Local spin susceptibility in the metallic phase of the quasi-one-dimensional conductor $\beta$-Li$_{0.33}$V$_2$O$_5$

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Abstract. $^{51}$V NMR measurements have been made on a single crystal to study local spin susceptibility in the metallic phase of the quasi-one-dimensional conductor $\beta$-Li$_{0.33}$V$_2$O$_5$ which undergoes the metal-insulator transition at $T_{MI}\sim 170$ K. In the metallic phase we observe five sets of NMR spectra split by the electric quadrupole interaction coming from the V1B, V2A, V2B, V3A, and V3B sites that appear due to the Li cation ordering. The $^{51}$V Knight shift $K$ tensors are determined. From the analysis of $K$ and bulk magnetic susceptibility, we estimate the local spin susceptibility at each V site. A model of the electron distribution in the metallic phase is proposed on the basis of the weakly coupled three ladders.

1. Introduction
The discovery of the metal-insulator (MI) transition accompanied by the charge ordering (CO) and the pressure induced superconductivity has renewed interests in the quasi-one-dimensional conductors $\beta$-A$_{0.33}$V$_2$O$_5$ (A$^+$= Li, Na, and Ag) with a mixed-valence state of V$^{4+}$ ($3d^1$):V$^{5+}$ ($3d^0$)=1:5 [1, 2, 3, 4]. In order to understand the mechanisms of the MI transition and superconductivity, it is important to clarify the electronic structure in the metallic phase of $\beta$-A$_{0.33}$V$_2$O$_5$. In the monoclinic $\beta$-type structure, there are three vanadium sites, V1, V2, and V3. The V1 and V3 sites form zig-zag chains along the $b$ axis sharing the edges of V1O$_6$ octahedra and V3O$_5$ pyramids, whereas the V2 sites form a two-leg ladder along the $b$ axis sharing the corner of the V2O$_6$ octahedra. The A cation is located in a tunnel of the V$_2$O$_5$ framework. Recent NMR and theoretical studies revealed that these V sites form the weakly coupled three ladders composed of two V1-V3 and one V2-V2 ladders from the aspect of the electronic structure [5, 6]. This electronic structure is considered to play an essential role for the MI transition and superconductivity of $\beta$-A$_{0.33}$V$_2$O$_5$ [4, 7, 8]. Physical properties of these oxides such as pressure versus temperature diagrams, $T_{MI}$, and so on show an A-cation dependence. Therefore it is important to know the A-cation dependence of the local magnetic properties closely related to the electronic structure. However, detailed NMR studies useful in studying them have not been made except $\beta$-Na$_{0.33}$V$_2$O$_5$ [5, 9, 10].

In this paper we performed $^{51}$V NMR measurements on a single crystal to study the local susceptibility in the metallic phase of $\beta$-Li$_{0.33}$V$_2$O$_5$ which undergoes the MI transition at
$T_M \sim 170$ K. The Knight shift $K$ tensors at 300 K are determined from the angular dependence of $^{51}$V NMR spectra. Also we estimate the local magnetic susceptibility at each V site and propose a model of the electronic structure with the 2$b$ modulation of the electron density.

2. Experimental procedure
The single crystal of $\beta$-Li$_{0.33}$V$_2$O$_5$ used in the present NMR experiments was grown by the rf heating Czochralski method [8]. Fourier-transformed (FT) NMR spectra of spin-echo signals were measured with the sample rotated in a magnetic field $H_0$ of 5.8709 T using a coherent pulsed spectrometer. The $^{51}$V Knight shift $K$ was determined by using a relation as $K = (\nu_{\text{res}} - \nu_0) / \nu_0$ where $\nu_{\text{res}}$ and $\nu_0$ (=65.7048 MHz) are $^{51}$V resonance frequencies in $\beta$-Li$_{0.33}$V$_2$O$_5$ and aqueous NaVO$_3$, respectively.

3. Experimental results and discussion

![Figure 1](image1.png)

Figure 1. Angular dependence of the $^{51}$V Knight shift $K$ at 300 K in the (a) $a^*b$, (b) $bc$, and (c) $ca^*$ planes of $\beta$-Li$_{0.33}$V$_2$O$_5$. The solid and broken lines are the fitted results of the data to Eq. (1).

![Figure 2](image2.png)

Figure 2. Temperature dependence of the $^{51}$V Knight shift components, $K_X$, $K_Y$, and $K_Z$, at the (a) V1B, (b) V2A, V2B, (c) V3A, and V3B sites in $\beta$-Li$_{0.33}$V$_2$O$_5$.

We observed five sets of $^{51}$V (the nuclear spin $^{51}I=7/2$) resonance lines, one central and six satellite ones, split by the electric quadrupole interaction coming from the V1B, V2A, V2B, V3A, and V3B sites, which appear due to the Li ordering along the 2$b$ lattice modulation [11], in the metallic phase of $\beta$-Li$_{0.33}$V$_2$O$_5$. The spectra could be well explained by the first order electric quadrupole effect with the anisotropic $K$ tensor. Figure 1 shows the angular dependence
of $K$ in the $a^*b$, $bc$, and $ca^*$ planes where $a^* \perp b$ and $c$. When $H_0$ is rotated in the $bc$ plane, $K$ is expressed as [9]

$$K = k_{1,a^*} + k_{2,a^*} \cos 2\theta_{a^*} + k_{3,a^*} \sin 2\theta_{a^*},$$

with $k_{1,a^*} = \frac{(K_{bb} + K_{cc})}{2}$, $k_{2,a^*} = \frac{(K_{bb} - K_{cc})}{2},$ and $k_{3,a^*} = K_{bc}$, where $K_{\alpha\beta}$ ($\alpha, \beta = a^*, b,$ and $c$) are components of the $K$ tensor. Similar relations for $H_0$ rotations in the $ca^*$ and $a^*b$ planes are obtained by cyclic permutation. In order to determine the principal components of the $K$ tensor $K_X$, $K_Y$, and $K_Z$, we fitted the experimental data in Fig. 1 to Eq. (1) and diagonalized the $K$ tensor expressed in the $a^*bc$ coordinate system. The results are presented in Fig. 2 that shows the $T$ dependence of $K_X$, $K_Y$, and $K_Z$ at each V site. One should note that $K$ at each V site has almost an axial symmetry which is governed by the $d_{xy}$ orbital ordering due to the crystal field effect [5].

**Figure 3.** Temperature dependence of magnetic susceptibility of the powdered sample $\chi$ (Ref. 4) and isotropic local magnetic susceptibilities $\chi_{iso}(i)$ ($i = V1A, V1B, V2A, V2B, V3A, \text{and } V3B$) in $\beta$-Li$_{0.33}$V$_2$O$_5$.

**Figure 4.** Schematic electronic structure in the Li-ordered metallic phase of $\beta$-Li$_{0.33}$V$_2$O$_5$. The size of the circles is proportional to the electron number.

The Knight shift can monitor the local magnetic susceptibility at individual nuclear site. In transition metal oxides, $K$ is generally given by $K = K_{\text{orb}} + K_{\text{d}}$ where $K_{\text{orb}}$ is the shift due to Van Vleck orbital susceptibility independent on $T$ and $K_{\text{d}}$ is proportional to the 3$d$ electron spin susceptibility. We estimate the local magnetic susceptibilities at the six V sites from the magnetic susceptibility $\chi$ of a powdered sample [4] and the isotropic $^{51}$V Knight shift $K_{iso} = (K_X + K_Y + K_Z)/3$. In the present analysis, we neglect $K_{\text{orb}}$ and the orbital susceptibility which may be small and comparable to the diamagnetic susceptibility [5]. Thus $\chi$ is expressed as $\chi \sim \sum_i \chi_{iso}(i)/6$ where $\chi_{iso}(i)$ is the isotropic spin susceptibility of the $i$ ($= V1A, V1B, V2A, V2B, V3A, \text{and } V3B$) site. The isotropic Knight shift at the $i$ site $K_{iso}^{d}(i)$ is expressed as [12]

$$K_{iso}^{d}(i) = \frac{A_{hf}}{N\mu_B} \chi_{iso}(i),$$

where $A_{hf}$ is the hyperfine coupling constant of the Fermi contact interaction due to the core polarization effect, $N$ is the Avogadro’s number, and $\mu_B$ is the Bohr magneton. From Eq. (2)
and the assumption of $A_m \sim -100 \text{kOe}/\mu_B$ [13], we can obtain $\chi_{\text{iso}}(i)$ ($i = \text{V1B, V2A, V2B, V3A,}$

and V3B). Also $\chi_{\text{iso}}(\text{V1A})$ is evaluated by subtracting $\chi_{\text{iso}}(i)$ from $\chi$. Thus we can obtain the $T$ dependence of local magnetic susceptibility at each V site as displayed in Fig. 3. As seen in Fig. 3, the V1A site has the largest local magnetic susceptibility and there is the large difference between the local susceptibilities at the V1A and V1B sites.

On the basis of $\chi_{\text{iso}}(i)$, we estimate the 3$d$ electron number at each V site. By the procedure as discussed for $\beta$-Na$_{0.33}$V$_2$O$_5$ [5], the 3$d$ electron numbers at the V1A, V1B, V2A, V2B, V3A and V3B sites are roughly estimated as $\sim-0.44, 0.20, 0.14, 0.09, 0.08,$ and 0.06 electrons/V-ion, respectively. Thus, as a model of the electronic structure, we present in Fig. 4 the electron distribution on the weakly coupled three ladders composed of two V1-V3 and one V2-V2 ladders which are considered to be the basic structure in $\beta$-Na$_{0.33}$V$_2$O$_5$ [5, 9]. Comparing $\beta$-Li$_{0.33}$V$_2$O$_5$ with $\beta$-Na$_{0.33}$V$_2$O$_5$, the V1 sites in both the oxides commonly have the largest electron numbers. However, it should be noted that the difference between the electron numbers at the V1A and V1B ($i = 1, 2,$ and 3) sites is large in $\beta$-Li$_{0.33}$V$_2$O$_5$, whereas it is very small in $\beta$-Na$_{0.33}$V$_2$O$_5$. Also $\beta$-Sr$_{2+1}$V$_2$O$_5$ with one 3$d$ electron per three V ions is reported to have an electron distribution different from those in the $A^+$-cation compounds [14]. These facts show that the charge disproportionation between the V1A and V1B sites, which takes place even in the metallic phase, is strongly dependent on the A cation. Theoretical studies are desired to systematically understand the A-cation dependence of the charge disproportionation.

4. Conclusion

We have made $^{51}$V NMR measurements on a single crystal to study the local magnetic susceptibilities in the metallic phase of the quasi-one-dimensional conductor $\beta$-Li$_{0.33}$V$_2$O$_5$. We determined the $^{51}$V Knight shift tensors and estimated the local magnetic susceptibilities. Also a model of the electronic structure composing of the weakly coupled three ladders is proposed with the electron distribution.

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