7Li and 51V NMR Studies on Local Symmetry and Charge Disproportionation in Quasi-One-Dimensional Conductor $\beta$-Li$_{0.33}$V$_2$O$_5$

Ichiro Yamauchi$^1$, Masayuki Itoh$^1$, Touru Yamauchi$^2$, Jun-Ichi Yamaura$^2$ and Yutaka Ueda$^2$

$^1$Department of Physics, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan
$^2$Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa 277-8581, Japan

E-mail: yamauchi.ichihiro@f.mbox.nagoya-u.ac.jp

Abstract. We have made 7Li and 51V NMR measurements on a single crystal to investigate the local symmetry and the charge disproportionation in the metallic phase of the quasi-one-dimensional conductor $\beta$-Li$_{0.33}$V$_2$O$_5$. The electric quadrupole tensors at the Li sites are determined and the Li ordering is discussed on the basis of the recent X-ray diffraction results. We also report the temperature dependence of the 51V Knight shift and the 51V nuclear spin-lattice relaxation rate, indicating the presence of the charge disproportionation even in the metallic phase.

1. Introduction

Understanding the nature of anomalous metals located near Mott insulators has been one of the major interests in strongly correlated electron systems such as 3d transition metal oxides [1]. Quasi-one-dimensional conductors $\beta$-A$_{0.33}$V$_2$O$_5$ (A = Li, Na and Ag) with mixed valence of V$^{4+}$($3d^1$) and V$^{5+}$($3d^0$), which undergo the metal-insulator (MI) transition accompanied by the charge ordering and show pressure-induced superconductivity, have been intensively investigated as one of the anomalous metals [2, 3, 4, 5].

In the $\beta$ structure, there are three crystallographically inequivalent vanadium sites V1, V2 and V3, and one A-cation site is located in a tunnel structure of the V$_2$O$_5$ framework [2]. In $\beta$-Na$_{0.33}$V$_2$O$_5$, the zig-zag ordering of the Na atom in the tunnel structure changes the space group from C$2/m$ to P$2_1$ and splits the VI($I$=1, 2 and 3) site into two inequivalent VIA and VIB sites [6, 7]. Previously, we found that the Na order-disorder transition drastically changes the static and dynamical magnetic properties in the metallic phase of $\beta$-Na$_{0.33}$V$_2$O$_5$ [8, 9, 10]. These results suggest that the electrostatic potential and the charge fluctuations originating from the motion of the A cation affect the physical properties in the metallic phase of $\beta$-A$_{0.33}$V$_2$O$_5$.

$\beta$-Li$_{0.33}$V$_2$O$_5$, which undergoes the MI transition at $T_{MI}$$\sim$170 K [5], is one of the family member of $\beta$-A$_{0.33}$V$_2$O$_5$. A recent X-ray diffraction (XRD) experiment on a single crystal of $\beta$-Li$_{0.33}$V$_2$O$_5$ showed that the unit cell doubles along the a and b axes compared with the standard $\beta$-type structure [11]. The $2a\times2b\times c$ lattice modulation different from $a\times2b\times c$ in $\beta$-Na$_{0.33}$V$_2$O$_5$ allows us to systematically study the role of the A cation for the physical properties.
of $\beta$-$A_{0.33}V_2O_5$. Although we reported the brief $^{51}\text{V}$ NMR results of $\beta$-$\text{Li}_{0.33}V_2O_5$ [12], the $^7\text{Li}$ NMR has not been performed in order to clarify the local symmetry and the structure of the Li ordering.

In this paper, we have made $^7\text{Li}$ and $^{51}\text{V}$ NMR measurements to study the local symmetry and the charge disproportionation in the metallic state of $\beta$-$\text{Li}_{0.33}V_2O_5$. We determine the electric field gradient (EFG) tensor at the Li sites and discuss the local symmetry and the Li ordering on the basis of the recent XRD results. We also report the $^{51}\text{V}$ Knight shift $K$ and the $^{51}\text{V}$ nuclear spin-lattice relaxation rate $1/T_1$ at the V2 sites, indicating the presence of the charge disproportionation (CD) even in the metallic state.

2. Experiments
An as-grown $\beta$-$\text{Li}_xV_2O_5$ crystal with $x \sim 0.38$ was grown by the rf-heating Czochralski method [5]. A single crystal of $\beta$-$\text{Li}_{0.33}V_2O_5$ used in the present NMR study was prepared by washing the as-grown crystal in hot hydrochloric acid and calcination of the crystal with a large amount of powdered $x=0.33$ sample in an evacuated quartz tube. The Fourier-transformed $^7\text{Li}$ and $^{51}\text{V}$ NMR spectra of spin-echo signals were measured with the sample rotated in a magnetic field $H_0=5.8709$ T. $1/T_1$ for $^{51}\text{V}$ was measured by the inversion recovery method.

3. Results and discussion

Figure 1. Fourier-transformed $^7\text{Li}$ NMR spectra at 300 K with the external field $H_0=5.8709$ T applied along (a) the $b$ axis ($\theta_c=90^\circ$) and (b) $\theta_c=81^\circ$, where $\theta_c$ is the angle from the $a^*$ axis in the $a^*b$ plane, in $\beta$-$\text{Li}_{0.33}V_2O_5$. The S(a) and S(b) [$S'(a)$ and $S'(b)$] are shown as the red (blue) shaded spectra.

Figure 2. Angular dependence of the $^7\text{Li}$ nuclear quadrupole splitting $\Delta\nu_{3/2-1/2}$ at 300 K in the (a) $a^*b$, (b) $bc$ and (c) $ca^*$ planes of $\beta$-$\text{Li}_{0.33}V_2O_5$.

We can expect that the ordering of the Li ions lowers the lattice symmetry and changes the electronic and magnetic properties. In order to study the local symmetry, we have measured
the angular dependence of $^7$Li NMR spectra at 300 K. Figure 1 shows typical $^7$Li NMR spectra with $H_0$ applied along the $b$ axis and a direction of $\theta_c$-Li$_0$, where $\theta_c$ is the angle between $H_0$ and the $a^*$ axis, which is perpendicular to the $b$ and $c$ axes, in the $a^*b$ plane. We observed four sets of $^7$Li spectra, S(a), S(b), S'(a) and S'(b), split by the electric quadrupole interaction. Each spectrum has equally spaced three lines, one central line, $\nu_{1/2-1/2}$, and two satellite lines, $\nu_{3/2-1/2}$ and $\nu_{-3/2-1/2}$, as presented by the solid and dashed lines in Fig. 1. Figure 2 shows the $^7$Li quadrupole splitting frequencies, $\delta\nu_{3/2-1/2}=\nu_{3/2-1/2}-\nu_{-3/2-1/2}$, as a function of the direction of $H_0$ rotated in the $a^*b$, $bc$ and $ca^*$ planes. We fitted the results in Fig. 2 using eqs. (2) and (3) in Ref. [13] to determine the EFG tensors $V_{a,b}$($\alpha$, $\beta$ = $a^*$, $b$, $c$) in the $a^*bc$ coordinate system. We obtained the values of the electric quadrupole frequency $\nu_Q$, the asymmetry parameter $\eta=|V_{XX}-V_{YY}|/V_{ZZ}$, where $V_{XX}$, $V_{YY}$ and $V_{ZZ}$ are principal components of the EFG tensor, and directions for the principal axes $X_Q$, $Y_Q$ and $Z_Q$ by diagonalizing the EFG tensors in the $a^*bc$ coordinate system. The obtained values are listed in Table 1. Note that the $Z_Q$ and $X_Q$ axes for S(a) [S'(a)] and S(b) [S'(b)] are tilted to the opposite directions from the $b$ axis but they have almost the same $\nu_Q$ and $\eta$ values. These features show the presence of the zig-zag Li ordering along the $b$ axis as discussed in the $^{23}$Na NMR study on $\beta$-Na$_{0.33}$V$_2$O$_5$ [13].

In addition to the 2$a$ modulation due to the Li ordering, the 2$a$ lattice modulation was observed in the XRD experiment [11] where the Li$_2$ and Li$_3$ sites among the three Li sites, Li$_1$-Li$_3$, are proposed to be located in the same tunnel and to stack along the $b$ axis alternatively, whereas Li$_1$ is located another tunnel. Thus we can reasonably consider that the broad S(a) and S'(b) spectra, which are the blue shaded spectra as shown in Fig.1, come from the Li$_2$ and Li$_3$ sites, while the narrow S(a) and S(b) spectra, the red ones, are originating from the Li$_1$ site.

Next we present the $^{51}$V NMR results in the metallic phase of $\beta$-Li$_0.36$V$_2$O$_5$. We observed five sets of $^{51}$V NMR spectra, one V1, two V2, and two V3 spectra as reported in Ref.[12]. These several V spectra indicate the presence of the CD. Previously, we analyzed the obtained V spectra on the basis of the standard $\beta$-type structure in the A ordered phase with the $a\times2b\times c$ superlattice structure and proposed the model of the CD with the $2b$ $d$ electron density modulation [12]. However, the recent XRD study found the 2$a$ lattice modulation in addition to the 2$b$ one [11]. This fact requires a new model of the CD. In this paper, in order to study the local magnetic properties related to the CD, we made temperature $T$ dependence of the $K$ and $1/T_1$. Figure 3(a) shows the $T$ dependence of the isotropic $^{51}$V Knight shift $K_{iso}$ of the V2 spectra, V2a and V2b, for example, whereas the $T$ dependence of $1/T_1$ with $H_0||Z$ is presented for V2a and V2b in Fig. 3(b). In general, $K$ has the spin part $K_{spin}$ and the $T$-independent orbital one $K_{orb}$. As pointed out in Ref. [8], we can neglect $K_{orb}$ in $\beta$-Li$_0.33$V$_2$O$_5$. Thus the local spin susceptibility is governed by $K_{iso}$. On the other hand, $1/T_1$ is proportional to the imaginary part of the dynamical susceptibility $\chi_{\perp}(q, \omega_n)$ where $q$ is the wave vector and $\omega_n$ is the NMR frequency [14]. As seen in Fig. 3, $K_{iso}$ at each V2 site increase with decreasing $T$ and $K_{iso}$ of V2a is only
Figure 3. Temperature dependence of (a) the $^{51}$V isotropic Knight shift $K_{iso}$ and (b) the $^{51}$V nuclear spin-lattice relaxation rate divided by temperature $1/T_1T$ for the V2 spectra, V2a and V2b, in $\beta$-Li$_{0.33}$V$_2$O$_5$.

a factor of $\sim 1.5$ larger than one of V2b. However, $1/T_1T$ of V2a is enhanced with decreasing $T$, while $1/T_1T$ is almost $T$-independent for V2b. This can be interpreted as the enhancement of the $\mathbf{q} \neq 0$ component of $\chi(\mathbf{q}, \omega_n)$ for V2a. Thus it is concluded that the difference in the local magnetic property at each V2 site is governed by the CD in the metallic state of $\beta$-Li$_{0.33}$V$_2$O$_5$.

4. Conclusion
We have conducted $^7$Li and $^{51}$V measurements to study the local symmetry and the charge disproportionation in the metallic phase of the quasi-one-dimensional conductor $\beta$-Li$_{0.33}$V$_2$O$_5$. The $^7$Li NMR results indicated the presence of the Li zig-zag ordering along the $b$ axis and three Li sites due to the $2a$ lattice modulation observed by the recent X-ray experiment. We also found the site difference in the local spin susceptibility due to the charge disproportionation.

Acknowledgement
This study was supported by Grants-in-Aid (Nos. 18104008 and 19340097) for Scientific Research from the Japan Society for the Promotion of Science (JSPS). One of the authors (I. Y.) also thanks the JSPS for the financial support through the Grant-in-Aid for JSPS Fellows.

References
[1] Imada M, Fujimori A and Tokura Y 1998 Rev. Mod. Phys. 70 1039
[2] Yamada H and Ueda Y 1999 J. Phys. Soc. Jpn. 68 2735
[3] Yamauchi T, Ueda Y and Môri N 2002 Phys. Rev. Lett. 89 057002
[4] Yamauchi T, Isobe M and Ueda Y 2005 Solid State Sciences 7 874
[5] Yamauchi T and Ueda Y 2008 Phys. Rev. B 77 104529
[6] Yamaura J, Isobe M, Yamada H, Yamauchi T and Ueda Y 2002 J. Phys. Chem. Solids 63 957
[7] Nagai S, Nishi M, Kakurai K, Oohara Y, Yoshizawa H, Kimura H, Noda Y, Grenier B, Yamauchi T, Yamaura J, Isobe M, Ueda Y and Hirota K 2005 J. Phys. Soc. Jpn. 74 1297
[8] Suzuki T, Yamauchi I, Itoh M, Yamauchi T and Ueda Y 2006 Phys. Rev. B 73 224421
[9] Yamauchi T, Itoh M, Yamauchi T and Ueda Y 2006 Phys. Rev. B 74 104410
[10] Yamauchi I, Itoh M, Yamauchi T and Ueda Y 2008 J. Phys. Soc. Jpn. 77 104715
[11] Yamaura J, Yamauchi T and Ueda Y, unpublished data
[12] Yamauchi I, Itoh M, Shimizu Y, Yamauchi T, Yamaura J and Ueda Y 2009 J. Phys. : Conference Series 150 042236
[13] Itoh M, Yamauchi I, Kozuka T, Suzuki T, Yamauchi T, Yamaura J and Ueda Y 2006 Phys. Rev. B 74 054434
[14] Moriya T 1963 J. Phys. Soc. Jpn. 18 516