Nuclear Magnetic Relaxation in a Quasi-one-dimensional Conductor $\beta$-Ag$_{0.33}$V$_2$O$_5$

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Abstract. $^{51}$V nuclear-magnetic-resonance (NMR) measurements were performed on $\beta$-Ag$_{0.33}$V$_2$O$_5$, a quasi-one-dimensional conductor with three crystallographically inequivalent V sites (V1, V2, and V3). We observed the site difference between the V1 and V2 sites. The nuclear quadrupole frequency ($\nu_Q$) shows different temperature dependence between the V1 and V2 sites, and the values of the relaxation rate (1/$T_1$) are also different between the two sites in the metallic phase. These facts suggest that a non-uniform metallic state is realized: a 3$d$ electron shared within a V1-V3 or V2-V2 rung in the CO phase could move in the quasi-one-dimensional direction in the metallic phase.

1. Introduction

Since the discovery of superconductivity under high pressure, a quasi-one-dimensional (q1D) conductor $\beta$-Ag$_{0.33}$V$_2$O$_5$ (A=Li, Na, Ag) has attracted much interest in its electric and magnetic properties.[1, 2] This series exhibits various phases, such as a metallic phase, a charge-ordered (CO) insulating phase, and an antiferromagnetic (AF) phase at ambient pressure. Besides the superconductivity, the successive charge and magnetic orderings are also interesting because these phenomena are realized although the electron density is very low: a 3$d$ electron exists among six V sites as formally expressed as $\beta$-Ag$_{0.33}$(V$^{4+}$+5V$^{5+}$)$_{0.33}$O$_5$, V$^{4+}$ being a magnetic ion with spin $S=1/2$ and V$^{5+}$ being a nonmagnetic ion. The fact that the superconducting (SC) phase is adjacent to the CO phase on the pressure-temperature phase diagram suggests that a charge fluctuation is important for the superconductivity.[3] Therefore, further studies of local electric and magnetic properties are highly desired. Nuclear magnetic resonance (NMR) is one of the most powerful techniques because it offers site-selective microscopic information.

The compound consists of three kinds of crystallographically inequivalent Vi (i=1, 2, and 3) sites. Although the structure is complicated, a simple theoretical model has been presented by Doublet and Lepetit based on extended Hückel tight-binding calculations.[4] In their model, the V1O$_5$ and V3O$_5$ pyramids form corner-shared two-leg ladders along the b axis, and the two V2O$_5$ pyramids also form the other ones independently as shown in Fig.1. In the previous study on $\beta$-Ag$_{0.33}$V$_2$O$_5$, we performed $^{51}$V-NMR measurements mainly in the CO phase and zero field resonance (ZFR) measurements in the AF phase, and proposed a simple charge-distribution model:[5] a 3$d$ electron is located on a V1-V3 or V2-V2 rung like a proton molecular orbital in the CO phase.
2. Experimental results

We measured $^{51}$V-NMR spectra at a frequency of 59.00 MHz for the field ($H$) perpendicular to the chain direction as well as the $H$ parallel to the chain direction. Figure 2 shows the NMR spectra for the $H$ parallel to the first principal axis of the electric field gradient (EFG) tensor for the V1 sites. Temperatures of 200, 90, and 27 K correspond to the cation-, charge-, and antiferromagnetic ordering temperatures, respectively. As shown in Fig.2, seven peaks appear owing to EFG at each $^{51}$V (I=7/2) site above 27 K. In this $H$ direction, the separation of seven peaks for the V1 sites becomes the largest. The frequency span between the two first satellite peaks is given as $2\nu_Q$. The direction also corresponds to the second principal axis for the V2 sites.

Figure 3 shows the temperature ($T$) dependence of $\nu_Q$ for the V1, V2, and V3 sites. The dotted lines represent the three transition temperatures mentioned above. The $T$ dependence of $\nu_Q$ for the V1 sites is similar to that for the V3 sites. Both of them show step-like increase at the charge-ordering temperature ($T_{CO}$). On the other hand, $\nu_Q$ for the V2 sites is almost constant throughout whole temperature range, although there appears a slight change in the vicinity of the transition temperatures.

Figure 4(a) shows the $T$ dependence of $1/T_1$ for the V1 and V2 sites measured for $H \parallel b$. $1/T_1$ for both sites obeys $T$-linear dependence in the metallic phase, and no anomaly is observed for the V2 sites at the cation-ordering temperature. This $T$ dependence is different from that for an isostructural compound $\beta$-Na$_{0.33}$V$_2$O$_5$. Figure 4(b) shows the $T$ dependence of $1/T_1 T$. The values of $1/T_1 T$ for the V1 sites are twice as large as those for the V2 sites in the metallic phase.
phase, and they are almost constant. This result is attributable to the Korringa relation. In the vicinity of $T_{CO}$, there appears a hump only for the V2 sites. This may be caused by critical spin fluctuation at the transition temperature. The reason why the hump appears only for the V2 sites is not clear at present.

3. Discussion

The frequency $\nu_Q$ reflects EFG for each Vi site. As far as the $T$ dependence of $\nu_Q$ is concerned, the V1 and V3 sites show similar electric property in both the metallic and CO phases, while the V2 sites are likely to be different from them. The difference between the V1 and V2 sites is also seen in the relaxation rate. $1/T_1 T$ for the V1 and V2 sites is in a ratio of 2:1 in the metallic phase. When the relaxation rate obeys the Korringa relation, $1/T_1 T$ is proportional to square of a hyperfine coupling $A_{hf}$ and the density of state at the Fermi energy $D(E_F)$, $1/T_1 T \sim A_{hf}^2 D(E_F)^2$. Therefore, $A_{hf} D(E_F)$ for the V1 and V2 sites is calculated to be in a ratio of 7:5. The hyperfine coupling $A_{hf}$ is proportional to $K_{spin}/\chi_{spin}$, $K_{spin}$ and $\chi_{spin}$ being the spin parts of the NMR shift and the susceptibility, respectively. $A_{hf}$ for each Vi site ($A_{hf}(Vi)$) is hardly determined from the $K-\chi$ plot because the susceptibility itself is macroscopic quantity. However, for $H \parallel b$, $A_{hf}(V1) \approx A_{hf}(V2)$ is expected from the result that the values of $1/T_1 T$ for the V1 and V2 sites are almost the same in the CO phase where a 3$d$ electron is shared within a rung (see Fig. 4(a)). As a result, $D(E_F)$ for the V1 and V2 sites would be in a ratio of 7:5.
In the previous work, we have proposed a charge model in which a 3d electron is shared within a V1-V3 or V2-V2 rung and explained the similarity between the V1 and V3 sites in both the AF and CO phases.\[5\] If localized electrons in the CO phase start to move in the quasi-one-dimensional direction in the metallic phase, a non-uniform metallic state would be realized and local electric properties may be different between the V1 and V2 sites. Such a peculiarity is expected from the tight-binding model in which the V1 and V3 orbitals are diagonal to the V2 orbitals.\[4\] The microscopic model also explain semiconducting resistivity along the a and c axes in the metallic phase.

4. Summary
We performed $^{51}$V-NMR measurements on $\beta$-Ag$_{0.33}$V$_2$O$_5$, and investigated the $T$ dependence of $\nu_Q$ and $1/T_1$. We found that the $T$ dependence of $\nu_Q$ for the V1 sites is similar to that for the V3 sites, however, that for the V2 sites is almost $T$ independent. Moreover, the values of $1/T_1$ are also different between the V1 and V2 sites in the metallic phase. These facts suggest that a non-uniform metallic state is realized. This peculiar metallic state could be explained based on our previous model: a 3d electron shared within a V1-V3 or V2-V2 rung in the CO phase could move in the quasi-one-dimensional direction in the metallic phase.

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