Zigzag Charge Ordering in $\alpha'$-NaV$_2$O$_5$

Tetsuo OHAMA$^{1,*}$, Atsushi GOTO$^2$, Tadashi SHIMIZU$^2$, Emi NINOMIYA$^3$, Hiroshi SAWA$^3$, Masahiko ISobe$^4$ and Yutaka UEDA$^4$

$^1$Department of Physics, Faculty of Science, Chiba University, Chiba 263-8522
$^2$National Research Institute for Metals, Tsukuba 305-0003
$^3$Graduate School of Science and Technology, Chiba University, Chiba 263-8522
$^4$Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8566

(Received )

$^{23}$Na NMR spectrum measurements in $\alpha'$-NaV$_2$O$_5$ with a single-crystalline sample are reported. In the charge-ordered phase, the number of inequivalent Na sites observed is more than that expected from the low-temperature structures of space group $Fmm\bar{2}$ reported so far. This disagreement indicates that the real structure including both atomic displacement and charge disproportionation is of lower symmetry. It is suggested that zigzag ordering is the most probable. The temperature variation of the NMR spectra near the transition temperature is incompatible with that of second-order transitions. It is thus concluded that the charge ordering transition is first-order.

KEYWORDS: $\alpha'$-NaV$_2$O$_5$, NMR, charge ordering, crystal structure, spin-ladder, trellis lattice

Since the phase transition into a spin-gapped phase in $\alpha'$-NaV$_2$O$_5$ was reported,¹ a lot of experimental efforts have been devoted to understand the nature of this transition. Although it was initially identified as a spin-Peierls transition, a recent room-temperature structural study² questioned this interpretation: it concluded that the real structure including both atomic displacement and charge disproportionation is of lower symmetry. It is suggested that zigzag ordering is the most probable. The temperature variation of the NMR spectra near the transition temperature is incompatible with that of second-order transitions. It is thus concluded that the charge ordering transition is first-order.

$^{23}$Na NMR spectrum measurements in $\alpha'$-NaV$_2$O$_5$ with a single-crystalline sample are reported. The number of Na sites observed is more than that expected from the low-temperature structures of space group $Fmm\bar{2}$ reported so far. This disagreement indicates that the real structure including both atomic displacement and charge disproportionation is of lower symmetry. It is suggested that zigzag ordering is the most probable. The temperature variation of the NMR spectra near the transition temperature is incompatible with that of second-order transitions. It is thus concluded that the charge ordering transition is first-order.

In this letter, we report $^{23}$Na NMR spectrum measurements with a single-crystalline sample. The obtained NMR spectra in the charge-ordered phase disagree with the space group $Fmm\bar{2}$, indicating lower symmetry. We will discuss possible low-temperature structures and charge ordering patterns, and will show that zigzag patterns are the most probable. The temperature variation of the NMR spectra near $T_C$ is incompatible with that of second-order transitions, suggesting that the charge ordering is first-order.

The single-crystalline sample preparation was described in ref. 15. The NMR measurements were done using a high-resolution NMR spectrometer with a magnetic field $H \sim 63.382$ kOe. The $^{23}$Na NMR spectra were obtained as power spectra by Fourier-transforming FID signals with the Gaussian multiplication for resolution enhancement and apodization.¹⁶ Line width and intensity in the obtained spectra are thus inaccurate.

NMR spectrum in a crystal is generally determined by the number of crystallographically inequivalent nuclear sites, and electrical field gradient and NMR shift tensors at each site. These are closely related to the crystal structure and the site symmetry. The room-temperature structure of $\alpha'$-NaV$_2$O$_5$ belongs to space group $Pnnm$,³⁻⁴ in which structure Na ions occupy a unique atomic position of site symmetry $mm\bar{2}$. The principal axes of the electrical field gradient and NMR shift tensors are identical to the crystallographic axes accordingly. For the low-temperature structure of space group $Fmm\bar{2}$,¹² Na ions occupy six different atomic positions. Among 32 Na atoms in a unit cell, 16 atoms occupy four...
positions (4a) of site symmetry mm2, and the other 16 do two positions (8d) of site symmetry m.. For the 4a sites, the principal axes are identical to the crystallographic axes, whereas for the 8d sites, one of the principal axes is identical to b axis, but the other two are not determined only by the site symmetry.

We present 23Na NMR spectra in the charge-ordered and uniform (above TC) phases for H || b, c, and a in Figs. 1(a), 1(b), and 2, respectively. In the spectra in the uniform phase, three resonance lines (the central and two satellite lines) are observed corresponding to 23Na nuclear spins (I = 3/2) at the unique Na position. Quadrupolar splitting, nuclear quadrupolar frequency νQ, and quadrupolar asymmetry parameter η at 50 and 295 K are deduced (Table I), in agreement with a previous measurement with a powder sample.17) Since electrical field gradient is a traceless tensor, and the principal axes at the Na site are identical with the crystallographic axes, νb − (νa + νc) should vanish. This is confirmed in Table I, indicating accurate alignments of the crystallographic axes along the magnetic field.

We observed slight splitting of the resonance lines for H || b above TC. The splitting of the central line remains unchanged down to 10 K. We have no plausible explanation for its origin. For the Na site in the Pmmm structure, misalignment of the applied magnetic field from the crystallographic axes cannot cause any line splitting. Further, since the splitting of the central and satellite lines is comparable, it is not of quadrupolar origin and thus can be ascribed to neither inequivalent Na sites nor a twin sample.

In the charge-ordered phase, each satellite line splits into eight lines for H || a and b, or four for H || c. A similar result has been reported in ref. 18. As listed in Table II, these satellite lines can be assigned to eight Na sites with different quadrupolar splitting. Each of the
Table III. Possible subgroups of \( \text{Fmm2} \) (order 16) for low-temperature structure and charge ordering patterns. A: alternating chains along \( a \) axis, C: four-\( V^{4+} \) clusters, and Z1, Z2, Z3: zigzag chains.

| order | subgroups                              |
|-------|----------------------------------------|
| 8     | \( \text{Ama2}(C)\) \( \text{Bma2}(C)\) \( \text{Cc2}(Z1)\) |
| 4     | \( \text{Pna21}(A, C, Z2)\) \( \text{Pbn21}(C, Z2, Z3)\) \( \text{Pca21}(A, C, Z2)\) \( \text{Pbc21}(C, Z2, Z3)\) |

four lines for \( H \parallel c \) was considered as superposition of two lines, since these four lines have comparable intensities. This assignment in Table II is not unique and other assignments of satellite lines for \( H \parallel c \) are possible: two adjacent lines with \( \nu_c \) of 580 and 583 kHz can be assigned to the sites B, D, E and G alternatively.

The observation of the eight inequivalent Na sites disagrees with the low-temperature structures of \( \text{Fmm2} \), which has the six Na sites. Crystallographically equivalent sites, in general, can be observed as split resonance lines in NMR spectrum for some crystal structures. However, this is not the case for the Na sites in the \( \text{Fmm2} \) structure with the magnetic field along the crystallographic axes. To explain this disagreement between the NMR and x-ray measurements, it is reasonable to suppose that the space group determined by the x-ray diffraction is correct as far as major atomic displacement is concerned, and further that the charge disproportionation of V ions is responsible for the disagreement, since usual x-ray diffraction measurements are sensitive to atomic displacement but not to charge disproportionation of V ions. This supposition is supported by the fact that \( \text{Fmm2} \) contains all the subgroups of \( \text{Pmma} \), the room-temperature structure, with the unit cell of \( 2a \times 2b \times 4c \). Since the observed atomic displacement through the phase transition is small, it is unlikely that a new symmetry element arises at the transition. Then the real low-temperature structure consistent with the present NMR result should belong to a proper subgroup of \( \text{Fmm2} \).

In Table III, the subgroups compatible with the NMR spectra and possible charge ordering patterns in a plane of trellis lattice are listed. The following subgroups and patterns are here excluded: (1) the subgroups which are a proper subgroup of the subgroups of \( \text{Fmm2} \) listed in Table III and include only structures with more than eight Na sites, since there is no experimental evidence for such lower symmetry, (2) the patterns without charge modulation along \( b \) axis, which disagree with the x-ray anomalous scattering measurements, (3) the patterns expected to contain \( V^{4+} \) sites with very different magnetic properties, for example, a pattern containing both zigzag and linear chains, since all the \( V^{4+} \) sites have the same nuclear relaxation rate well below \( T_C \). The remaining possible patterns are classified in two groups according to the arrangement of \( V^{4+} \) and \( V^{5+} \) sites in two-leg ladders: (1) the patterns in which a part of rungs of ladders have both the V sites occupied and consequently another part of rungs are empty. This group consists of several patterns of alternating chains along \( a \) axis (A) and of clusters composed of four \( V^{4+} \) sites (C). (2) the patterns which contain no doubly occupied rung. This group consists of three types of zigzag patterns (Z1, Z2, Z3). These zigzag patterns and examples of the patterns with doubly occupied rungs are shown in Figs. 3(a)–3(e).

The double occupancy of the rungs contained in the former group of charge ordering patterns is unfavorable because it has higher energy per rung by the order of the hopping parameter along the rung \( t_\perp \sim 0.3 \text{ eV} \). We therefore concluded that the zigzag patterns are the most probable. Although this conclusion is consistent with neutron scattering and dielectric susceptibility measurements, it should be directly confirmed by an x-ray diffraction measurement.

We next discuss complicated behavior experimentally observed near \( T_C \). Some experiments suggest the transition is second-order. X-ray diffraction measurements observed the superlattice reflection intensity continuously vanish at \( T_C \) as \( (T_C - T)^\beta \) (\( \beta \sim 0.16,22,23 \)). It was reported that \( \nu_c \) for the \( ^{23}\text{Na} \) NMR obeys the power law with \( \beta \sim 0.19 \). On the contrary, Köppen et al have found two adjacent phase transitions by a thermal-expansion measurement: a first-order transition at \( T_h \sim 33.0 \text{ K} \) and the other at \( T_l \sim 32.7 \text{ K} \). In the \( ^{51}\text{V} \) NMR spectrum, the resonance lines in the uniform and charge-ordered phases were observed to coexist in the temperature range between 33.4 and 33.8 K with a similar width to the separation between \( T_h \) and \( T_l \). Recent measurements of dielectric and magnetic properties under high pressure clearly show two separated transitions under pressure.
we measured the temperature variation of the NMR spectrum is less than 0 K. We found that the lines in the uniform and charge-ordered phases coexist near a narrow temperature range between 33.4 and 33.8 K without any hysteresis. This temperature range agrees with the temperature range near 33.9 K. This indicates that the analysis for the ordinary transition is first-order. The present result does not rule out the other adjacent transition, but its existence is unclear.

To investigate these characteristics of the transition, we measured the temperature variation of the NMR spectrum for $H \parallel a$ near $T_C$ as shown in Fig. 2. The experimental error of the absolute value of the temperature is less than 0.2 K. We found that the lines in the uniform and charge-ordered phases coexist in a narrow temperature range between 33.4 and 33.8 K without any hysteresis. This temperature range agrees with the $^{51}$V NMR measurements with a different single-crystalline sample.

In Fig. 4, we show the temperature dependence of the satellite splitting for $H \parallel a$. We can fit this temperature dependence to the power law $\propto (T_C - T)^{\beta}$, $\beta \sim 0.29$, and $T_C \sim 34.04$ K. Dashed lines show the boundaries between which the resonance lines of the uniform and charge-ordered phase coexist.

In summary, we have measured the $^{23}$Na NMR spectrum in $\alpha'$-NaV$_2$O$_5$ with a single-crystalline sample. We have observed eight Na sites in the charge-ordered phase in disagreement with the low-temperature structure of space group $Fmn2$ determined by the x-ray diffraction measurements. We discussed possible space groups and charge ordering patterns, and have concluded that zigzag patterns are the most probable. We also observed the resonance lines in the uniform and charge-ordered phase coexist near $T_C$. Furthermore, the temperature dependence near $T_C$ of the satellite line splitting is inconsistent with that of a second-order transition. We thus conclude that the transition is first-order.

**Acknowledgment**

We would like to thank H. Nakao, Y. Ohta, Y. Itoh and T. Yamauchi for helpful discussions.