$^{51}$V-NMR study of low-temperature phase in \(\delta$-Ag$_{2/3}$V$_2$O$_5$

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Abstract. \(^{51}\)V-NMR experiments have been performed to investigate the local magnetic and electronic properties on the phase transition in the mixed-valence oxide \(\delta$-Ag$_{2/3}$V$_2$O$_5\). We have observed the abrupt loss of \(^{51}\)V-NMR signal coming from the non-magnetic V$^{5+}$-like ions above \(T_c = 225\) K. It indicates that the majority of V ions are magnetic above \(T_c\) and that the phase transition is accompanied by the charge separation and charge ordering of 3$d$ electrons on V sites. In the charge ordered state below \(T_c\), the magnetic V$^{4+}$-like ions are located at both V1 and V2 sites with equal distribution.

1. Introduction

A rich variety of exotic phenomena due to spin, charge, lattice and orbital degrees of freedom have attracted much attention in strongly correlated electron systems [1]. Among them, the charge ordering (CO) is one of the most intriguing and extensively studied phenomena because of its strong impact on electron transport properties. In the vanadium bronzes \(A_xV_2O_5\) ($A$: alkali, alkaline-earth or other metals), mixed-valence oxides of V$^{4+}$ (3$d^1$) and V$^{5+}$ (3$d^0$), the CO appears in its stoichiometric composition, where the number of 3$d$ electrons may be controlled as a function of $x$. The first discovery of CO in this system has been made on \(\alpha'$-NaV$_2$O$_5$ [2, 3]. For the last decade, the CO in \(\beta$-A$_{1/3}$V$_2$O$_5\) has been intensively investigated in connection with the superconductivity that appears when the CO is suppressed by applying pressure for \(A = \text{Li, Na and Ag}\) [4, 5]. For example, \(\beta$-Na$_{1/3}$V$_2$O$_5$ shows the successive phase transitions at ambient pressure; the ordering of Na atoms at 242 K, the metal-insulator (MI) transition at 135 K and the antiferromagnetic one at 24 K. Various experiments have clarified that the MI transition is accompanied by the CO or the charge disproportionation. The proposed electronic structure, however, is not a simple Wigner crystal [6, 7, 8, 9].

We focus on \(\delta$-Ag$_{2/3}$V$_2$O$_5$ with the nominal V valence ratio of V$^{4+}$ : V$^{5+} = 1 : 2$. The crystal structure of the \(\delta$-phase compound is expressed as V$_2$O$_5$ double trellis layers and Ag ions located between the double trellis layers (Fig. 1) [10, 11]. There are two V sites denoted as V1 and V2,

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and each V forms a distorted octahedron, V1O6 (mauve octahedra in the figure) and V2O6 (blue ones). The V2O5 double trellis layers are formed by sharing the edges and the corners of V1O6 and V2O6 octahedra. Ag ions (orange balls) occupy one of two nearest-neighboring sites between the double trellis layers.

Onoda and Arai have reported that $\delta$-Ag$_2$/3V$_2$O$_5$ in the range $0.65 \leq x \leq 0.75$ shows the first-order transition accompanied by the jumps in resistivity and magnetic susceptibility $\chi$ around 220 K [11]. The transport properties become more insulating below $T_c$, which may be associated with a CO in the nearly 1/6-filling condition of 3d electrons. For the nominal composition with $x = 0.65$, $\chi$ significantly decreases on cooling below around 100 K, i.e., the spin ground state may be characterized by a spin-singlet one with an energy gap. Quite recently, Baba et al. have revealed that the phase transition in $\delta$-Ag$_{2/3}$V$_2$O$_5$ is a novel CO phenomenon induced by cation order, i.e., the ordering of Ag ions at $T_c$ triggers the transition accompanied by the $V^{4+}/V^{5+}$ CO [12]. It differs from the case in $\beta$-Na$_{1/3}$V$_2$O$_5$ where the CO and the Na ordering take place separately. They have also found that the spin state remains paramagnetic without the spin-gap behavior in $\chi$ at low temperature, when the sample is rapidly cooled down from the high-temperature phase. These results indicate that the magnetic $V^{4+}$ ions have a specific geometrical arrangement required for the spin-gap state and that the geometrical arrangement is closely related to the ordering of Ag ions. In this study, we have performed the $^{51}$V-NMR experiments to investigate the local magnetic and electronic properties of $\delta$-Ag$_{2/3}$V$_2$O$_5$, which may provide information on the geometrical arrangement of $V^{4+}$ ions or the CO structure.

2. Experimental

A powder sample of $\delta$-Ag$_{2/3}$V$_2$O$_5$ was prepared by a solid state reaction method. The detailed preparation method of this material has been reported elsewhere [12]. X-ray diffraction and magnetic susceptibility confirm that the structural and magnetic properties obtained are consistent with the published data [11, 12]. The transition temperature $T_c$ on warming process for our sample is determined to be 225 K from the inflection point on the $^{51}$V-NMR signal intensity vs. temperature curve, where the signal intensity abruptly decreases as mentioned later.

Because the magnetic behavior of this material appears dependently on cooling rate, we cooled the sample down to 5.0 K with sufficiently slow rate of 2 K/min and subsequently measured the $^{51}$V-NMR spectrum at elevated temperature. The spin-echo signal of $^{51}$V nuclei was recorded by using a phase-coherent pulsed NMR spectrometer. To observe the spin-echo signal, we used a silver coil instead of the usual copper coil to avoid the $^{63}$Cu background signal, because the
nuclear gyromagnetic ratio of $^{63}\text{Cu}$ nucleus is very close to that of the $^{51}\text{V}$ nucleus. The $^{51}\text{V}$-NMR spectrum was obtained by tracing the intensity of the spin-echo signal as a function of the external magnetic field at the fixed frequency of 67.1 MHz.

3. Results and discussion
In Fig. 2, we show the field-swept $^{51}\text{V}$-NMR spectrum at 5.0 K in the low-temperature phase. The spectrum consists of two typical powder patterns (S1 and S2) for the nuclear spin of $I = 7/2$ with different NQR frequencies, which are indicated by the blue dotted and the red dashed lines, respectively, in the figure. The NQR frequencies for S1 and S2 are estimated to be $\nu_{Q1} = 0.29$ MHz and $\nu_{Q2} = 0.43$ MHz, respectively, where the respective asymmetric parameter is nearly zero for both. One may consider that S1 and S2 are associated with non-magnetic $\text{V}^{5+}$-like ions located at the V1 and V2 sites ($\text{V}^{5+}_1$ and $\text{V}^{5+}_2$) from the experimental results described next, although it is unclear whether S1 (S2) comes from $\text{V}^{5+}_1$ or $\text{V}^{5+}_2$ at present. A short nuclear spin-spin relaxation time $T_2$ may prevent us from clearly observing the $^{51}\text{V}$-NMR signals of magnetic $\text{V}^{4+}$-like ions.

The non-magnetic nature of V ions associated with S1 and S2 is indicated by the facts: (i) the positions of central peak for S1 and S2 are almost same and the corresponding Knight shifts are nearly zero, (ii) $T_2$’s for S1 and S2 are comparable, which indicates that the V ions associated with S1 and S2 are magnetically similar, (iii) $T_2$’s for S1 and S2 are long and these values are about a few hundreds microsecond, which are comparable to the value of $T_2 \sim 100 \mu$s for the $\text{V}^{5+}$-like site in the CO phase of $\text{Ag}_{2/3}\text{V}_3\text{O}_5$ [13] and (iv) for both S1 and S2, the signal intensity abruptly decreases at $T_c = 225$ K, above which the $\text{V}^{5+}$-like ions are expected to be almost absent due to the collapse of the charge separation and CO.

The relative signal intensities of S1 and S2 are almost comparable, which indicates that the non-magnetic $\text{V}^{5+}$-like ions are located at both V1 and V2 sites with equal distribution. It means that the magnetic $\text{V}^{4+}$-like ions occupy both V1 and V2 sites with equal distribution, because the multiplicities of V1 and V2 sites are the same. Considering that the ground state is the spin-singlet one with the energy gap, the spin singlet is formed on the $\text{V}^{4+}$-$\text{V}^{4+}$ pair at low
temperature. To discuss a model of the CO structure from the NMR results, further experiments on a single crystal may be required. However, we notice that the present result is consistent with the CO structure containing the “cluster” with four $3d$-electrons, proposed on the basis of the Ag ion ordering pattern [12], in which the V1 and V2 sites have the same number of V$^{4+}$ ions.

Next, we show the $^{51}$V-NMR spectra at elevated temperatures including the data above $T_c = 225$ K in Fig. 3. The arrows for the data at 150 K indicate the positions of the central, the 1st, the 2nd, the 3rd satellite peaks for S1 and S2. In Fig. 4, we show the temperature dependencies of the Knight shifts, $K_1$ and $K_2$, (a) and the NQR frequencies, $\nu_{Q1}$ and $\nu_{Q2}$, (b) for S1 and S2, respectively, which are estimated from the peak positions. Here, $K_1$ and $\nu_{Q1}$ are plotted by blue open circles, while $K_2$ and $\nu_{Q2}$ are plotted by red filled circles in the figure. Above $T_c$, it was unable to estimate the Knight shifts and the NQR frequencies for two V sites, because the $^{51}$V-NMR signal is drastically reduced.

At 5.0 K, $K_1$ is almost same as $K_2$, yielding the very sharp peak at the center of the measured spectrum. Nearly zero values of $K_1$ and $K_2$ indicate that both NMR signals come from the non-magnetic V$^{5+}$-like ions. With increasing temperature, $K_1$ is almost independent of temperature, while $K_2$ becomes larger very slightly up to 100 K. As a result, the very sharp peak at the center splits into two and the measured spectral shape largely changes at higher temperature. The very slight increase in $K_2$ up to 100 K may be related to the significant change in $\chi$ due to the formation of spin singlet on the magnetic V$^{4+}$-like sites, because $K_2$ is proportional to $\chi$ with a positive hyperfine coupling constant. Here, one may exclude a possibility that some $3d$ electrons remain on the V$^{5+}$-like site above 100 K and move to the other sites at lower temperature. It is because the on-site hyperfine coupling constant of the V site is generally negative, about $-100$ kOe/$\mu_B$ for a VO$_2$ system [14, 15], which is inconsistent with the present case. Regarding the NQR frequency, $\nu_{Q1}$ and $\nu_{Q2}$ are almost independent of temperature from $T_c$ to 100 K, but both frequencies become larger at low temperature, as shown in Fig. 4(b). Because both S1 and S2
come from the non-magnetic V$^{3+}$-like ions, the changes in $\nu_{Q1}$ and $\nu_{Q2}$ may be ascribed not to the on-site 3$d$ electrons but to the anions surrounding V$^{5+}$-like ions. The present result may, therefore, indicate that the V1O$_6$ and the V2O$_6$ octahedra become more distorted below 100 K, which is possibly related to the formation of spin singlet in the same temperature range.

In Fig. 5, we show the temperature dependence of $IT$, the sum of signal intensities $I$ for S1 and S2 multiplied by temperature $T$. Here, the measurement of $IT$ was made on the warming process and the effect of the temperature variation in $T_2$ on the signal intensity is compensated. With increasing temperature, $IT$ is gradually reduced and drastically decreases above $T_c = 225$ K. This result indicates that the non-magnetic V$^{5+}$ ions almost disappear and that the majority of V ions are magnetic above $T_c$, most probably, due to the collapse of the charge separation and CO. It is, therefore, considered that the phase transition at $T_c$ is associated with the charge separation and CO of 3$d$ electrons on the V1 and V2 sites. It should be mentioned that we observe the signal even above $T_c$, which is about 5% of that at 100 K, and that $T_2$ for the observed signal is as long as that below $T_c$. This fact may imply that there remain the non-magnetic V$^{5+}$-like ions and the charge separation partly occurs above $T_c$.

4. Conclusion
We have made $^{51}$V-NMR measurements to investigate the local magnetic and electronic properties of the mixed-valence oxide $\delta$-Ag$_{2/3}$V$_2$O$_5$ with the nominal V valence ratio of V$^{4+}$ : V$^{5+}$ = 1 : 2. It has been microscopically confirmed that the phase transition is accompanied by the charge separation and most probably charge ordering at $T_c = 225$ K, above which the $^{51}$V-NMR signal coming from the non-magnetic V$^{5+}$-like ions is significantly reduced. In the charge ordered state below $T_c$, the non-magnetic V$^{5+}$-like ions are located at both V1 and V2
sites with equal distribution, which is consistent with the CO structure proposed on the basis of the Ag ion ordering manner [12].

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