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NMR study of ^{51}V in quasi-one-dimensional integer spin chain compound $SrNi_2V_2O_8$

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NMR studies of ^{51}V in $SrNi_2V_2O_8$, a $S=1$ quasi-one-dimensional antiferromagnet, reveal no magnetic long-range order down to 3.75 K, in contradiction to the prediction from the inelastic neutron scattering data. The temperature dependence of the NMR frequency shift leads to spin gap, $\Delta \sim 25$ K, in the low energy excitations. The spin-lattice relaxation rates suggest a temperature dependence of a spin gap with $\Delta \sim 38$ K in $80K < T < 15K$ and are dominated by the spin diffusion term below 10 K. Thus the ground state of $SrNi_2V_2O_8$ is more correctly described as a disordered "spin liquid" Haldane state as in isomorphous $PbNi_2V_2O_8$.

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A remarkable feature in the low-dimensional magnetic system is the appearance of a spin gap between the singlet ground state and the first excited triplet state in quasi-one-dimensional (quasi-1D) $S=1$ Heisenberg antiferromagnet (HAF) because of their peculiar quantum effect as predicted by Haldane.[1] The most important property of such systems is the high stability of the singlet ground state. A complete phase diagram of this ground state in the D-J_1 plane, [where D is the single ion anisotropy and J_1 is the ratio of the interchain ($J_\perp$) over intrachain (J) exchange coupling] was studied by Sakai and Takahashi.[2] The possibility of a quantum phase transition between the spin-liquid and ordered states was identified when the magnitude of $J_\perp$ and/or D overcomes a certain critical value. A direct way to investigate such transition is to focus on a series of isostructural compounds with small variation in the values of $J_\perp$ and D. However, most of the known quasi-1D $S=1$ antiferromagnetic (AF) materials either lie well inside the spin-liquid regime of the phase diagram, or in the three-dimensional (3D) Néel-like or XY-like ordered phases. $CsNiCl_3$ and related compounds[3–5] are perhaps the only system close to the phase boundary that have been extensively studied. Unfortunately, these compounds exhibit 3D ordering and have no isostructural counterpart with a spin-liquid ground state.

In this respect, a series of isostructural compounds viz., ANi$_2$V$_2$O$_8$ (A=Pb,Sr), with $S=1$ belonging to HAF have attracted much attention.[6–10] The Pb compound, studied extensively, is located at the extreme vicinity of the borderline between the Haldane (spin-liquid) phase and 3D ordered Ising-like phase in the Sakai-Takahashi phase diagram.[7] It is quite plausible that a small perturbationlike replacement of Pb by Sr can drive the system from one side of the phase diagram to the other side. In fact, it was suggested from inelastic neutron scattering that while $PbNi_2V_2O_8$ has a spin-liquid ground state,[7] $SrNi_2V_2O_8$ falls into the Ising-like ordered state of the SK phase diagram and orders into a weak ferromagnetic state below 7 K. Prediction of the spin-liquid ground state in the former was also confirmed by dc susceptibility measurements.[6] However, the 3D ordered ground state in $SrNi_2V_2O_8$ is not yet supported from magnetic susceptibility or elastic neutron scattering results. As both the compounds lie very close to the phase boundary, it is necessary to have a clear knowledge about the true low temperature electronic state of $SrNi_2V_2O_8$ to predict whether a substitution of Pb by Sr could result in a transition from a spin-liquid to a 3D ordered state. Moreover, the prediction of the different ground states has some validity as their phase diagram has its roots in the peculiar topology of the chemical structure. (Pb/Sr)$Ni_2V_2O_8$ belongs to the tetragonal space group I4$_1$cd,[11] where slightly distorted NiO_6 octahedra are edge shared around the fourfold screw axis along the c direction. Intrachain nearest neighbor Ni-Ni AF interactions are expected to dominate. Because of the intertwining of the Ni^{2+} chains, $J_\perp$ seems to be quite large as the screw chains are bridged by VO_4 tetrahedra. The V^{5+} sites are presumed nonmagnetic. Thus, the recent ^{51}V NMR study of the doped compounds $PbNi_{2-x}Mg_xV_2O_8$ reveal that VO_4 tetrahedra serve as a superexchange bridge between Ni^{2+} chains.[12]

Ideally, a well-characterized, single crystal specimen should be used to clarify the different properties. However, a suitable single crystal of $SrNi_2V_2O_8$ is still not available. Study of the nuclear magnetic resonance (NMR) even in polycrystalline sample could provide quite unambiguous information about the electronic ground state and the low energy electron spin dynamics through the measurement of the shift parameter and the relaxation rate of the probed nucleus, as a function of temperature. The present paper reports the static and dynamic properties of Ni^{2+} spins in the polycrystalline sample of $SrNi_2V_2O_8$ using ^{51}V NMR, in the range 3.75–300 K. In addition, the result of the dc magnetic susceptibility in the range 4.9–300 K is also reported.

Figure 1 shows the magnetic susceptibility of $SrNi_2V_2O_8$ measured in a superconducting quantum interference device (SQUID) magnetometer in a magnetic field of 0.1 T. As expected, for a 1D AF chain, the susceptibility exhibits a broad maximum around 140 K and then decreases rapidly with decreasing temperature. Below 10 K, an upturn appears, which is common to most of the quasi-1D magnetic system and explained in most cases due to the Curie-Weiss contribution arising from isolated magnetic ions present possibly as lattice defects. From similar argument, we have subtracted $\chi_0+\chi_{cw}(T)$ from $\chi(T)$ and the contribution due to $\chi_{spin}(T)$ has been obtained. χ_0 is the temperature independent term and $\chi_{cw}(T)=C/(T-\Theta)$, the Curie-Weiss term. The parameters are $\chi_0=-2.0\times10^{-5}$ emu/mol Ni and $\theta=-1$ K, $C=2.1\times10^{-2}$ emu K/mol Ni. Thus the fraction of the iso-

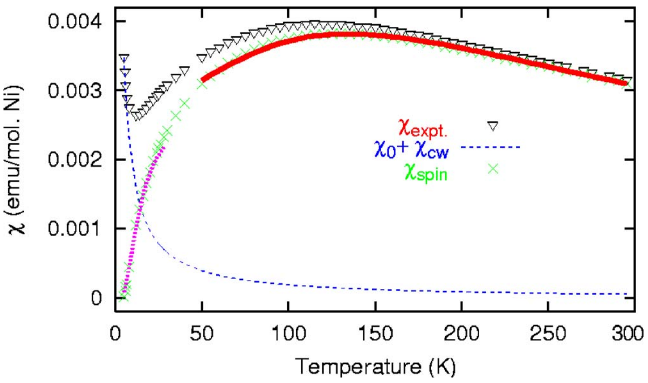

FIG. 1. (Color online) Temperature dependence of magnetic susceptibility of $SrNi_2V_2O_8$. The solid lines represent the theoretical fitting: (1) thin line follows Eq. (1) below 25 K and (2) thick line corresponds to Eq. (2) above 50 K.

lated Ni^{+2} ions estimated from C is 2.1%. The theoretical expression of $\chi_{\text{spin}}(T)$, derived by Jolicoeur and Golinelli[13] for the Haldane system, in the low temperature limit $(T \ll \Delta)$, is given by

$$\chi_{\text{spin}}(T) = \frac{2(g\mu_B)^2}{v\sqrt{2\pi}} \sqrt{\frac{\Delta}{T}} \exp(-\Delta/T). \tag{1}$$

A comparison with the derived $\chi_{\text{spin}}(T)$ (Fig. 1) gives thermal activation energy, $\Delta = 25$ K in the Sr compound, which is in close agreement with that found in the grain aligned $PbNi_2V_2O_8$ sample ($\Delta \sim 28$ K).[6] Above 25 K, $\chi(T)$, however, deviates from the simple exponential relation.

The intrachain exchange J is obtained from the expression of the susceptibility for 1D-HAF $(S=1)$ using high temperature series expansion[14]

$$\chi_{\text{spin}}(T) = \frac{Ng^2\mu_B^2}{k_B T} \frac{2 + 0.0194\chi + 0.777\chi^2}{3 + 4.346\chi + 3.232\chi^2 + 5.834\chi^3}, \tag{2}$$

where $\chi = |J|/k_B T$ and all other notations carry their usual meanings. As shown in Fig. 1, the best fit has been achieved for $T > 50$ K when $|J|/k_B = 102$ K$=8.8$ meV. The numerical calculation[2,15] for the noninteracting $S=1$ chains gives $\Delta = 0.41J = 42$ K, which is considerably higher than that obtained from Eq. (1) applied to low temperature susceptibility data in $SrNi_2V_2O_8$. Therefore, with respect to magnetic susceptibility data there is little difference between Sr and Pb-vanadite, in particular, J and Δ for Sr and Pb are very close to each other, respectively.[6]

NMR has an important advantage over the bulk susceptibility in determining the behavior of the magnetic parameters. For example, the Curie-Weiss term due to a dilute concentration of defect related spins hinder the accurate measurement of χ_{spin} at low temperatures. For random distribution of defect spins this paramagnetism broadens the NMR line, but does not contribute to the NMR shift. NMR measurements have been made at 2 and 7 T. Figure 2 shows some typical ^{51}V NMR spectra in $SrNi_2V_2O_8$ at different temperatures. The resonance line at each temperature corresponds to the powder pattern relevant to central transition superimposed with the first order quadrupolar satellites. At 300 K, the line position is shifted toward the high frequency side with respect to the ^{51}V reference position. This finding unambiguously proves the existence of nonzero interchain exchange between the two consecutive Ni^{2+} chains through the VO_4 tetrahedra, producing a nonzero hyperfine field at the vanadium site suggesting an important role of VO_4 units in determining the magnetic properties of $SrNi_2V_2O_8$. In the range 60–300 K, the line shape remains almost unaltered; however, the resonance line shifts toward the reference position.

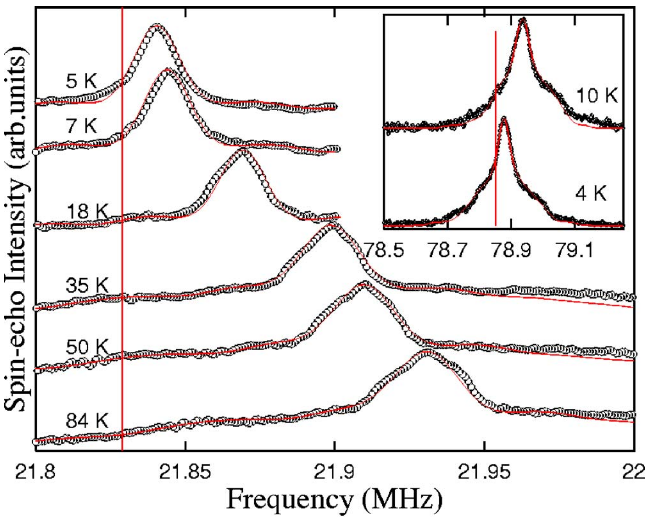

FIG. 2. (Color online) NMR study of ^{51}V spectra at different temperatures at 22 MHz. The inset shows ^{51}V spectra at 79 MHz. Theoretically simulated spectra are shown by the continuous lines. The vertical lines represent ^{51}V reference positions.

The values of the shift and the quadrupolar interaction parameters are determined from the theoretical simulation of the experimental spectra using the same method followed in $BaCu_2V_2O_8$.[16] The quadrupolar splitting frequency (ν_Q) and η for V site are 0.078 MHz and 0.18, respectively. These small values reveal highly symmetric environment around the vanadium site. Furthermore, these parameters remain almost unaltered down to 3.75 K, indicating no further structural deformation of the VO_4 tetrahedra. A similar finding was also observed from ^{51}V NMR in $PbNi_2V_2O_8$.[12]

The temperature variation of the isotropic shift (K_{iso}) is shown in Fig. 3. Inset (a) shows variation of axial shift (K_{ax}). Similar to the bulk susceptibility, both the parameters show a very broad peak around 140 K and starts to decrease sharply from below 60 K. However, it is emphasized that, unlike the bulk susceptibility which shows a Curie-Weiss tail due to Ni^{2+} free spins, both the parameters show no upturn until 3.75 K. This finding suggests that the hyperfine field at the vanadium nuclear site decreases continuously below 60 K, indicating a reduction of the Ni^{2+} spin susceptibility toward a very small value near 3.75 K presumably due to the existence of the Haldane spin gap. Gradual line narrowing starts below 60 K and this continues until 3.75 K, where the magnitude of $K_{\text{iso}} \sim 0.024\%$ and arises mainly from temperature-independent orbital contribution. An almost similar finding was reported in the Pb compound.[12] Therefore, the NMR

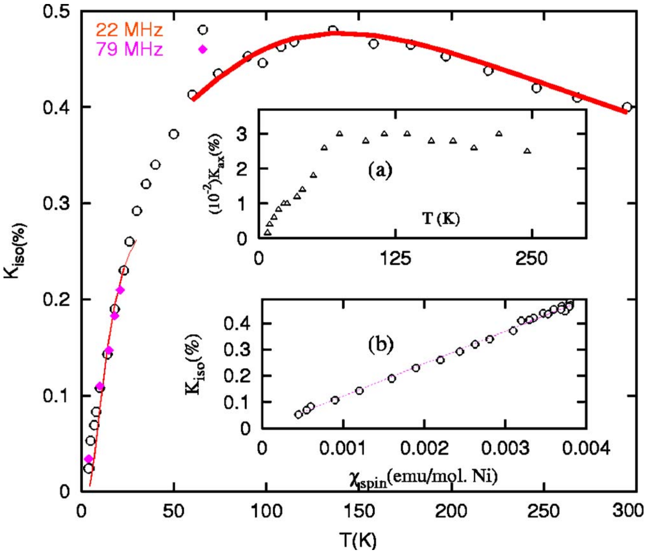

FIG. 3. (Color online) Temperature variation of K_{iso}. The continuous lines represent theoretical fitting as discussed in the text. Inset (a) variation of K_{ax} against T, (b) variation of K_{iso} with χ_{spin}. The solid line represents Eq. (3).

shift data confirms that the system does not show any magnetic ordering at 7 K, rather it gradually approaches a nonmagnetic state and contradicts the previously published result.[7] Occurrence of a 3D magnetic ordering at 7 K should give rise to an enhancement of the resonance linewidth close to this temperature due to the critical slowing down of the Ni^{2+} spin fluctuations, and also due to the development of large hyperfine field below T_N.

K_{iso} follows a linear relation with $\chi_{\text{spin}}(T)$ [Fig. 3(b)],

$$K = K_0 + \frac{H_{\text{hf}}}{N\mu_B}\chi_{\text{spin}}(T). \tag{3}$$

The linearity suggests a unique isotropic part of the hyperfine coupling constant $H_{\text{hf}}=6.9\ \text{kOe}/\mu_B$ over the whole temperature range. This parallelism between K_{iso} and χ_{spin} allows us to determine Δ and the intrachain exchange constant J independently from the shift data using appropriate expressions for K_{iso} very similar to Eqs. (1) and (2), respectively.

Theoretical fit using the similar Eq. (1) as shown by the thin line in Fig. 3 leads to $\Delta=25$ K. This value is the same to that determined from the bulk susceptibility, whose behavior at low temperature is, however, dominated by the Curie term. Furthermore, by fitting the high temperature ($T>50$ K) part of the K_{iso} versus T curve (thick line of Fig. 3) with similar Eq. (2), the magnitude of J is found to be 106 K=9.1 meV which is slightly higher than that determined from the bulk susceptibility ($J=8.8$ meV).

Figure 4 shows the variation of the spin-lattice relaxation rate, $1/T_1$ with $1/T$ in the range 240–4.7 K at 79 MHz and 3.9–80 K at 22 MHz. At both the frequencies, $1/T_1$ decreases by two orders of magnitude with the lowering of temperature revealing a remarkable decrease in the magnetic fluctuations at low temperature. Again at low T, $1/T_1$ appears to have magnetic field dependence, suggesting the possibility of the spin diffusion in this material. Moreover, there is no enhancement in $1/T_1$ until 4 K. This excludes the possibility of the occurrence of a 3D magnetic ordering at 7 K. The relaxation rate in this vanadite should be governed by the thermal excitations of Ni^{2+} chains, and an appropriate starting point for the analysis of the nuclear spin-lattice relaxation data is the expression[17]

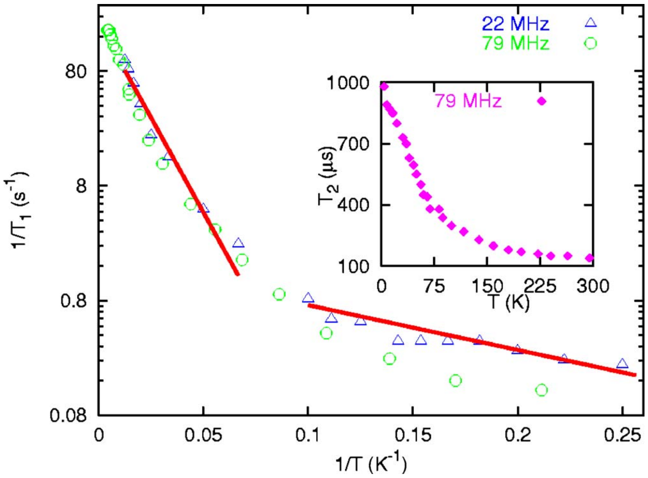

FIG. 4. (Color online) Variation of $1/T_1$ with $1/T$. △: 22 MHz. ○: 79 MHz. The continuous line segment represent theoretical fitting. Inset shows T dependence of spin-spin relaxation time, T_2 at 79 MHz.

$$1/T_1 = \Sigma|A_\alpha(\mathbf{q})|^2 S_\alpha(\mathbf{q},\omega_n) n_\alpha(q), \tag{4}$$

where $A(\mathbf{q})$ is the $\mathbf{q}$-dependent hyperfine coupling constant at site i defined by $A(\mathbf{q})=\Sigma A_{ij}\exp[i\mathbf{q}(r_i-r_j)]$. A_{ij} is the interaction between ith nuclear spin and jth electronic spin. $S_\alpha(q)$ is the corresponding occupation function for the magnetic excitation. From field theoretical calculation of $1/T_1$ in Haldane systems in the low T limit, $T \ll \Delta$, it was shown that, $1/T_1$ follows an activated behavior $1/T_1=C\exp[-\Delta_r/T]$, with $\Delta_r \sim 2\Delta(0)$.[13,18] Since, the present data do not fit with a single Δ_r, we have estimated the same by fitting the experimental $1/T_1$ in the temperature range 80–15 K and 10–4 K, giving $\Delta_r=78$ K and 9 K, respectively. The magnitude of the gap parameter, $\Delta(0)=38$ K in $80K<T<15K$ and 4.5 K in $10K<T<4K$. These values differ appreciably from that obtained from the shift parameter. However, if spin diffusion term[19] contributes to $1/T_1$, then $\Delta_{1/T_1}=\frac{3}{2}\Delta_{\text{Shift}}$, where $\Delta_{\text{Shift}}=25$ K is obtained from shift parameters. This leads to $\Delta_{1/T_1}=37.5$ K, which is close to the observed value 38 K obtained from $1/T_1$.

The spin-spin relaxation time (T_2) was measured at the resonance frequency of 79 MHz in the range 295–3.9 K using the two-pulse Hahn echo sequence ($\pi/2-\tau-\pi$). Throughout the whole temperature range, instead of following a Gaussian behavior, the decay of the spin echo amplitude can be fitted well to $[M(2\tau)/M(0)]=\exp[-2\tau/T_2]$ with a single value T_2. This suggests that the vanadium nuclear magnetic dipolar interaction is not dominating the T_2 process, rather the contribution due to the Ni^{2+} electron spin fluctuation dominates through the electron nuclear hyperfine interaction. Inset of Fig. 4 shows the variation of T_2 with temperature. Initially T_2 increases slowly with the lowering of temperature. From below 60 K (from where the χ_{spin} or ^{51}V shift decreases sharply with temperature), this increment is appreciably enhanced. This finding microscopically further establishes the fact that there is a change of magnetism of this compound around this temperature. Appreciable enhancement of T_2 below 60 K clearly indicates that the electron nuclear hyperfine contribution to the spin-spin relaxation process is reduced considerably below this temperature similar to the shift data. Absence of any reduction in the magnitude of T_2 near 7 K again confirms the absence of a 3D ordering.

In summary, the present results of the static and the dynamic parameters of ^{51}V NMR in $SrNi_2V_2O_8$ provide important information regarding the low temperature phase of this material. In particular, NMR shift and T_2 do not give any evidence of 3D magnetic long-range order, rather suggests a nonmagnetic Haldane spin liquid state with a definite gap of 25 K in the low energy excitations of the Ni^{2+} spins. This explains why powder diffraction experiments on $SrNi_2V_2O_8$ failed to detect any magnetic Bragg reflections at low temperatures. T_1 is dominated by the spin diffusion term at low temperature. Intrachain exchange J, obtained from susceptibility and NMR shift, is almost the same as that for $PbNi_2V_2O_8$. Thus we conclude that the interchain exchange in $SrNi_2V_2O_8$ is not strong enough to give rise to an ordered state in the presence of the small gap in the spin excitations. Further investigations of the low temperature phase with a single crystal and theoretical models are necessary to explain all the issues raised from our observation.

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[1] F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).

[2] T. Sakai and M. Takahashi, Phys. Rev. B **42**, 4537 (1990).

[3] W. J. L. Buyers, R. M. Morra, R. L. Armstrong, M. J. Hogan, P. Gerlach, and K. Hirakawa, Phys. Rev. Lett. **56**, 371 (1986).

[4] T. Inami, K. Kakurai, H. Tanaka, M. Enderle, and M. Steiner, J. Phys. Soc. Jpn. **63**, 1530 (1994).

[5] Z. Tun, W. J. L. Buyers, A. Harrison, and J. A. Rayne, Phys. Rev. B **43**, 13331 (1991).

[6] Y. Uchiyama, Y. Sasago, I. Tsukada, K. Uchinokura, A. Zheludev, T. Hayashi, N. Miura, and P. Boni, Phys. Rev. Lett. **83**, 632 (1999).

[7] A. Zheludev, T. Masuda, I. Tsukada, Y. Uchiyama, K. Uchinokura, P. Boni, and S. H. Lee, Phys. Rev. B **62**, 8921 (2000).

[8] K. Uchinokura, Y. Uchiyama, T. Masuda, Y. Sasago, I. Tsukada, A. Zheludev, T. Hayashi, N. Miura, and P. Boni, Physica B **284–288**, 1641 (2000).

[9] A. Zheludev, T. Masuda, K. Uchinokura, and S. E. Nagler, Phys. Rev. B **64**, 134415 (2001).

[10] A. Zorko, D. Arcon, A. Lappas, J. Giapintzakis, C. Saylor, and L. C. Brunel, Phys. Rev. B **65**, 144449 (2002).

[11] R. Wichmann and H. Muller-Buschbaum, Rev. Chim. Miner. **23**, 1 (1986).

[12] D. Arcon, A. Zorko, and A. Lappas, Europhys. Lett. **65**, 109 (2004).

[13] T. Jolicoeur and O. Golinelli, Phys. Rev. B **50**, 9265 (1994).

[14] V. Gadet, M. Verdaguer, V. Briois, A. Gleizes, J. P. Renard, P. Beauvillain, C. Chappert, T. Goto, K. LeDang, and P. Veillet, Phys. Rev. B **44**, 705 (1991).

[15] O. Golinelli, T. Jolicoeur, and R. Lacaze, J. Phys.: Condens. Matter **5**, 7847 (1993).

[16] K. Ghoshray, B. Pahari, B. Bandyopadhyay, R. Sarkar, and A. Ghoshray, Phys. Rev. B **71**, 214401 (2005).

[17] T. Moriya, Prog. Theor. Phys. **16**, 23 (1956).

[18] J. Sagi and I. Affleck, Phys. Rev. B **53**, 9188 (1996).

[19] K. Damle and S. Sachdev, Phys. Rev. B **57**, 8307 (1998).