# Low-Temperature *Zigzag* Charge Ordering Structure of $\alpha'$-$NaV_2O_5$

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**Abstract**

The low-temperature (LT) superstructure of $NaV_2O_5$ was determined by synchrotron radiation X-ray diffraction. Below the phase transition temperature at 34 K, the LT structure is monoclinic. It was determined that the LT structure is $(a-b)\times 2b\times 4c$ with the space group $A112$, where $a$, $b$ and $c$ represent the high-temperature orthorhombic unit cell. The valence estimation of V ions shows that the V sites are clearly separated into two groups of $V^{4+}$ and $V^{5+}$ with a zigzag charge-ordering pattern.

*Key words:* $NaV_2O_5$; spin-singlet state; charge order transition; low-temperature structure

## 1. Introduction

Physical properties are subject to four degrees of freedom of charge, spin, orbital, and lattice. In the case of a correlation among these properties, it is not easy to determine what the dominant parameter is with regard to the physical properties.

$\alpha$'-$NaV_2O_5$ has a quarter-filled two-leg ladder structure at room temperature. This system has a novel transition in which the charge-ordering, spin singlet, and lattice-distortion occur simultaneously at $T_C \sim 35$K[1–3]. The crystal structure in the high-temperature phase is described by space group P$mmn$ ($a_p$, $b_p$, $c_p$), and the direction of the ladders is given by the crystallographic $b_p$ axis[4]. The $^{51}$V NMR measurement indicates that the single V site above the $T_C$ split into two groups of $V^{4+}$ and $V^{5+}$ states[3]. Recently, several X-ray diffraction studies of the low-temperature (LT) structure have been reported[5,6]. The results of these studies have given qualitatively the same structure with space group F$mm2$, including three different electronic states of the V sites, $V^{4+}$, $V^{5+}$ and $V^{4.5+}$. This charge distribution is incompatible with $^{51}$V NMR results. In the present study, we have determined by the synchrotron radiation that the real LT structure as a monoclinic with space group A2. The charge ordering pattern in the $ab$ plane consists of only $V^{4+}$ and $V^{5+}$ sites forming a zigzag pattern intra-ladder.[7]

## 2. Experiments

$NaV_2O_5$ single crystals were grown by the flux method. Small high-quality single crystals were used for the X-ray diffraction experiments. All experiments were carried out at the photon factory of KEK. In order to determine the lattice system below $T_C$, high-resolution scattering measurements were performed at

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BL-4C used HUBER four-circle diffractometer with a closed-cycle helium refrigerator. For the crystal structure analysis, the reflection data set was measured by MPD system with a two-dimensional (2D) cylindrical imaging-plate detector on BL-1B.

## 3. Results and Discussions

From the BL-4C experiments, a peak splitting was observed below $T_C$ with (0 2 0) reflection, and this splitting disappeared above $T_C$. The splitting width increases with decreasing temperature, and saturated to $\Delta\omega = 0.07$ degrees at the lowest temperature. The splittings of (h00) and (00l) reflections were not observed. Consequently, the symmetry of the LT structure must be the lower than orthorhombic. We determined the symmetry in the LT phase is A112 monoclinic, with the unit cell being revised as $(a_m, b_m, c_m) = (a_p - b_p, 2b_p, 4c_p)$.

Because of the observation of the peak-splitting on BL-4C, leading us to assume that the crystal would be a twin structure that includes the domain as $(-a_m, b_m, c_m) = (b_p - a_p, 2b_p, 4c_p)$. The resulting structure refined with A112 including domain ratio is different from the previously reported LT structure. This LT structure consists of eight inequivalent V sites constructed by a similar pyramid structure. The valence of each V site is calculated by the bond-valence sum method[8]. These sites are clearly separated into two groups, and the between the number of the sites of each region is 4:4. We conclude that these are estimated as $V^{4+}$ and $V^{5+}$ sites. This result that shows the two separated V sites is in good agreement with the V NMR result.

Figure 1 shows the crystal structure in the LT charge-ordered phase. One ladder consists of the zigzag pattern by $V^{4+}$ and $V^{5+}$ in the sequence along the $b$ axis alternately as 4+ 5+ 4+ 5+, with the pattern being out of phase between the two legs. This intra-ladder pattern is good agreement with the results of the theoretical calculations, including the long-range Coulomb repulsion[9].

The next important problem to be solved is the spin singlet state in the LT phase. The *ab* plane has a simple structure, and the crystal structure essentially consists of one kind of ladder. In the feature, it is important to consider two situations in which the nearest neighbor is the $V^{4+}$ dimmer inter-ladder or the electronic state intra-ladder. In the LT phase, the nearest neighbor $V^{4+}$ atoms keep away from each other and the change in the distance between V-V is small compared with in the HT phase. However, in the two-leg ladder system of $V^{4.5+}$ in the HT phase where the transition temperature is lowered by the charge frustration, the singlet

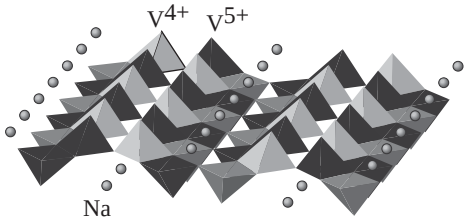


Fig. 1. The low-temperature structure in ab plane (only $z \sim 0$). Each ladder consists of a zigzag pattern of $V^{4+}$ and $V^{5+}$ ordering alternately along the b axis as 4+ 5+ 4+ 5+. Dark and light pyramids indicate $V^{4+}O_5$ and $V^{5+}O_5$, respectively.

state occurs simultaneously with the charge-ordering transition and the spin gap appears to be caused by the formation of an isolated dimmer structure. In contrast, with the inter-ladder situation the $V^{4+}$ array is not uniform along the $b$ axis. This alternation array suggests the appearance of a spin gap. In either case, we would be able to obtain information about the spin-singlet state by the band calculation in the LT phase.

In conclusion, the charge-ordering of $NaV_2O_5$ in the LT phase realized by a *zigzag*-pattern intra-ladder appears to be caused by a long-range Coulomb interaction. The crystal structure consists of only two types of $VO_5$ pyramids, as $(V^{4+})O_5$ and $(V^{5+})O_5$.

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