Spin Diffusion in the Quasi-One-Dimensional Conductor $\beta$-Na$_{0.33}$V$_2$O$_5$

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Abstract. We have measured the $^{51}$V nuclear spin-lattice relaxation rate $1/T_1$ at various magnetic fields $H$ to study the spin dynamics in the metallic phase of the quasi-one-dimensional conductor $\beta$-Na$_{0.33}$V$_2$O$_5$. We find the $H$ dependence of $1/T_1$ due to the spin diffusion. The Na ordering is found to suppress at the V$_2$ site the diffusive behavior with the diffusion constant $D_s$ which increases rapidly down to the MI transition temperature. On the other hand, the diffusive contribution to $1/T_1$ is small at the V$_3$ site and the $q=2k_F$, where $k_F$ is the Fermi wave vector, spin fluctuations dominantly contribute to it.

1. Introduction
The vanadate $\beta$-Na$_{0.33}$V$_2$O$_5$ with a mixed-valence state of V$^{4+}(3d^1)$ and V$^{5+}(3d^0)$ has been intensively investigated from the aspects of the metal-insulator (MI) transition accompanied by the charge ordering (CO) [1, 2, 3, 4, 5, 6]. This oxide crystallizes in a monoclinic crystal structure with the space group $C2/m$ at room temperature [1]. There are three vanadium sites V1, V2, and V3, and the Na site is located in a tunnel of the V$_2$O$_5$ framework. It successively undergoes the Na order-disorder transition at $T_{Na}\sim$242 K, the MI transition at $T_{MI}\sim$135 K and the antiferromagnetic (AF) transition at $T_N\sim$24 K [1, 7]. Recent NMR and theoretical studies revealed that these V sites form an electronic structure composed of the weakly coupled three ladders [4, 8]. Thus this vanadate is interesting from the aspect of a quasi-one-dimensional (quasi-1D) conductor. We discussed the dynamical magnetic properties from the experimental results of the $^{51}$V nuclear spin-lattice relaxation rate $1/T_1$ in the metallic phase of $\beta$-Na$_{0.33}$V$_2$O$_5$ [9, 10]. However, the spin dynamics still remains unclear particularly in the wave vector $q$ dependence. In quasi-1D conductors, the low-energy spin excitation spectrum is governed by the $q\sim0$ and $q\sim2k_F$, where $k_F$ is the Fermi wave vector, spin fluctuations [11]. The $q\sim0$ contribution to $1/T_1$ is expected to exhibit a magnetic field $H$-dependent behavior due to the spin diffusion effect, whereas the $2k_F$ contribution is not $H$-independent.

In this paper, we have measured the $H$ dependence of $1/T_1$ to study the spin diffusion in the metallic phase of $\beta$-Na$_{0.33}$V$_2$O$_5$. We find the presence of the $1/\sqrt{H}$ term due to the spin diffusion at $q\sim0$. The spin dynamics at the V2 site is reported to be governed by both $q\sim0$ and $q\sim2k_F$ fluctuations, whereas it is at the V3 site by the $q\sim2k_F$ fluctuations.

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2. Experimental procedure
A single crystal of \(\beta\)-Na_{0.33}V_{2}O_{5} \) used in the present NMR measurements was prepared by the rf heating Czochralski method [6]. The \( ^{51}V \) nuclear spin-lattice relaxation rate \( 1/T_{1} \) was measured with magnetic fields \( H \) of 1.23-7.98 T applied along the direction of magic angles, \( \theta_{b} \sim 172^\circ \) (139\(^\circ\)), for the V2 (V3) sites where \( \theta_{b} \) is the angle between \( H \) and the \( c \) axis in the \( ca \) plane. In these conditions, the electric quadrupole interaction vanishes and the nuclear magnetization recovers exponentially with a single time constant \( T_{1} \).

3. Experimental results and discussion

![Figure 1](image1.png)  
**Figure 1.** Temperature dependence of \( 1/T_{1} \) at the (a) V2, V2A, V2B, (b) V3, V3A, and V3B sites measured at various magnetic fields in the metallic phase of \( \beta\)-Na_{0.33}V_{2}O_{5}.

![Figure 2](image2.png)  
**Figure 2.** \( 1/T_{1} \) versus \( 1/\sqrt{H} \) plots for the (a) V2, V2A, V2B, (b) V3, V3A, and V3B sites at various temperatures in \( \beta\)-Na_{0.33}V_{2}O_{5}. The solid and dashed lines are the results of the data fitted to the relation \( 1/T_{1}=(1/T_{1})_{0}+C/\sqrt{H} \). 

We observed \( ^{51}V \) NMR spectra from the V2 and V3 sites and no spectrum from the V1 site due to the short spin-spin relaxation time above \( T_{Na} \). Below \( T_{Na} \), two spectra from the V3A and V3B sites were observed owing to the Na ordering, whereas the difference between the spectra from the V2A and V2B sites was not detected [4]. In Fig. 1, we present the \( T \) dependence of \( 1/T_{1} \) at the V2 and V3 sites in the metallic phase of \( \beta\)-Na_{0.33}V_{2}O_{5}. The \( 1/T_{1} \) shows the \( H \) dependence which is more clearly seen in Fig. 2 where \( 1/T_{1} \) versus \( 1/\sqrt{H} \) plots are shown at various temperatures. All data of \( 1/T_{1} \) at the V2 and V3 sites can be well fitted by the relation \( 1/T_{1}=(1/T_{1})_{0}+C/\sqrt{H} \) where \( (1/T_{1})_{0} \) and \( C \) are fitting parameters. The fitted results of \( (1/T_{1})_{0} \) and \( C \) are shown in Fig. 3. At the V2 sites, \( C \) rapidly reduces with decreasing \( T \) below \( T_{Na} \) and \( (1/T_{1})_{0} \) shows a jump at \( T_{Na} \). The \( (1/T_{1})_{0} \) at the V3A and V3B sites show the upwards and downwards concave \( T \) dependence, respectively, below \( T_{Na} \), whereas \( C \) shows the weak \( T \) dependence.
Figure 3. Temperature dependence of $C$, $(1/T_1)_\text{diff}$, and $(1/T_1)_0$ at the (a) V2, V2A, V2B, (b) V3, V3A, and V3B sites in the metallic phase of $\beta$-Na$_{0.33}$V$_2$O$_5$. The dashed curve represents the average of $(1/T_1)_0$ at the V3A and V3B sites.

Figure 4. Temperature dependence of the diffusion constant $D_s$ (a) at the V2, V2A, V2B, (b) V3, V3A, and V3B sites in the metallic phase of $\beta$-Na$_{0.33}$V$_2$O$_5$.

In general, $1/T_1$ in 1D conductors are given by $1/T_1=(1/T_1)_{q\sim 0}+(1/T_1)_{q\sim 2k_F}$ where the first and second terms are due to the $q\sim 0$ and $2k_F$ spin fluctuations, respectively [11]. The spin dynamics at $q\sim 0$ is expected to become diffusive. Based on the 1D spin diffusion model, the transverse component of the spin correlation function $S^{xx}(q,t)$ at $q \sim 0$ is given by

$$S^{xx}(q,t) = k_B T \frac{\chi(q)}{g^2 \mu_B^2} \exp(-D_s q^2 t) \exp(-i \omega_e t),$$

where $k_B$ is the Boltzmann’s constant, $\chi(q)$ is the $q$-dependent susceptibility, $D_s$ is the diffusion constant, $g$ is the electron $g$ value, $\mu_B$ is the Bohr magneton and $\omega_e = g \mu_B H/\hbar$ is the electron Larmor frequency [11, 12, 13, 14]. Using Eq. (1), $1/T_1$ due to the spin diffusion $(1/T_1)_\text{diff}$ is expressed as

$$\left( \frac{1}{T_1} \right)_\text{diff} = A_{hf}^2 \frac{k_B T}{\hbar^2 g^2 \mu_B^2} \frac{1}{\sqrt{2D_s} \sqrt{\omega_e}},$$

where $A_{hf}$ is the hyperfine coupling constant, $\chi_{\text{spin}}$ is the spin susceptibility and $\hbar$ is the Planck’s constant [11, 12, 13, 14]. As seen in Eq. (2), $(1/T_1)_\text{diff}$ is proportional to $1/\sqrt{\omega_e}$ ($\propto 1/\sqrt{H}$). On the other hand, $(1/T_1)_{2k_F}$ is independent of $H$. Thus the $H$ dependence of $1/T_1$ observed in the metallic phase of $\beta$-Na$_{0.33}$V$_2$O$_5$ can be well explained by the spin diffusion model. That is, $C/\sqrt{H} \sim (1/T_1)_\text{diff} \sim (1/T_1)_{q\sim 0}$ and $(1/T_1)_0 \sim (1/T_1)_{q\sim 2k_F}$. The $T$ dependence of $(1/T_1)_\text{diff}$, which
is obtained by subtracting \((1/T_1)\) from \(1/T_1\), is also presented in Fig. 3. As seen in Fig. 3, we can conclude that both \(q=0\) and \(q=2k_F\) fluctuations at the V2 sites contribute to \(1/T_1\), whereas \(1/T_1\) at the V3 sites is not governed by the \(q=0\) fluctuations.

Based on Eq. (2), we can calculate the \(D_s\) values from the experimental \(C\) values, \(A_{hf}^{\beta} = -100 \text{kOe}/\mu_B\), \(q = 1.95\), and \(\chi_{\text{spin}}\) estimated in Ref. 4. The results are presented in Fig. 4, which shows the \(T\) dependence of \(D_s\) at the V2 and V3 sites. One notes that \(D_s\) at the V2 sites shows a steep increase towards \(T_{\text{MI}}\), whereas \(D_s\) at the V3 sites is larger than \(D_s\) at the V2 sites and shows a little increase below \(T_{\text{Na}}\). Previously, Soda et al. discussed \(D_s\) in quasi-1D organic conductor TTF-TCNQ and concluded that \(D_s\) is related to the electric conductivity parallel to the chain direction. However, \(D_s\) at the V2 and V3 sites is not scaled to the conductivity. On the other hand, \(D_s\) at quasi-1D antiferromagnets is reported to be proportional to the AF correlation length according to the dynamical scaling hypothesis. The development of the AF correlation might be an origin of the increase of \(D_s\) at the V2 sites of \(\beta\)-Na\(_{0.33}\)V\(_2\)O\(_5\). The origin is, however, not clear and theoretical studies are desired to understand the \(T\) dependence of \(D_s\).

4. Conclusion
We have measured the \(H\) dependence of the \(^{51}\text{V}\) nuclear spin-lattice relaxation rate \(1/T_1\) in the metallic phase of the quasi-one-dimensional conductor \(\beta\)-Na\(_{0.33}\)V\(_2\)O\(_5\). We found the spin diffusion expected to appear in quasi-one-dimensional systems. The Na ordering was found to suppress the diffusive behavior at the V2 sites and the diffusion constant \(D_s\) increases rapidly down to the MI transition temperature. On the other hand, the diffusive contribution to \(1/T_1\) is small at the V3 site, indicating the dominant contribution of the \(q=2k_F\) spin fluctuations.

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