# $^{51}V$ NMR study of the quasi-one-dimensional alternating chain compound $BaCu_2V_2O_8$

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$^{51}V$ nuclear magnetic resonance (NMR) studies in polycrystalline sample of $BaCu_2V_2O_8$ reveal the existence of nonzero spin densities, with unequal magnitudes, at the two vanadium sites, viz., $V_1$ and $V_2$ and hence the participation of $VO_4$ tetrahedra to the intrachain and interchain exchange interaction. The behavior of $K_{iso}$ below 200 K provide a clear signature of the reduction of $Cu^{2+}$ spin susceptibility within the chain. Furthermore, there exist unique hyperfine coupling constants for $V_1$ and $V_2$ sites. This data also confirms the existence of only one spin component and the ground state corresponds to a nonmagnetic spin singlet. The $T$ dependence of $K_{iso}$ above 120 K follows the nature of $\chi_{spin}(T)$ proposed by Hatfield for alternating chain model. While below 80 K, it follows the expression for $\chi_{spin}$ of a one-dimensional chain with a spin gap $\Delta$. From the $K_{iso}$ data we have obtained $\Delta = 215 \pm 5$ K, which is smaller than that determined from the magnetic susceptibility ($\Delta = 230$ K) data. The hyperfine field for $V_1$ and $V_2$ sites are 24.6 and $14.4 \pm 1.0$ kOe/$\mu_B$, respectively, with a ratio of 1.7 between them. Thus the exchange path Cu-O-$V_2$-O-Cu in $BaCu_2V_2O_8$ is not negligible. The spin-lattice relaxation time, $T_1$, for both the sites are identical in the range 300–40 K and vary from 3 ms to 10 s. $1/T_1$ follows an activated behavior and provides a gap parameter $\Delta = 380$ K, which is much higher than that obtained from shift data. Moreover, the magnitude of $1/T_1T$ decreases more rapidly than that of $K_{iso}$ below 75 K.

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## I. INTRODUCTION

One-dimensional (1D) quantum spin systems with antiferromagnetic (AF) interactions have been a very active field of research in condensed matter physics, due to the discoveries of various magnetic phenomena related to spin and charge correlations. Examples of such systems are those which exhibit the spin-Peierls (SP) transition, the two-leg spin ladders, the spin alternating chain and charge ordering.[1] They are characterized by ground states of the spin singlet with a finite spin gap ($\Delta$) due to their spin quantum effect. An AF alternating–exchange Heisenberg chain is one in which nearest neighbor spins in the chain interact via a Heisenberg interaction, but with two AF exchange constants $J_2 \leqslant J_1$, $J_1$, $J_2 \geqslant 0$ which alternate from bond to bond along the chain; the alteration parameter $\alpha = J_2/J_1$. The uniform AF Heisenberg chain is one limit of the alternating chain in which the two exchange constants are equal ($\alpha = 1$, $J_1 = J_2 = J$). The other limit is the isolated dimer in which one of the exchange constants is zero ($\alpha = 0$). Among all 1$D$ spin systems, the linear spin chain compounds have attracted much theoretical and experimental interest. In the uniform linear spin chain compound, $CuGeO_3$[2] ($S = 1/2$) the opening of a spin gap is due to a structural phase transition from a gapless state into a gapped state, which accompanies a spontaneous lattice dimerisation below its critical temperature. While the Haldane gap, taking place in an AF Heisenberg chains of integer spins, has purely electronic origin.[3] For the alternating spin chain compound $(VO)_2P_2O_7$, it was found that two different spin gaps coexist, and the second gap is about twice as large as the first one.[4]

The magnitude of the gap parameter known in case of linear spin chain compounds are $\ll 200$ K. Recently He *et al.*,[5] suggested a spin gap of 230 K in a new linear chain compound viz., $BaCu_2V_2O_8$, from specific heat and magnetic susceptibility measurements on a powder sample. This is the highest value of the gap parameter reported for a spin-1/2 Heisenberg AF alternating chain compound. In this compound due to a strong Jahn-Teller effect, the $Cu^{2+}(d^9, S = 1/2)$ ions have quasiplanar $(4+1+1)$ coordination bridged by oxygen ions, while the $V^{5+}$ ions ($d^0$, $S = 0$) have two crystallographic sites $V_1$ and $V_2$, which are tetrahedrally coordinated by oxygen ions. Each type of vanadium site contains eight atoms.[6] The one-dimensional linear chains are made of edge-sharing pairs of $CuO_4$ square-plaquettes and the $VO_4$ tetrahedra ($V_1$ site) along the $c$ axis, and the linear chains are separated by another $VO_4$ tetrahedra ($V_2$ site). The magnetic susceptibility was well reproduced by alternating AF chain model with $J_1 = 260$ K and $J_2 = 52$ K, which results in a large spin gap of about 230 K. It was suggested that the two major AF interactions, viz., $J_1$ and $J_2$ are important similar to those in $(VO)_2P_2O_7$. $J_1$ and $J_2$ correspond to the interactions along the almost linear Cu-O-$V_1$-O-Cu path and the orthogonal Cu-O-Cu path, respectively. The interchain interactions resulting from their 90° Cu-O-$V_2$-O-Cu paths are negligible.

The present paper reports the results of $^{51}V$ NMR as a microscopic probe of $Cu^{2+}$ spin susceptibility and magnetic excitations in polycrystalline sample of $BaCu_2V_2O_8$. New data for magnetic susceptibility would be presented very briefly for clarity. In the Cu-O-$V_1$-O-Cu bond, a mixing of the vanadium 4$s$ orbital with oxygen 2$s$ and 2$p$ orbital, would produce a transfer of magnetic $d$-spin from the $Cu^{2+}e_g$ orbital onto $V^{5+}4s$ orbital. Therefore, $^{51}V$ NMR studies would be very useful to investigate microscopically the $Cu^{2+}$ electronic state, the spin dynamics and to determine the magnitude of $\Delta$ through the effect of transferred hyperfine interaction. Moreover, from NMR the two types of V atoms, as mentioned above can probe the intrachain as well as the in-

 

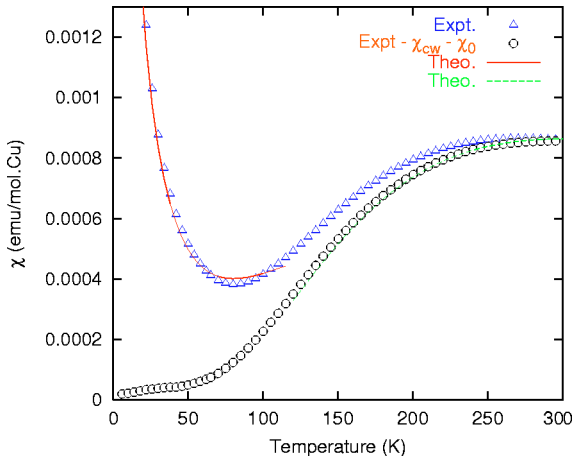


FIG. 1. (Color online) Temperature dependence of magnetic susceptibility of $BaCu_2V_2O_8$. △: the raw data; ○: the data after subtraction the $\chi_0$ and the Curie term. The thick solid line below 120 K represents the result of fitting to the equation $\chi(T)=\chi_0+\chi_{cw}(T)+\chi_{spin}(T)$. The thin dotted line above 120 K represents the results of the fitting to the chain model given by Eq. (1).

terchain exchange interactions. NMR has an important advantage over the bulk magnetic susceptibility. For example, the Curie-Weiss term due to a dilute concentration of defect related spins hinders measurement of $\chi_{spin}$ at low temperatures. For a random distribution of defect spins this paramagnetism broadens the NMR line but does not contribute to the NMR shift tensor.[7]

## II. EXPERIMENT

The polycrystalline sample of $BaCu_2V_2O_8$ was prepared by solid state reaction using high purity reagents of $BaCO_3$, CuO and $V_2O_5$ as starting materials following the method described by He *et al.*[5] Results of the powder x-ray diffraction using Cu $K\alpha$ radiation show no impurity phase. The cell parameters refined by the Rietveld method using the FullProf program[8] agree very well with the tetragonal space group $I$-42d with $a=12.77$ Å, and $c=8.14$ Å as reported previously.[6,9] The dc magnetic susceptibility was measured with a SQUID magnetometer (MPMSXL 7T, Quantum Design) in a magnetic field of 1 T from 2–300 K in the heating cycle. NMR studies were performed at 79 MHz in a Bruker MSL100 pulse spectrometer with a 7.04 T superconducting magnet. A home built NMR probe with a rf coil made of silver was used to avoid spurious $^{63,65}$Cu signals. The spectrum was recorded by applying a $\pi/2$-$\tau$-$\pi/2$ solid echo sequence. Temperature variation studies in the range 4.2–380 K were performed in the Oxford continuous flow He cryostat with ITC503 controller.

## III. RESULTS AND DISCUSSION

### A. Magnetic susceptibility measurement

Figure 1 shows the temperature dependence of magnetic susceptibility of the powder sample $BaCu_2V_2O_8$ in the range 2–300 K. The nature of the curve is similar to that reported

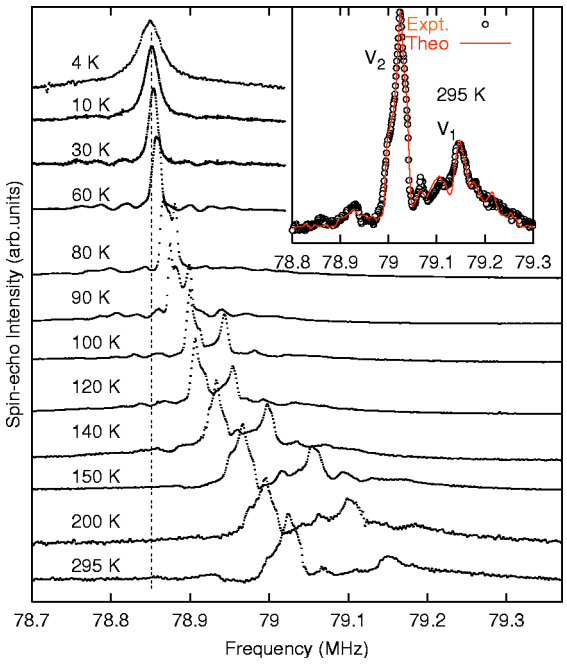


FIG. 2. (Color online) Typical $^{51}$V NMR spectra of polycrystalline $BaCu_2V_2O_8$ at different temperatures recorded at 7 tesla. The dotted vertical line represents the $^{51}$V reference position. Inset shows the $^{51}$V NMR spectrum at 295 K along with a theoretically fitted line obtained as mentioned in the text.

by He *et al.*[5] where the measurements were done up to 900 K. 1D nature in magnetism is revealed from the broad maximum around 250 K. A sharp upturn appearing below 70 K originates due to the contribution of the Curie-Weiss term arising from the isolated $Cu^{2+}$ ions present in the lattice. The data below 120 K is fitted to the relation $\chi(T)=\chi_0+\chi_{cw}(T)+\chi_{spin}(T)$ as shown in Fig. 1, where $\chi_0$ is the temperature independent term, and $\chi_{spin}(T)=aT^{-0.5}\exp(-\Delta/T)$ the susceptibility of one dimensional chain systems with a finite spin gap.[10] The most important parameters are $C=0.026$ emu K/mol Cu and $\Delta=235\pm5$ K. The fraction of the isolated $Cu^{2+}$ spins estimated from the $C$ value is ~6.4%, which is nearly twice that of the reported data.

The susceptibility data corrected for $\chi_{cw}$ and $\chi_0$ term is shown by circles in Fig. 1 and $\chi_{spin}$ above 120 K is found to be well fitted to the equation of the alternating chain model[11,12] for $\alpha=0.2$

$$\chi_{spin}(T)=\frac{Ng^2\mu_B^2}{k_BT}\frac{0.25-0.08\chi+0.004\chi^2}{1+0.39\chi-0.006\chi^2+0.49\chi^3}, \quad (1)$$

where the symbols have their usual meaning. The value of $\Delta$ is found to be $227\pm5$ K. Thus the present sample shows an average gap parameter of $231\pm5$ K which agrees with that ($\Delta=230$ K) reported by He *et al.*[5]

### B. NMR spectra and the shift parameters

$^{51}$V NMR spectra of polycrystalline $BaCu_2V_2O_8$ at different temperatures are shown in Fig. 2. Well resolved characteristic powder pattern typical of the combined anisotropic

magnetic shift and the first order quadrupolar interaction corresponding to the central transitions of the two inequivalent vanadium sites have been obtained in the range 100–380 K. As there are equal number of vanadium atoms in each site, the difference in the intensity (S/N ratio) of the two signals must be due to the difference in their linewidth and/or the anisotropic shift. With lowering of temperature, both the lines shift towards the reference position in such a way that the separation between the two lines is gradually reduced. Below 100 K, the two lines overlap. Structures due to satellite transitions can be seen in all the spectra. However, from below 30 K, width of the resonance lines starts to increase such that the satellites could not be detected in the range 4–10 K. This broadening could be due to the effect of the $Cu^{2+}$ free spins in the magnetic susceptibility (as mentioned in Sec. III A), which is enhanced appreciably in this temperature range.

Thus the observation of the NMR spectra unambiguously proves the existence of non zero spin densities at both sites, and hence the participation of the $VO_4$ tetrahedra to the exchange interaction between the $Cu^{2+}$ ions within the chain and between the chains. The resonance line having larger shift can be assigned to the site $V_1$, belonging to the Cu-O-$V_1$-O-Cu bond within the chain, where the exchange interaction is stronger, while the line with a smaller shift could be ascribed to $V_2$ site, belonging to 90° Cu-O-$V_2$-O-Cu bond connecting the two chains, where the strength of the exchange interaction is expected to be weaker.

In order to determine the shift and the quadrupolar interaction parameters, the experimental spectra are fitted to the equation with magnetic hyperfine and the quadrupolar interactions as first order perturbations over the nuclear Zeeman term:

$$\nu(m \rightarrow m-1) = \nu_{\mathrm{ref}}[1 + K_{\mathrm{iso}} + K_{\mathrm{ax}}(3\cos^2\theta - 1) + K_{\mathrm{an}}\sin^2\theta\cos 2\phi] + \frac{\nu_Q}{2}(m-1/2)[(3\cos^2\theta - 1) + \eta\sin^2\theta\cos 2\phi]. \quad (2)$$

Inset of Fig. 2 shows the simulated powder pattern generated using Eq. (2) superimposed on the experimental data obtained at 295 K. For both the sites, the anisotropic contribution is considerably smaller compared to the isotropic part. The values of the quadrupolar splitting frequency, $\nu_Q$ and $\eta$ for $V_1$ and $V_2$ sites thus obtained are 0.082, ≃0.0 and 0.197 MHz, ≃0.0 respectively. This suggests that both the vanadium sites, are located in highly symmetric environment, most probably at the center of the $VO_4$ tetrahedra. Over and above, it also indicates that $V_1$ is located in a more symmetric environment than that of $V_2$. Furthermore, the quadrupolar interaction parameters for both the sites remain almost unaltered in the range 4.2–380 K indicating no further structural deformation of the $VO_4$ tetrahedra, and hence rules out the possibility of any lattice distortion as was observed in case of spin-Peierls transition in $CuGeO_3$.[2]

Figure 3 shows the variation of the isotropic shift, $K_{\mathrm{iso}}$ with temperature for two vanadium sites. Each of them follow the similar behavior as that of $\chi_{\mathrm{spin}}$ in the range 60–380 K. However, the decrement for $V_1$ site is much faster than that of $V_2$. Hence, the two curves almost superimpose around 60 K. Thus the sharp decrease in the value of $K_{\mathrm{iso}}$ below 200 K, is a clear signature in the reduction of $Cu^{2+}$ spin susceptibility within the chain, indicating the opening of a spin gap, and hence a decrease in the hyperfine field at the vanadium nuclear site. For $V_2$ site an almost unaffected linewidth and the reduced (50%) shift, along with a comparatively slower rate of decrement in $K_{\mathrm{iso}}$ below 200 K, indicate a considerably weaker exchange path in between the chains. In the range 4.2–60 K, the shift of $V_1$ and $V_2$ sites, reduces very slowly towards $K_{\mathrm{iso}} \sim 0$ demonstrating the existence of the nonmagnetic ground state. This has been confirmed by the observation of $^{63}$Cu NMR below 30 K.[29] Furthermore, the shift data clearly differentiate between the effect of $Cu^{2+}$ spins in the chains and the defect spin. This confirms that the observed large enhancement in the bulk susceptibility, below 60 K, is not an intrinsic feature.

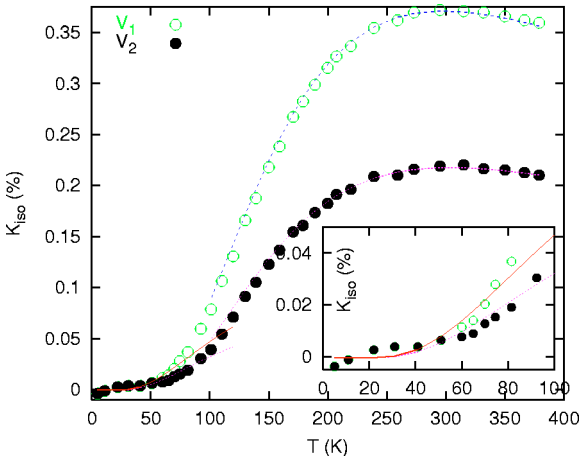


FIG. 3. (Color online) Temperature dependence of $K_{\mathrm{iso}}$ for $^{51}$V NMR in $BaCu_2V_2O_8$. ○: $V_1$; ●: $V_2$. The dotted lines above 100 K represent the functional form given by Hatfield [Eq. (1)]. Inset shows the functional form given by the spin term $\chi_{\mathrm{spin}}(T) = aT^{-0.5}\exp(-\Delta/T)$.

### *1. Hyperfine coupling constant*

The shift is related to $\chi_{\mathrm{spin}}$ by the relation

$$K = K_0 + \frac{A_{\mathrm{hf}}}{N\mu_B\gamma\hbar g}\chi(T), \quad (3)$$

where $A_{\mathrm{hf}}$ is the total hyperfine coupling constant. As long as $A_{\mathrm{hf}}$ remains constant, $K$ should follow $\chi(T)$. Contributions to $A_{\mathrm{hf}}$ arise from the transferred hyperfine interaction, which is a property of the electronic structure, and the dipolar interaction, neither of which is temperature dependent. Although $K(T)$ need not have the same symmetry as $\chi(T)$, the temperature dependence of $K$ should reflect that of $\chi$.

Figure 4 shows the linear dependence of the variation of $K$ with respect to $\chi_{\mathrm{spin}}$ corrected for $\chi_0 + \chi_{\mathrm{cw}}(T)$. This linearity suggests a unique hyperfine coupling constant over the whole temperature range for each vanadium site. The hyperfine field, $H_{\mathrm{hf}} = A_{\mathrm{hf}}/(\gamma\hbar g)$ for $V_1$ and $V_2$ sites are 25.3 and 14.5±1.0 kOe/$\mu_B$ respectively.

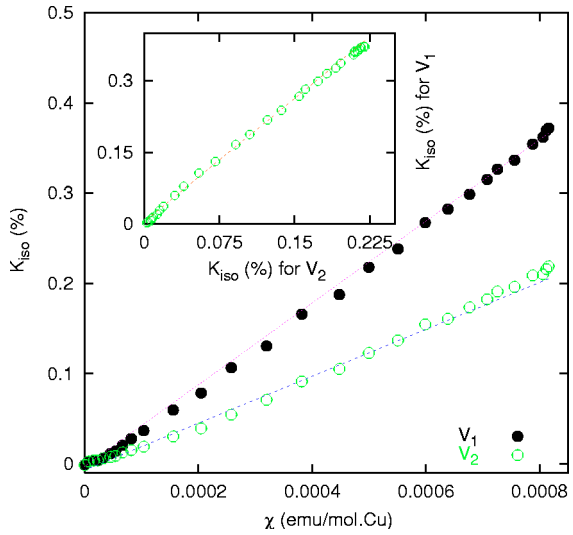


FIG. 4. (Color online) Variation of $^{51}$V NMR shift against $\chi_{spin}$, determined as mentioned in Sec. III A, with temperature as implicit parameter. Inset shows the variation of shift for $V_1$ site against $V_2$ site.

Inset of Fig. 4 shows the shift of $V_1$ versus the shift of $V_2$ with temperature as an implicit parameter. The linear behavior indicates that the $T$ dependence of $K_{iso}$ for both sites are identical. The slope of this straight line gives the ratio of the coupling constants $A_1/A_2=1.7$, which is exactly the ratio of the absolute values of the coupling constants determined from Fig. 4. Agreement of the value of this ratio from these two different approaches confirms (1) the correctness of the extraction of the $\chi_{spin}$ contribution from the measured $\chi$, and (2) the existence of only one spin component in this compound rather than two spin components found from NMR studies in $(VO)_2P_2O_7$.[13]

### *2. Gap parameter*

In order to estimate the magnitude of the spin gap from the shift data, we use the expression [Eq. (1)] for $\chi_{spin}$ as a function of temperature proposed by Hatfield in Eq. (3). Then the $K_{iso}$ versus $T$ curves for $V_1$ and $V_2$ above 100 K are theoretically fitted (indicated by the dotted lines in Fig. 3) to Eq. (3) with $\chi_{spin}$ as an implicit parameter. The magnitude of the spin gap thus obtained is $\Delta=215\pm5$ K for $V_1$ and $V_2$. $H_{hf}$ determined from this functional form are 24.0± 1.0 and 14.3± 1.0 kOe/$\mu_B$ for $V_1$ and $V_2$ sites respectively, which are consistent with that calculated from $K_{iso}$ vs $\chi_{spin}$ graph (Fig. 4).

$\Delta$ in the temperature region $T\ll\Delta$ is obtained from the behavior of susceptibility of a gapped one-dimensional spin system.[14,15] If the magnon dispersion along the chain is approximated by the quadratic form $\epsilon(\mathbf{k})\simeq\Delta+c^2k^2/2\Delta$ near the bottom of the dispersion ($k=q$, $\pi\sim0$), the $T$ dependence of the susceptibility $\chi$ in the low temperature limit $T\ll\Delta$ is expressed as

$$\chi=\sqrt{2\Delta/(\pi^2T)}\exp(-\Delta/T), \tag{4}$$

where c is the spin velocity. $K_{iso}$ for both site are fitted well when $\chi$ in Eq. (3) is replaced by the form given by Eq. (4).

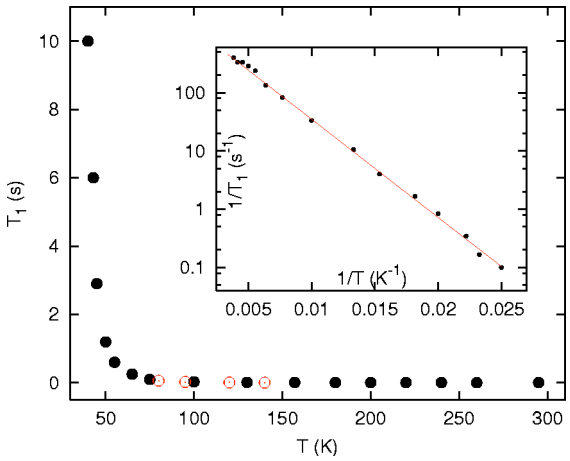


FIG. 5. (Color online) Temperature dependence of $^{51}$V spin-lattice relaxation time ($T_1$); ●: at 7 tesla; ○: at 2.14 tesla. Inset shows variation of $1/T_1$ with $T^{-1}$.

The results of these fits are shown in the inset of Fig. 3. The $K$ versus T curve for $V_1$ satisfies the above equation in the temperature range 4–80 K. Whereas, for $V_2$ site, it is satisfactory in the range 4–100 K. The value of $\Delta=215\pm5.0$K for $V_1$ and $V_2$, thus determined from the $K$ versus T curves in the two temperature regions, agree quite well. This value is lower than that derived from $\chi_{spin}$ data ($\Delta=230\pm5.0$ K). One possible reason for the difference in the value of the energy gap measured from the susceptibility and the NMR shift may be due to the fact that shift data measures intrinsic susceptibility not contaminated by the Curie term due to impurities and thus accurate estimation of the spin gap is possible. Any other possibility, if any, is not known.

### C. Nuclear spin-lattice relaxation rates

It was revealed that the hyperfine fields at $V_1$ and $V_2$ sites differ appreciably in the range 300–100 K, resulting in two well resolved resonance lines. This provides the opportunity to check whether the nuclear spin-lattice relaxation rates, $1/T_1$ for the two vanadium sites are also different in the above temperature region. $1/T_1$ were measured by saturating the central line only with a single $\pi/2$ pulse and monitoring the growth of the solid echo at variable delays. $1/T_1$ is extracted from a fit to the data to the recovery law

$$\frac{M(\infty)-M(t)}{M(\infty)}=C\left[0.012\exp\left(\frac{-t}{T_1}\right)+0.068\exp\left(\frac{-6t}{T_1}\right)+0.206\exp\left(\frac{-15t}{T_1}\right)+0.714\exp\left(\frac{-28t}{T_1}\right)\right], \tag{5}$$

which is obtained from the solution of the master equations[16] in case of a magnetic relaxation of a nucleus with spin I =7/2. It was found that the experimental recovery curves for both the $^{51}$V nuclear sites are reasonably reproduced by Eq. (5). However the values of $T_1$ are found to be same for both the sites within the experimental error.

Figure 5 shows the variation of $T_1$ between 40 and 300 K,

where the magnitude of $T_1$ changes from 10 s to 3 ms. Thus $T_1$ becomes too large to measure below 40 K. The relaxation rate in this compound is governed by the thermal excitations of $Cu^{2+}$ chains, and can be written in the form[17]

$$1/T_1 = 2\gamma_n^2 k_B T \sum |A(\mathbf{q})|^2 \chi''(\mathbf{q},\omega_n)/\omega_n, \quad (6)$$

where $\gamma_n$ is the nuclear gyromagnetic ratio, $A(\mathbf{q})$ is the wave vector dependent hyperfine coupling, and $\chi''(\mathbf{q},\omega_n)$ is the dissipative component of the chain dynamic susceptibility evaluated at the nuclear Larmor frequency $\omega_n$. Calculation of $\chi''(\mathbf{q},\omega_n)$ which is related to the dynamical structure factor of the particular system is the main problem.

In this paper, we did not attempt to calculate the $T$ dependence of $1/T_1$ for $BaCu_2V_2O_8$ in terms of a suitable model. However, we shall discuss some of the theoretical models which were successful in explaining the behavior of $1/T_1$ in some 1D spin chain compounds having similar topological configuration like $BaCu_2V_2O_8$. For example Troyer *et al.*[18] had calculated $1/T_1$ for an AF Heisenberg ladder with $S=1/2$. Instead of simple activated behavior, $1/T_1$ follows the relation

$$(T_1)^{-1} \approx \frac{3\gamma^2 A^2}{16a\pi^2}\exp(-\Delta/T)[0.80908 - \ln(\omega_n/T)] \quad (7)$$

in the temperature range $\omega_n \ll T \ll \Delta$. In addition to the usual exponential drop there is a logarithmic divergence in $\omega_n$. Inset of Fig. 5 shows the linear relation of $1/T_1$ with $T$ indicating the existence of an energy gap $\Delta$ between nonmagnetic ground state and magnetic excited states. $\Delta$ obtained by fitting the relaxation data to Eq. (7) is 380 K, which is considerably higher than $\Delta_S$, obtained from the shift ($215\pm5$ K) and susceptibility data ($230\pm5$ K). Thus the value of $\Delta_{1/T_1}$ obtained from the relaxation data differ appreciably from the shift data though the measurements were done at $T \ll \Delta$. It may also be pointed out that such deviations were also observed in case of Haldane gap antiferromagnets having ladder structures, such as $Y_2BaNiO_2$,[19] $CaV_2O_5$,[20] $SrCu_2O_3$,[21] and $AgVP_2S_6$.[22] On the other hand, comparable gap values were obtained from susceptibility and $1/T_1$ in organometallic compound $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP).[23]

Various types of excitation processes can contribute to the nuclear spin-lattice relaxation, as well as the low lying excitations with different $q$ modes in the Brillouin zone.[17] It has been shown earlier by Sagi *et al.*,[24] that for integer spin 1D antiferromagnets, which exhibit Haldane gap, the dynamic fluctuations near $q=0$ provide dominant contribution to $1/T_1$ for $T \ll \Delta$, despite the strong short range AF correlations at $q=\pi/a$ Thus $A(q)$ in Eq. (6) can be replaced by $A(0)$, which is determined accurately from the shift data, that probes the uniform spin-spin correlation. However, this situation is significantly different in case of half integer spin chain, where spin fluctuations near $q=\pi/a$ play the dominant role in $1/T_1$.[25]

The puzzling discrepancies in some cases for the value of the energy gap obtained from Knight shift–susceptibility data on the one hand, and $1/T_1$ on the other was successfully removed by Damle and Sachdev.[15] From the knowledge of space and time dependent two point correlation function of the conserved magnetization density, they computed the field and temperature dependent $1/T_1$ for $S=1$ for the strong coupling limit in the regime $T \ll \Delta$ for 1D Heisenberg antiferromagnet. They have shown that the overall scale of $1/T_1$ is set by the ratio $T\chi_u/\sqrt{D_s}$. Where $\chi_u$ is the uniform spin susceptibility of the system and $D_s$ is the spin diffusion constant. This leads to an activation gap for $1/T_1$ given by

$$\Delta_{1/T_1} = \tfrac{3}{2}\Delta_S, \quad (8)$$

where $\Delta_S$ is the activation gap for $\chi_u$ or shift. Close agreement with this relation is observed for a large number of gapped spin chains,[26] e.g., $(VO)_2P_2O_7$($S=1/2$),[13] $Y_2BaNiO_5$($S=1$), and $AgVP_2S_6$.[22] Whereas, $\Delta_{1/T_1}$ in $SrCu_2O_3$($S=1/2$) is 50 K higher than $3/2\Delta_S$ and $\Delta_{1/T_1}$ is 80 K lower than that of $3/2\Delta_S$ in case of $CaV_2O_5$($S=1/2$). In the present case of $BaCu_2V_2O_8$, however, $\Delta_{1/T_1}$ is 58 K higher. It may be mentioned that $1/T_1$ did not show any field dependence measured in the field 2.1 (75–150 K) and 7.0 tesla. However, the importance of the spin diffusion could not be ascertained as the field dependence was done in a very limited range of temperature. On the other hand, this $\Delta_{1/T_1}$ shows a close agreement (within 7 K) with the relation

$$\Delta_{1/T_1} = 1.73\Delta_S, \quad (9)$$

as proposed by Kishine and Fukuyama[27] for weakly coupled Heisenberg spin ($S=1/2$) chains in terms of Majorana fermion excitations.[28] This theory demonstrate that not only the triplet process but also the triplet-singlet process contributes to the $1/T_1$ through the hyperfine coupling. The temperature dependence of $\exp(-\Delta_S)$ due to the triplet process is predominant in $1/T_1$ at low $T$, while at high $T$, $\exp(-3\Delta_S)$ due to the triplet-singlet process is predominant. Then their crossover gives rise to an apparent dependence of $\exp(-1.73\Delta_S)$ in $1/T_1$. They have shown that the increase in the interchain exchange $J_\perp$ reduces the magnitude of the ratio $\Delta_{1/T_1}/\Delta_s$. The presence of a weak interchain exchange in $BaCu_2V_2O_8$ is already established from the present NMR result through the observation of nonzero shift at the $V_2$ site connecting two consecutive chains. Finally, it may be pointed out that the theory of nuclear spin-lattice relaxation are available for uniform AF spin chain for $S=1$ and $S=1/2$ ladder system which exhibit spin gap. However, the same is not available for gapped alternating spin chain compound with $J_\perp \sim 0$.

Figure 6 shows the temperature dependence of $(T_1T)^{-1}/K_{iso}$ which remains constant above 75 K, but decreases considerably below this temperature, which is much lower than the gap energy ($\Delta$). This behavior demonstrates that the local dissipative susceptibility $\chi''(\mathbf{q},\omega_n)$, sampled by $(T_1T)^{-1}$, has stronger temperature dependence (i.e., exhibits a larger gap) than the uniform susceptibility $\chi'(\mathbf{q}=0,\omega_n=0)$, sampled by $K_{iso}$. Whereas, above 75 K, both the static and the dynamic susceptibility follow the same temperature dependence resulting in an almost temperature independent behavior of the ratio $(T_1T)^{-1}/K_{iso}$. Such a behavior was also observed in the Haldane gap compound $Y_2BaNiO_5$ near a temperature which is close to the gap parameter.[19]

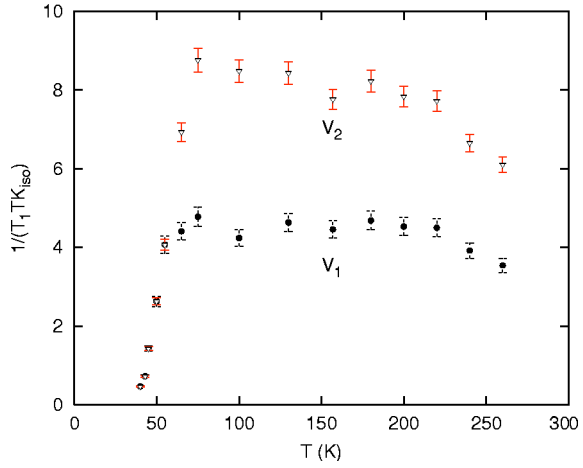


FIG. 6. (Color online) Temperature dependence of $1/(T_1TK_{iso})$ corresponding to $V_1$ and $V_2$ sites of $^{51}V$ NMR.

## IV. SUMMARY

$^{51}V$ NMR studies in quasi-one-dimensional alternating chain compound $BaCu_2V_2O_8$ reveal the existence of nonzero spin densities at both the vanadium sites, and hence the participation of $VO_4$ tetrahedra to the intrachain and interchain exchange interaction. A sharp decrease of $K_{iso}$ for $V_1$ site, below 200 K, provide a clear signature of the reduction of $Cu^{2+}$ spin susceptibility within the chain. On the other hand, almost unaffected linewidth and half the magnitude of $K_{iso}$ with comparatively slower rate of reduction in its magnitude below 200 K for the line corresponding to the $V_2$ site, indicate a comparatively weaker exchange path in between the chains. Furthermore, there exists unique hyperfine coupling constants over the whole temperature range for each vanadium site. The shift data further confirms that there is only one spin component in this compound rather than two spin components as found from NMR in a similar type of compound $(VO)_2P_2O_7$ and there exists a nonmagnetic ground state. The temperature dependence of shift above 120 K follows the behavior of $\chi_{spin}(T)$ proposed by Hatfield for alternating chain model. While below 80 K, it follows the expression for $\chi_{spin}$ of a one-dimensional chain with a spin gap, $\Delta$. Its value $215\pm5$ K, determined from the shift data of $V_1$ and $V_2$ is smaller than that derived from the magnetic susceptibility ($\Delta=230$ K). The hyperfine field for $V_1$ and $V_2$ sites are 24.6 and $14.4\pm1.0$ kOe/$\mu_B$, respectively, with a ratio of 1.7 between them. Thus the exchange path ($J_\perp$) Cu-O-$V_2$-O-Cu, which was not considered in the analysis of the susceptibility data, may have some role in the magnetic properties of $BaCu_2V_2O_8$.

The spin-lattice relaxation times for both the sites are identical throughout the range 40–300 K. It follows an activation behavior and provides a gap parameter $\Delta=380$ K, which is much higher than that obtained from shift data. The temperature dependence of $(T_1T)^{-1}$ is more prominent than that of $K_{iso}$ below 75 K. Moreover, $1/T_1$ did not show any field dependence in the range 75–150 K at 2.1 and 7.05 tesla. Since the field dependence has been made in a small temperature range, one cannot rule out the importance of spin diffusion in this system and therefore, further experiment is needed to account for the large difference between $\Delta_{1/T_1}$ and $\Delta_S$ in $BaCu_2V_2O_8$, a spin half alternating chain compound with weak interchain coupling.

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[29] We have detected a broad and complex $^{63}$Cu NMR spectrum for $BaCu_2V_2O_8$ at 7 tesla in the range 4–30 K. Intensity of the spectrum increases at lower temperatures. Detail would be reported elsewhere.