
[22] J. Boucher *et al.,* Phys. Rev. B **13**, 4098 (1976).
[23] G. Soda *et al.,* J. Phys. (Paris) **38**, 931 (1977).
[24] B. I. Halperin and P. C. Hohenberg, Phys. Rev. **177**, 952 (1969).
[25] We thank S. Chakravarty for bringing our attention to this point.