X-Ray Anomalous Scattering Study of a Charge-Ordered State in NaV_2O_5

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Charge ordering of V^{4+} and V^{5+} in NaV_2O_5 has been studied by an x-ray diffraction technique using anomalous scattering near a vanadium K-absorption edge to critically enhance a contrast between the two ions. A dramatic energy dependence of the superlattice intensities is observed below $T_C = 35$ K. The charge ordering pattern is the fully charged *zigzag*-type ladder with the unit cell $2a \times 2b \times 4c$, but not the *chain*-type originally proposed for the spin-Peierls state. Charge disproportionation suggested in our model as the average valence $V^{4.5\pm\delta_c/2}$ is observed below T_C, showing continuous variation of δ_c as a function of temperature.

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The inorganic crystal α'-NaV_2O_5 has attracted much attention as a quasi-1D spin-$\frac{1}{2}$ Heisenberg antiferromagnet (AF) system, which exhibits a steep decrease of its magnetic susceptibility below $T_C = 35$ K suggesting a spin-Peierls (SP) transition [1]. According to the original structure analysis [2], the space group was a noncentrosymmetric $P2_1mn$, with magnetic chains of V^{4+} ($s = \frac{1}{2}$), separated by nonmagnetic chains of V^{5+} ($s = 0$) running along the b axis. The magnetic chains were playing a role as those of the Heisenberg AF model above T_C to cause the SP phase transition at T_C. Moreover, the observation of atomic displacements with the modulation wave vector $\boldsymbol{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$ by x-ray and spin gap formation at the $(1, \frac{1}{2}, 0)$ by neutron scattering strongly suggested the SP state below T_C [3]. NMR [4] and Raman scattering [5] experiments also supported this transition.

In 1998, the structural refinement at room temperature ($>T_C$) revealed the space group as $Pmmn$. This symmetry allows only one kind of V sites where the ions have an average valence of $V^{4.5+}$ [6,7], and they form spin ladders oriented along the b axis, resulting in the so-called quarter filled ladder. On the basis of this new structure, the V-O-V orbital which forms a rung along the a axis has only one d electron, so that the insulating state is retained, and the chains along the b axis behave as the Heisenberg AF above T_C [6,8]. The NMR experiment indicated existence of two inequivalent V sites of V^{4+} and V^{5+} below T_C, since the signals merge into the one signal of $V^{4.5+}$ sites above T_C [9]. This phase transition is no longer an ordinary SP transition but is a spin-charge-lattice-coupled system, which is of a novel case. Lüdecke *et al.* [10] and Boer *et al.* [11] have recently succeeded in analysis of the structure below T_C as the space group $Fmm2$. In their analysis, however, the charge ordered state of the V ions was not directly determined.

Two models of the charge order have been theoretically proposed; the one is based on the 1D V^{4+} chains along the b axis [*chain model* shown in Fig. 1(a)], and the other is characterized as the *zigzag* pattern formed by V^{4+} ions along the ladders [zigzag model 1 shown in Fig. 1(b)]. Based on these two models, the interplay between the charge ordering and the spin-gap formation was studied, indicating that the charge degree of freedom plays an important role in NaV_2O_5 [12–14].

In this Letter, we study the structure of charge ordering in NaV_2O_5 by using x-ray anomalous scattering near the vanadium K-absorption edge ($E_A \sim 5.465$ keV) to preferentially probe the V ions. Dramatic energy dependence of superlattice reflections with wave vector $\boldsymbol{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$ is observed, and hence the unit cell relevant to charge order is $2a \times 2b \times 4c$, which rules out the chain model ($a \times b \times c$). Therefore, we consider the following two models to explain our experimental data: one assumes a fully charge-ordered state as shown in Fig. 1(b) (zigzag model 1), and the other has a charge disordered ladder to satisfy the space group $Fmm2$ as shown in Fig. 1(c) (zigzag model 2). The former is based on the NMR results [9] and inconsistent with the space group $Fmm2$ [10], and the latter involves the three kinds of V ions, V^{4+}, V^{5+}, and $V^{4.5+}$. The model calculation of the fully charged zigzag model 1 can reproduce our results better. The order parameter of the charge-ordered state δ_c is also determined as a function of temperature.

High-quality NaV_2O_5 single crystals were grown by a flux method [15]. A typical crystal is $1 \times 5 \times 0.6$ mm^3 ($a \times b \times c$) in size. The crystal has an orthorhombic

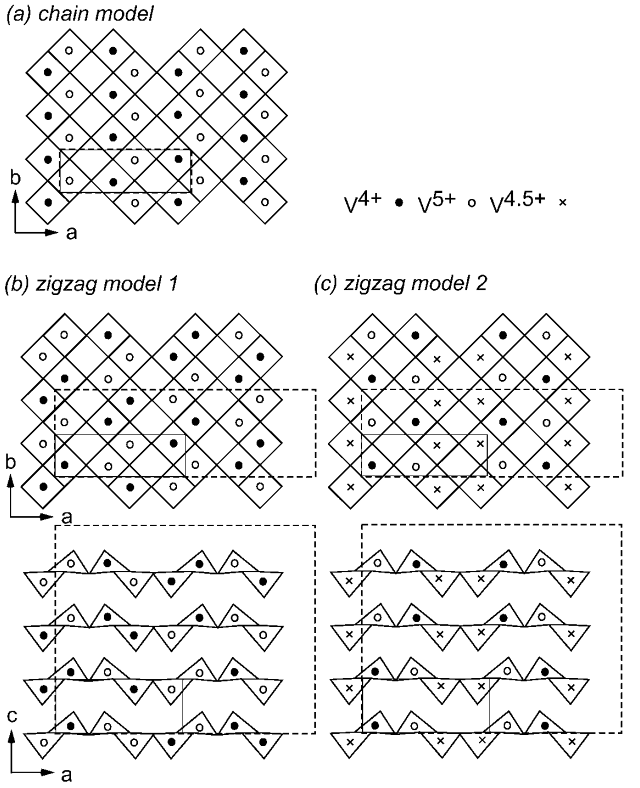

FIG. 1. Schematic drawing of charge ordering in α'-NaV_2O_5 below T_C projected onto the *ab* and *ac* planes. The filled circles, open circles, and cross marks show V^{4+}, V^{5+}, and $V^{4.5+}$ sites, respectively. The solid and broken rectangles indicate the unit cell at room temperature and low temperature phase, respectively. (a) Chain model, (b) zigzag model 1, and (c) zigzag model 2.

structure with the lattice constants $a = 11.3$ Å, $b = 3.61$ Å, and $c = 4.80$ Å at room temperature. The experiments were carried out both at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory and at the Photon Factory (PF) of KEK. The absorption spectrum was measured on the beam line X23A2(NSLS) with a Si(311) monochromator. The x-ray scattering experiments were performed at X22C(NSLS) with a Ge(111) monochromator and at multipole-wiggler beam line 16A2 (PF) with a Si(111) monochromator. A four-circle diffractometer equipped with a closed-cycle helium refrigerator was used.

In order to determine the charge-ordered structure in NaV_2O_5, anomalous scattering techniques were applied to enhance the slight difference of atomic scattering factors between V^{4+} and V^{5+}. The incident energy dependence of atomic scattering factor is generally described by $f(E) = f_0 + f'(E) + if''(E)$, where f_0 is the Thomson scattering factor. The f' and f'' are real and imaginary parts of the anomalous scattering factor, respectively. The f'' can be obtained directly from an absorption spectrum $\mu(E)$, while the f' is obtained by the Kramers-Krönig transformation of the f'' [16]. Fortunately, CaV_2O_5 and V_2O_5 have the same crystal structure as NaV_2O_5 and contain only V^{4+} and only V^{5+} ions, respectively. Their spectra are shown in Figs. 2(a) and 2(b). The absorption edge energy (E_A) of two ions differ by about 1.8 eV due to a chemical shift. A peak in f'' at 5.47 keV is a preedge feature corresponding to the $1s \rightarrow 3d$ transition of the V ion, consistent with a previous report [17]. Such a strong anomalous scattering intensity is influenced by the lack of local inversion symmetry on the vanadium sites. This state allows hybridization of vanadium $4p$ with the $3d$ states, leading to a significant dipole transition at the energy [18]. As indicated in Fig. 2(c), a difference between the two spectra is small at $E \ll E_A$, while it is critically enhanced with a large modulation near E_A. Therefore, the difference of one electron between the V^{4+} and V^{5+} sites should be easily detected from the scattering intensity as a function of the energy across E_A.

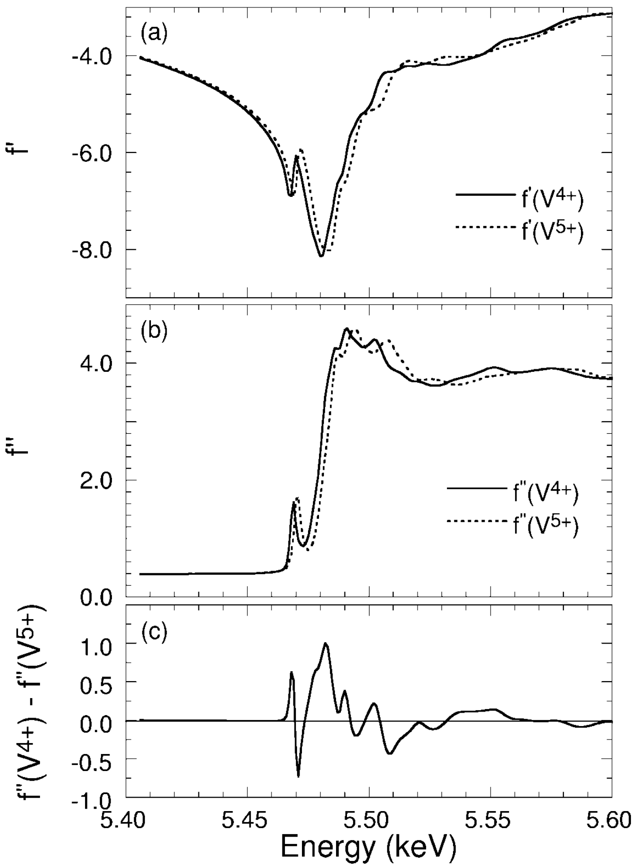

FIG. 2. (a),(b) The energy dependence of anomalous scattering factors f' and f'' for V^{4+} (solid line) and V^{5+} (broken line), respectively. (c) The energy dependence of the difference $f''(V^{4+}) - f''(V^{5+})$.

The energy dependence of the $(\frac{h}{2}, \frac{k}{2}, \frac{\ell}{4})$-type structure factor is calculated as follows:

$$F(\tfrac{h}{2}, \tfrac{k}{2}, \tfrac{\ell}{4}) \propto i(\boldsymbol{\delta} \cdot Q)\{a(\boldsymbol{Q})[f(V^{4+}) + f(V^{5+})] + b(\boldsymbol{Q})[f(V^{4+}) - f(V^{5+})]\} + c(\boldsymbol{Q})\delta_c[f(V^{4+}) - f(V^{5+})] + D(\boldsymbol{Q}). \tag{1}$$

The first three brackets are directly related to the V ions. $a(\boldsymbol{Q})$, $b(\boldsymbol{Q})$, and $c(\boldsymbol{Q})$ are phase factors related to V atomic positions in the unit cell. The f indicates the atomic scattering factors of V^{4+} and V^{5+}. $D(\boldsymbol{Q})$ is a structure factor related to the other ions which are approximately independent of E near the V edges. $\boldsymbol{\delta}$ is an atomic displacement of the V ions for $T < T_C$. The first two brackets are multiplied by δ, the so-called "δ term." δ_c is the order parameter of charge ordering so that $\delta_c = 1$ corresponds to full charge disproportionation. The third bracket arising from the charge disproportionation is called the "δ_c term." The nonzero δ_c term making the intensity contribution of $f(V^{4+}) - f(V^{5+})$ is crucial to determine the charge ordering pattern. The difference term is also included in the δ term. However, its contribution is negligible since the term is multiplied by the atomic displacement δ, and the first bracket including $f(V^{4+}) + f(V^{5+})$ is $10^{1\sim2}$ times larger. As a result, any intensity from the δ_c term near E_A, which is comparable to the δ term, should provide direct information about charge ordering.

The intensities observed at $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$ and $(\frac{13}{2}, \frac{1}{2}, \frac{1}{4})$ as a function of x-ray energy are given by the dots in Fig. 3. A large intensity modulation has been observed at $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$ near E_A. This result evidences the dominant contribution from the δ_c term, indicating that the unit cell size for charge order is $2a \times 2b \times 4c$. On the other hand, the intensity at $(\frac{13}{2}, \frac{1}{2}, \frac{1}{4})$ is not enhanced near E_A, so that the intensity is dominated by the δ term. The charge ordering pattern below T_C is discussed in the following paragraph on the basis of these results.

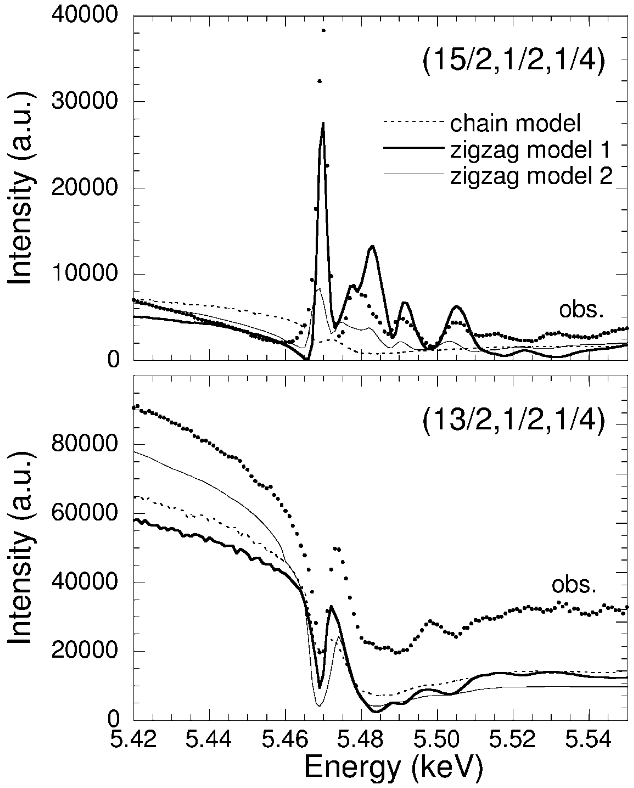

FIG. 3. Energy dependence of the superlattice reflections $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$ and $(\frac{13}{2}, \frac{1}{2}, \frac{1}{4})$ near E_A observed at $T = 8$ K. Solid, thin solid, and dotted curves are the calculations based on the zigzag model 1, 2 and chain model, respectively.

Considering the results of the NMR [9,19] and x-ray structure analysis [10] below T_C, the space group $Fmm2$ allows three kinds of V ions in the ab plane, one $16e$ site and two $8d$ sites. If V^{4+} (V^{5+}) occupies the $16e$ site, both $8d$ sites must be occupied by V^{5+} (V^{4+}). As a result, the V^{4+} and V^{5+} ladders are formed in the ab plane. However, such charge ordering does not satisfy doubling of the period along the b axis observed experimentally. In fact, this model calculation does not reproduce the nonzero δ_c term at $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$. Therefore we consider two other models. The first model is based on the NMR result with a fully charge-ordered state, i.e., $\delta_c = 1$. As the structural restriction, we also use the extinction rule and the rule of charge ordering; one V ion on a rung is V^{4+} (V^{5+}) and the other one is V^{5+} (V^{4+}) because the V-O-V orbital on a rung has one electron above T_C to keep the insulating state [6,8]. As a result, we obtain the charge-ordered state as shown in Fig. 1(b) (zigzag model 1) [13,14], with the unit cell of $2a \times 2b \times 4c$ as shown by a broken rectangle. The unit cell at room temperature is shown by the thin solid rectangle. Because of a disappearance of the mirror symmetry in the ab plane, this model is inconsistent with the space group $Fmm2$. In the second model based on the structure analysis, three kinds of V atoms, V^{4+}, V^{5+}, and $V^{4.5+}$, are considered; the $16e$ site is occupied by $V^{4.5+}$, and the two $8d$ sites are occupied by V^{4+} and V^{5+}. Then, two types of ladders, a charge disordered ladder of $V^{4.5+}$ and the zigzag ladder of V^{4+} and V^{5+}, coexist below T_C as shown in Fig. 1(c) (zigzag model 2), which is a half of charge ordering, i.e., average $\delta_c \sim 0.5$. The unit cell is again $2a \times 2b \times 4c$ as shown by the broken rectangle. This ordered state is also consistent with recent x-ray structure analysis [11]. Consequently, results of the NMR and the structure analysis lead to two different models, but the existence of a zigzag-type charge-ordered ladder along the b axis is common to both models. The scattering intensity of the δ_c term has a similar energy dependence in both models, but the intensity and its Q dependence must be different so that the two models can be assessed.

The superlattice intensities are calculated based on the zigzag model 1, 2 and also on the chain model indicated by solid, thin solid, and broken lines in Fig. 3. We used the atomic displacement as $\delta \sim 0.02$ Å for zigzag model 1, and the structural parameters determined by Lüdecke *et al.* for zigzag model 2. The values of δ in both models are the same order. At $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$ the strong intensity modulation resulting from the δ_c term near E_A can be explained by the calculation of zigzag model 1, 2, and is entirely absent in the chain model. As mentioned above, the shape of modulations is almost independent of the atomic displacement patterns, namely, zigzag model 1, 2, because the intensity modulation results solely from the δ_c term. On the other hand, the ratio of the intensity near E_A to that at $E \ll E_A$ is different, which depends on the value of δ_c. As a result, the zigzag model 1 with $\delta_c = 1$ can reproduce the observation

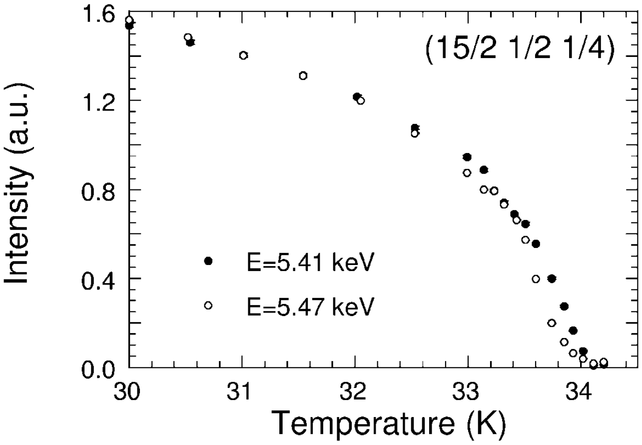

FIG. 4. Temperature dependence of superlattice reflection $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$ as measured at $E = 5.41$ keV $\ll E_A$ to probe atomic displacement (δ), and at $E = 5.47$ keV $\sim E_A$ to enhance the charge contribution.

better than the zigzag model 2. Also at $(\frac{13}{2}, \frac{1}{2}, \frac{1}{4})$, the small intensity modulation around $E \sim 5.5$ keV is reproduced only by the zigzag model 1, although the intensity is dominated by the δ term. We also measured the energy dependence of several other superlattice peaks, which is also consistent with the zigzag model 1.

We measured the temperature dependence of the order parameter for this charge ordering. The difference of anomalous scattering factor between V^{4+} and V^{5+} is so small at $E \ll E_A$ that the superlattice intensity is dominated by the δ term. On the other hand, the intensity of $(\frac{15}{2}, \frac{1}{2}, \frac{1}{4})$ at $E \sim 5.47$ keV results dominantly from the δ_c term. Therefore the order parameters of atomic displacement (δ) and charge ordering (δ_c) can be separately observed as a function of temperature at $E = 5.41$ ($\ll E_A$) and 5.47 keV ($\sim E_A$), respectively. These intensities normalized at 7 K are shown in Fig. 4. Both behave similarly, and are consistent with a continuous second order transition at T_C. This is the first direct observation of δ_c. It is clear that charge ordering gradually develops below T_C as the atomic displacement. The present result is in contrast to the NMR data indicating δ_c varying slightly with temperature [19]. One can see that the slightly different behavior appears near T_C. There are two possibilities. One is that the charge order and the atomic displacement take place at different temperatures. The other is that δ and δ_c terms may have different critical exponents. It is important to understand in this regard that the charge and lattice are coupled in this system. Such a detailed work is under way.

In conclusion, we have reported direct evidence of the fully charged zigzag-type ordered state below T_C by monitoring a dramatic energy dependence of the superlattice intensities at the vanadium K-absorption edge. Charge ordering (δ_c) was observed to gradually develop below T_C, manifesting a second order transition.

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