# NMR Study of Charge Ordering and Magnetic Correlation in Vanadium Oxide Bronzes

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We have made <sup>51</sup>V NMR experiments to study the charge ordering and the magnetic correlation in vanadium oxide bronzes  $\beta$ -AV<sub>6</sub>O<sub>15</sub> (A = Na, Ag and Ca). We observed a drastic change in the <sup>51</sup>V NMR spectrum accompanied by the charge ordering. Thus we can confirm from the microscopic point of view that the charge ordering commonly takes place in  $\beta$ -AV<sub>6</sub>O<sub>15</sub> (A = Na, Ag and Ca). A charge ordering structure is also discussed with a magnetic structure.

KEYWORDS: charge ordering, NMR, one-dimensional metal, NaV<sub>6</sub>O<sub>15</sub>, AgV<sub>6</sub>O<sub>15</sub>, CaV<sub>6</sub>O<sub>15</sub>

### §1. Introduction

Recently combined phenomena due to charge, spin and orbital degrees of freedom have attracted much attention in various 3d transition metal oxides from both experimental and theoretical aspects. One of the most characteristic phenomena due to the charge degree of freedom is a charge ordering observed in manganese oxides, nickel oxides and so on. The sodium vanadium oxide  $\alpha'$ - $NaV_2O_5$ , a mixed valence oxide of  $V^{4+}$  (3d<sup>1</sup>) and  $V^{5+}$  $(3d^0)$ , was recently discovered as the second example of an inorganic spin-Peierls (SP) compound.<sup>1)</sup> Several experimental studies, however, reveled that the transition at 35 K is not the SP transition but a charge ordering transition.<sup>2-4</sup>) This oxide, which has the crystal structure consisting of ladders along the b-axis on the twodimensional ab-plane, is considered to be a quarter-filled spin-ladder system. Several theoretical studies were performed to understand the charge ordering in  $NaV_2O_5$ . A zigzag type structure was proposed on the basis of the Hartree approximation in an extended Hubbard model.<sup>5)</sup> Also it was pointed out that the intersite Coulomb repulsion plays an important role in formation of the charge ordering. The same charge ordering structure was proposed from the exact diagonalization method for a finitesize cluster based on the trellis-lattice t-J ladder at quarter filling.<sup>6)</sup>

This finding of the charge ordering in NaV<sub>2</sub>O<sub>5</sub> has led to intensive studies of the charge ordering in mixedvalence vanadium oxides. To study the charge ordering mechanism in low-dimensional quantum spin systems with a characteristic structure we searched various vanadium oxides. Although vanadium bronzes  $A_x V_2 O_5$  (A = alkali, alkaline earth and metals), mixed valence oxides of V<sup>4+</sup> and V<sup>5+</sup>, are known to have various structural, magnetic and electric properties dependent on the concentration and the kind of the A cation,<sup>7-10)</sup> the physical properties have not been clearly understood. The oxide NaV<sub>2</sub>O<sub>5</sub> in the  $\alpha$ ' phase is an end compound of the sodium vanadium bronzes Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub> ( $0 \le x \le 1$ ). There is the  $\beta$  phase around x=1/3, the stoichiomeric concentration, in A<sub>x</sub>V<sub>2</sub>O<sub>5</sub>. In this paper we will concentrate our attention on the stoichiometric compounds  $\beta$ -A<sub>1/3</sub>V<sub>2</sub>O<sub>5</sub> ( $\beta$ -AV<sub>6</sub>O<sub>15</sub>).



Fig. 1. Crystal structure of  $\beta$ -AV<sub>6</sub>O<sub>15</sub> ( $\beta$ -A<sub>1/3</sub>V<sub>2</sub>O<sub>5</sub>).

The crystal structure<sup>11, 12)</sup> of  $\beta$ -AV<sub>6</sub>O<sub>15</sub> is presented in Fig. 1. There are three kinds of vanadium sites, V1, V2

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and V3. The V1O<sub>6</sub> octahedra and the V3O<sub>5</sub> pyramids form zigzag chains along the *b*-axis, whereas the V2O<sub>6</sub> octahedra form ladders along the *b*-axis. The A cation occupies half of the A1 site in AV<sub>6</sub>O<sub>15</sub>. In particular the Na<sup>+</sup> ion was reported to order at 230 K in NaV<sub>6</sub>O<sub>15</sub>.<sup>13)</sup>

Magnetic and electric properties of  $\beta$ -A<sub>x</sub>V<sub>2</sub>O<sub>5</sub> were previously discussed on the basis of the bipolaron model.<sup>7-10</sup> However, recent studies revealed that the bipolaron model may be not applicable to understand magnetic and electric properties of NaV<sub>6</sub>O<sub>15</sub>.<sup>13)</sup> We recently found phenomena which seem to come form the charge ordering in  $AV_6O_{15}$  (A = Na, Ag and Ca).<sup>13,14</sup>) Figure 2 shows the temperature dependence of the magnetic susceptibility  $\chi$  of AV<sub>6</sub>O<sub>15</sub> (A= Na, Ag and Ca).<sup>13,14)</sup> As is seen in Fig. 2, there is at  $T_{co}$  an anomaly which seems to come from the charge ordering in the magnetic susceptibility of all samples. In  $NaV_6O_{15}$  and  $AgV_6O_{15}$  there is another anomaly due to an antiferromagnetic order at  $T_N$ . On the other hand,  $\chi$  of CaV<sub>6</sub>O<sub>15</sub> is different from the others. That is,  $\chi$  has a maximum around 50 K and reduces with decreasing temperature below  $\sim 50$  K. This difference between the two kinds of  $\chi$  in AV<sub>6</sub>O<sub>15</sub> (A= Na, Ag and Ca) is closely related to the  $V^{4+}$  filling. It should be noted that the  $V^{4+}$  filling is dependent on the valence of the A ion. In compounds with  $A^+$  (A = Na and Ag) the formal ratio of  $V^{4+}$  to  $V^{5+}$ is 1:5, whereas the ratio is 2:4 in compounds with  $A^{2+}$ (A = Ca and Sr). Thus we can systematically study the filling dependence of the charge ordering in  $\beta$ -AV<sub>6</sub>O<sub>15</sub>.

#### $T_N$ $T_CO$ $T_CO$

Fig. 2. Temperature dependence of the magnetic susceptibility of  $AV_6O_{15}$  (A= Na, Ag and Ca) [Refs. 13 and 14].

In this paper we have made <sup>51</sup>V NMR measurements to study local magnetic and electric properties related to the charge ordering in  $AV_6O_{15}$  (A= Na, Ag and Ca).

### §2. Experimental Procedure

Powder samples of  $AV_6O_{15}$  (A= Na, Ag and Ca) were prepared by a solid-state reaction method. On the other hand, single crystals of  $NaV_6O_{15}$  were grown by a self flux method as was described in Ref. 13. Many single crystals stacked parallel to the *b*-axis were mainly used in the NMR measurements for  $NaV_6O_{15}$ , whereas the powder samples were used for  $AgV_6O_{15}$  and  $CaV_6O_{15}$ .

Field-swept NMR spectra were taken by using a coherent pulsed spectrometer and a superconducting magnet, whereas frequency-swept NMR spectra were taken point by point of frequency by using a super-heterodyne coherent pulsed spectrometer in zero external field.

#### §3. Experimental Results and Discussion

#### 3.1 Na V<sub>6</sub> O<sub>15</sub>

As is seen in Fig. 2,  $\chi$  of NaV<sub>6</sub>O<sub>15</sub> shows anomalies at  $T_{\rm co} = 130$  K and  $T_{\rm N} = 24$  K. The increase of  $\chi$  below  $T_{\rm N}$  is ascribed to the weak ferromagnetism due to a canting of antiferromagnetic moments.<sup>13</sup> Recently it was reported from electric resistivity measurements on a single crystal that the *b*-axis resistivity has a metallic behavior above 130 K, whereas  $a^*$ - and *c*-axis resistivities are semiconducting.<sup>13</sup> Thus the transition at  $T_{\rm co}$  is accompanied by the metal-insulator transition in NaV<sub>6</sub>O<sub>15</sub>.



Fig. 3. NMR spectra taken at 40, 80 and 160 K with H parallel to the *b*-axis in NaV<sub>6</sub>O<sub>15</sub>. The arrows in each <sup>51</sup>V NMR spectrum (S1, S2, S1', S2<sub>a</sub>', S2<sub>b</sub>' and S3') represent central and/or satellite transitions due to the electric quadrupole interaction.

As is well known, NMR is a very powerful technique to study local magnetic and electric properties of a substance where there are several magnetic sites. Figure 3 shows the NMR spectra taken at 40, 80 and 160 K with an external field H parallel to the *b*-axis. Above 130 K there are two sets of NMR spectrum denoted by S1 and S2. Each spectrum is well explained by an electric quadruple effect. Below 130 K, however, the S2 spectrum is split into two NMR spectra denoted by S2<sub>a</sub>' and S2<sub>b</sub>'. There is an additional spectrum with a short nuclear spin-spin relaxation time  $T_2$  as is denoted by S3' in the 40 K spectrum. This means that the S3' spectrum comes from a magnetic V site. Satellite spectra were not clearly observed in the S3' spectrum.



Fig. 4. Temperature dependence of  $\omega/\gamma$ -H<sub>n</sub> taken at 65 MHz with H parallel to the *b*-axis in NaV<sub>6</sub>O<sub>15</sub>. H<sub>n</sub> is a field where the NMR spectrum has a peak.

Figure 4 shows the temperature dependence of  $\omega/\gamma$ - $H_{\rm n}$  taken at  $\omega/2\pi$  (= 65 MHz) with H parallel to the b-axis in NaV<sub>6</sub>O<sub>15</sub>. Here  $\gamma$  (=2 $\pi$ ×1.119×10<sup>3</sup> Hz/Oe) is the <sup>51</sup>V nuclear gyromagnetic ratio and  $H_n$  is a field where the NMR spectrum has a peak. Above 130 K there are two sets of resonance denoted by S1 and S2. On the other hand, below 130 K, there are four sets of resonance S1', S2a', S2b' and S3', although the S3' spectrum was not observed behind the S2a' and S2b' spectra above  $\sim 50$  K. To obtain Knight shift components, we have to know principal axes of the electric field gradient (EFG). We could confirm from the measurement of the angular dependence of  $H_n$  for the S1' spectrum at 77 K that the  $a^*$ -, b- and c-axes are principal axes of the EFG in this spectrum. This finding and the crystallographic consideration lead to a conclusion that the S1' spectrum comes from the V3 site. Thus we can obtain parameters of the Knight shift and the electric quadrupole interaction from the analysis of these data. The temperature dependence of the Knight shift parallel to the *b*-axis,  $K_b$ ,

is presented in Fig.5. We note that shifts of the S1',  $S2_a$ ' and  $S2_b$ ' spectra gradually increase with decreasing temperature below 130 K. This means that spin susceptibilities of S1',  $S2_a$ ' and  $S2_b$ ' decrease with decreasing temperature. On the other hand, the S3' shift decreases with decreasing temperature. Namely the spin susceptibility increases with decreasing temperature. Namely the spin susceptibility increases with decreasing temperature and obeys the magnetic susceptibility. The gradual temperature variation of the shift of S1',  $S2_a$ ' and  $S2_b$ ' may come from a gradual redistribution of the charge in the charge ordering state. Such a gradual temperature variation was also observed in the nuclear quadrupole frequency as is seen in Fig. 6. This figure shows the temperature dependence of the nuclear quadrupole frequency of the S1',  $S2_a$ ' and  $S2_b$ ' spectra parallel to the *b*-axis,  $\nu_D^b$ .



Fig. 5. Temperature dependence of the  ${}^{51}$ V Knight shift parallel to the *b*-axis in NaV<sub>6</sub>O<sub>15</sub>.

In a magnetically ordered state all the V nuclei associated with inequivalent sites are subjected by the hyperfine field from the ordered spin moments. Therefore NMR spectra can be in principle observed in zero external field. At 1.5 K we observed five NMR spectra located at 0.1, 3.7, 17.9, 30.3 and 81.0 MHz as is presented in Fig. 7. The spectra below  $\sim 10$  MHz is plotted by converting a field-swept powder spectrum at 13.5 MHz into the frequency-swept spectrum. The spectrum at 3.7 MHz is concluded from a comparison between the NMR spectra in  $NaV_6O_{15}$  and  $AgV_6O_{15}$  to be a <sup>23</sup>Na NMR spectrum. The four  ${}^{51}$ V spectra observed in the antiferromagnetic state correspond to the four paramagnetic spectra in the following. The <sup>51</sup>V NMR spectra at 0.1 and 81.0 MHz are concluded to come from the nonmagnetic  $V^{5+}$  (S1') and the magnetic  $V^{4+}$  (S3') sites, respectively. On the



Fig. 6. Temperature dependence of the  ${}^{51}$ V nuclear quadrupole frequency parallel to the *b*-axis,  $\nu_{\Omega}^{b}$ , in NaV<sub>6</sub>O<sub>15</sub>.



Fig. 7. Frequency-swept NMR spectrum at 1.5 K under zero external field in  $\rm NaV_6O_{15}.$ 

other hand, the spectra at 17.9 and 30.3 MHz are considered to be due to the V<sup>5+</sup> sites (S2<sub>a</sub>' and S2<sub>b</sub>') with a transferred hyperfine field from the V<sup>4+</sup> site.

Thus we can confirm from the microscopic level that the charge ordering takes place at  $T_{\rm co} = 130$  K. Based on the present NMR results mentioned above, we will discuss the charge ordering in this oxide. Above  $T_{\rm co}$  we observed only two V NMR spectra. The V1 and V2 sites seem to have a mixed valence state, leading to metallic conductivity, whereas the V3 site has an electronic state different from that of the V1 and V2 sites. Below  $T_{\rm co}$  the four V NMR spectra were observed. The V3 site is occupied by the nonmagnetic V<sup>5+</sup> ion. Therefore the magnetic V<sup>4+</sup> ion should occupy half of the V1 or V2 site. One possible model is a zigzag or single-chain structure of V<sup>4+</sup> located at the V2 site. Another is a single-chain structure located at the V1 chain site. In these structures the V<sup>4+</sup> site has two types of neighboring V site which provide the two NMR spectra with the transferred hyperfine field.

Magnetic and electric properties of  $NaV_6O_{15}$  were previously discussed on the basis of the bipolaron model where a  $V^{4+}-V^{4+}$  pairing is formed by a strong electronphonon interaction.<sup>7-10</sup> Main experimental evidences which were considered to support the bipolaron model were the singlet ground state and the lattice distortion due to the  $V^{4+}-V^{4+}$  paring. However the present NMR studies clearly show that the ground state of the  $V^{4+}$ site is not the spin singlet but the antiferromagetic order. The recent X-ray study showed that the  $1\times 2\times 1$  superstructure observed below 230 K is not due to a  $V^{4+}-V^{4+}$ paring but due to an order of  $Na^+$ .<sup>13</sup> Thus there are no experimental results to support the bipolaron model.

A characteristic point of the charge ordering in  $NaV_6O_{15}$  is that it is accompanied by the metal-insulator (MI) transition. This is much different from the charge ordering in  $NaV_2O_5$  without the MI transition. A onedimensional metallic character in NaV<sub>6</sub>O<sub>15</sub> may be important to understand the mechanism of the MI and the charge order transitions. It is well known that onedimensional metal has the Peierls instability which leads to the MI transition and a charge density wave. Band calculations are highly desired to understand electronic properties of NaV<sub>6</sub>O<sub>15</sub> from this aspect. The charge ordering in  $NaV_6O_{15}$  is similar to that in vanadium oxides such as  $V_6O_{13}$ , a mixed valence oxide of  $V^{4+}$  and  $V^{5+}$ . In  $V_6O_{13}$  the charge ordering and the MI transitions take place at 150 K. Above 150 K two sets of V signal coming from the  $V^{4+}$ - and  $V^{5+}$ -like sites were observed.<sup>15)</sup> In the antiferromagnetic state below 50 K, six NMR spectra with internal fields coming from  $V^{4+}$ , singlet spin-paired  $V^{4+}$  and  $V^{5+}$  site were observed. Therefore the charge ordering in  $NaV_6O_{15}$  may be understood in the similar framework to that in the vanadium oxides. The mechanism of the charge-ordering and MI transitions in  $NaV_6O_{15}$  is an interesting problem which should be further investigated.

# 3.2 AgV6 O15

The magnetic susceptibility of AgV<sub>6</sub>O<sub>15</sub> shows a behavior similar to  $\chi$  of NaV<sub>6</sub>O<sub>15</sub>. The  $\chi$  of AgV<sub>6</sub>O<sub>15</sub> shows an anomaly at  $T_{\rm co} = 90$  K and another anomaly at  $T_{\rm N} = 27$  K due to the antiferromagnetic order as is seen in Fig. 2.

Figure 8 shows powder  ${}^{51}$ V NMR spectra taken at 28 MHz and several temperatures. The powder sample prevented us from obtaining detailed information of each V site. The  ${}^{51}$ V Knight shift was determined from the field



Fig. 8.  $^{51}\mathrm{V}$  NMR power spectra taken at 28 MHz and several temperatures in  $\mathrm{AgV}_6\mathrm{O}_{15}.$ 

where the spectrum has a maximum. Figure 9 shows the temperature dependence of the <sup>51</sup>V Knight shift K taken at 28 MHz. A small jump of K is seen at 90 K. The shift moves towards zero with decreasing temperature below 90 K. Thus the V site we could observe above  $T_{\rm N}$  is only the nonmagnetic V<sup>5+</sup> site.

In the antiferromagnetic state below 27 K, we observed four <sup>51</sup>V NMR spectra with an internal field. The NMR spectra at 1.5 K in zero external field were found to be located at 0.03, 8, 21.5 and 72.0 MHz. The NMR spectra at 0.03 and 72.0 MHz are considered to come from the nonmagnetic V<sup>5+</sup> and the magnetic V<sup>4+</sup> sites, respectively, whereas the spectra at 8 and 21.5 MHz are due to the V<sup>5+</sup> sites with a transferred hyperfine field from the V<sup>4+</sup> site. Thus  $AgV_6O_{15}$  is concluded to have the same type of magnetic and charge-ordering structures as that in NaV<sub>6</sub>O<sub>15</sub>.

# 3.3 CaV6 O15

As is seen in Fig. 2,  $\chi$  of CaV<sub>6</sub>O<sub>15</sub> has a small jump at  $T_{\rm co}=149$  K and a maximum around 50 K, and decreases with further decreasing temperature below ~50 K. This behavior of  $\chi$  is different from the others.

Figure 10 shows powder <sup>51</sup>V NMR spectra taken at 10, 20, 80 and 170 K. Above  $T_{\rm co} = 149$  K the symmetric NMR spectrum coming from one V site was observed as is seen in Fig. 10. On the other hand, below 149 K, the spectrum is asymmetric due to the presence of two spectra. This is clearly seen in Fig. 11 which shows powder NMR spectra at 80 K taken for various values of the time interval between exciting and focusing rf pulses,  $\tau$ . The spectrum becomes symmetric with increasing  $\tau$ , because a spectrum with a short  $T_2$  which is located at the high field side vanishes in the spectrum taken at a long  $\tau$ . This means that the spectrum below 149 K consists of nonmagnetic and magnetic spectra. At low temperatures the spectrum at the high field side moves towards a low field as is seen in Fig. 10.



Fig. 9. Temperature dependence of the  $^{51}V$  Knight shift taken at 28 MHz in AgV6O15.



Fig. 10.  $^{51}\rm V$  NMR powder spectra taken at 28 MHz and several temperatures in  $\rm CaV_6O_{15}.$ 

The temperature dependence of the <sup>51</sup>V Knight shift is presented in Fig. 12. Above  $T_{\rm co} = 149$  K the sift (~ -0.21

%) is almost temperature-independent. Below 149 K the shift of one vanadium site moves to zero with decreasing temperature below ~50 K. This means that this V site is the V<sup>5+</sup> site. On the other hand, the shift of another site has a minimum around 50 K and moves to zero with decreasing temperature. This temperature dependence of the shift approximately obeys the magnetic susceptibility, indicating that this comes from the V<sup>4+</sup> site with a nonmagnetic ground state. Thus we can conclude that the charge ordering from a mixed-valence state to a order state of V<sup>4+</sup> and V<sup>5+</sup> takes place at 149 K.



Fig. 11.  ${}^{51}$ V NMR powder spectra taken at 80 K and 28 MHz for  $\tau = 16, 40$  and 100  $\mu$ sec in CaV<sub>6</sub>O<sub>15</sub>.

We propose a model of the charge ordering in  $CaV_6O_{15}$ . In the case of  $A^{2+}$  there are  $V^{4+}$  sites which can occupy perfectly one V site. We should note that the ground state of the magnetic  $V^{4+}$  is nonmagnetic. One possible structure is that the V2 ladder is perfectly occupied by  $V^{4+}$ , because the half-filling two-leg ladder has a nonmagnetic ground state.<sup>16)</sup> Otherwise the V1 zigzag chains should be perfectly occupied, if there is an antiferromagnetic exchange constant between the second nearest neighbors larger than ~0.24J where J is the nearest neighbor exchange constant.<sup>17)</sup>

#### §4. Summary

We have made <sup>51</sup>V NMR measurements to study local magnetic and electric properties related to the charge ordering in vanadium bronzes  $\beta$ -AV<sub>6</sub>O<sub>15</sub> (A= Na, Ag and Ca). We observed a clear change of the NMR spectra due to the charge ordering in all the samples. Thus we could confirm from the microscopic level that the charge ordering is a phase transition which commonly takes place in  $\beta$ -AV<sub>6</sub>O<sub>15</sub> (A= Na, Ag and Ca). Also charge ordering



Fig. 12. Temperature dependence of the  $^{51}$ V Knight shift taken at 28 MHz in CaV<sub>6</sub>O<sub>15</sub>.

structures dependent on the  $V^{4+}$  filling were proposed from the NMR experiments.

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