

## Two-dimensional charge fluctuation in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$

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We have investigated the critical phenomena of the metal-to-insulator (MI) transition of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ . The critical exponent  $\beta$  of 0.226(3) and anisotropic diffuse scattering suggest that the MI transition of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  is two dimensional in nature and that the dimension of the order parameter is not Ising. The non-Ising-like order parameter indicates that the MI transition is not a simple order-disorder type such as that of  $\alpha'\text{-NaV}_2\text{O}_5$  but charge-density-wave like, where the valence at each V site is continuous and the arrangement is modulated. This closely corresponds to the situation predicted by neutron diffraction measurements [Nagai *et al.*, *J. Phys. Soc. Jpn.* **74**, 1297 (2005)] and NMR measurements [Itoh *et al.*, *Phys. Rev. B* **74**, 054434 (2006)].

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### I. INTRODUCTION

The  $\beta(\beta')$ -vanadium bronzes,  $\beta\text{-}A_x\text{V}_2\text{O}_5$  ( $A = \text{monovalent Li}^+, \text{Na}^+, \text{Ag}^+$ , or divalent  $\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Pb}^{2+}$ ), are known to be quasi-one-dimensional (1D) conductors. All members except for  $A = \text{Pb}^{2+}$  undergo a charge-order type metal-insulator (MI) transition. The most striking property of the *monovalent* and *stoichiometric* ( $x = 0.33$ ) system is superconductivity (SC) under high pressure, where it competes with a charge-ordering phase at approximately 7 GPa for  $\text{Na}^+$  and  $\text{Ag}^+$  and 9 GPa for  $\text{Li}^+$ .<sup>1,2</sup>

Despite long and intensive research, however, arguments about the intrinsic mechanism for the MI transition and the appearance of the SC state are still unsettled because it is necessary to consider the complex structure of  $\beta\text{-}A_x\text{V}_2\text{O}_5$  and hydrostatic high pressures of up to 10 GPa at low temperatures. The former (complex nature) makes it difficult to create a theoretical model and the latter (the request for high pressures of up to 10 GPa) prevents the application of some effective experimental methods.

The structure is common to all  $\beta$ -vanadium bronzes. As shown in Fig. 1, there are three independent V sites forming a 1D network along the most conducting  $b$  axis: two zigzag chains formed by V1 and V3 and a two-leg ladder formed by V2. One  $A$  ion occupies two sites equally at high temperatures as shown in Fig. 1. The space group is  $C2/m$ .<sup>4</sup> One electron from the  $A$  site is doped to the V sites and the ratio of  $\text{V}^{4+}(3d^1)$  to  $\text{V}^{5+}(3d^0)$  of monovalent and divalent systems is 1 : 5 and 1 : 2, respectively.

The cations order below a certain temperature ( $T_A$ ) and occupy a single site in the new space group  $P2_1/a$ .<sup>5</sup> The unit cell along the  $b$  axis doubles and generates two inequivalent sites for each of the three vanadium sites. After the ordering of cations, the MI transition takes place with the unit cell tripling along the  $b$  axis and the generation of three inequivalent sites for each of the six vanadium sites in the space group  $P2_1/a$ .<sup>5</sup> The lattice finally becomes sixfold along the  $b$  axis, giving eighteen inequivalent vanadium sites. In the case of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ , the MI transition temperature is about  $T_{\text{MI}} \sim 130$  K.<sup>6</sup> The MI transition is believed to be a charge-order type;<sup>5,7,8</sup> however, the determination of the charge order

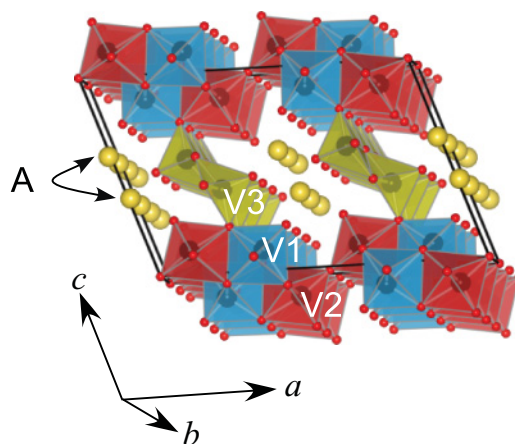


FIG. 1. (Color online) Crystal structure of  $\beta\text{-}A_x\text{V}_2\text{O}_5$  with  $C2/m$  space group. The solid lines show the unit cell.  $a = 15.44$  Å,  $b = 3.61$  Å,  $c = 10.08$  Å, and  $\beta = 109.6^\circ$  (when  $A = \text{Na}$ ). The crystal structure is drawn by VESTA (see Ref. 3).

pattern is proceeding with difficulty, and only the charge order pattern in the  $A = \text{Na}^+$  system has been proposed.<sup>9,10</sup> Both charge order patterns proposed by the neutron<sup>9</sup> and the NMR<sup>10</sup> measurements are complicated, i.e., the electron number at each V site is not an integer.

Thus, the structural background as well as the MI-transition mechanism of the  $\beta\text{-}A_x\text{V}_2\text{O}_5$  system is very complex. In this paper, by changing our point of view and to obtain an overall picture of the system, we focus on the critical phenomena of the MI transition of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ , which is a relatively well studied material in the  $\beta\text{-}A_x\text{V}_2\text{O}_5$  system.

Critical exponents describe the behavior of physical quantities near continuous phase transitions. Although it has not been proved, they are believed to be universal and independent of the details of the physical system and dependent only on the dimension of the system ( $d$ ), the dimension of the order parameter ( $n$ ), and the range of the interaction.

For example, for the well-known charge-ordering and spin-gap system  $\alpha'\text{-NaV}_2\text{O}_5$ ,<sup>11,12</sup> the critical exponent  $\beta$  has been reported to be  $\beta = 0.16(2)$ ,<sup>13</sup>  $0.17(3)$ ,<sup>14</sup> and  $0.18(3)$ .<sup>14</sup> Such

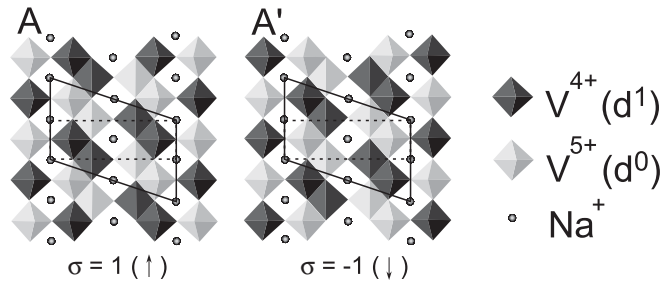


FIG. 2. Stripe charge order patterns A and A' of  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . Dotted and solid lines show the unit cell before and after charge ordering, respectively. A and A' correspond to the Ising spins  $\sigma = 1$  ( $\uparrow$ ) and  $-1$  ( $\downarrow$ ), respectively.

a low  $\beta$  value strongly indicates that the charge ordering in  $\alpha'$ - $\text{NaV}_2\text{O}_5$  is two-dimensional (2D) and Ising-like in nature. Note that the 2D Ising model gives  $\beta = 0.125$ .<sup>15</sup> Actually, a precise study of the structure under high pressure revealed that  $\alpha'$ - $\text{NaV}_2\text{O}_5$  is an ideal axial next-nearest-neighbor Ising (ANNNI) system and that the Ising spins ( $\uparrow$  and  $\downarrow$ ) closely correspond to the charge order patterns A and A' presented in Fig. 2.<sup>16–20</sup> The order-disorder phenomena of the electrons on the two adjacent V sites are well described by the Ising spin.  $\alpha'$ - $\text{NaV}_2\text{O}_5$  is known as a complex system having strong charge-spin-lattice coupling; however, the system simply reduces to the quasi-2D Ising system ( $d \approx 2$  and  $n = 1$ ).

## II. EXPERIMENTAL AND ANALYSIS

X-ray order parameter measurement of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  was performed by measuring the superlattice Bragg reflections originating from the bond alternation associated with the charge ordering, which give a suitable order parameter for describing the MI transition. The critical exponent  $\beta$  was obtained by power-law fitting with  $I \propto t^{2\beta}$ , where  $t$  is the reduced temperature defined as  $t = 1 - T/T_c$ , where  $T_c$  is the critical temperature. To obtain supplementary information about the MI transition, we also measured the temperature dependence of diffuse scattering intensities. The distribution of the diffuse scattering in the reciprocal space should provide information about the dimensionality of the interaction near  $T_c$ .

### A. X-ray diffraction measurement

X-ray diffraction measurements were performed on single crystals of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ , which were grown by an rf-heating Czochralski method<sup>21</sup> using  $\text{NaVO}_3$  as a solvent in a Pt crucible. The stoichiometry of the crystals was carefully checked by measuring the electrical resistivity and magnetic susceptibility, because the electric and magnetic properties are very sensitive to the stoichiometry.<sup>6</sup> The typical size of samples was  $5 \times 5 \times 1 \text{ mm}^3$  ( $a \times b \times c$ ).

The temperature dependence of the integrated intensities was measured using a conventional four-circle diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71 \text{ \AA}$ ) from a rotating anode x-ray generator (55 kV  $\times$  280 mA), which was monochromatized by the PG(002) reflection. The sample was mounted on a closed-cycle He-gas refrigerator and the temperature was controlled

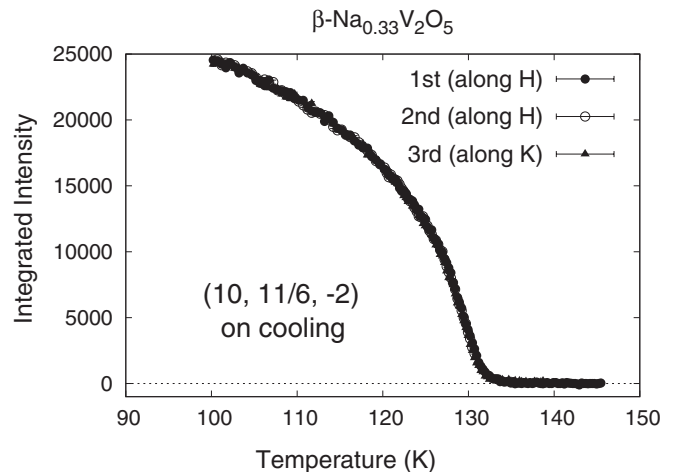


FIG. 3. Temperature dependence of the integrated intensities of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ .

within  $\pm 0.04 \text{ K}$ . The detector was a scintillation counter. The reciprocal lattice of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  at all temperatures was set using a high-temperature monoclinic cell ( $C2/m$ ,  $a \times b \times c$ ).

Figure 3 shows the temperature dependence of the integrated intensities measured at  $(10, 11/6, -2)$ . The integration of the superlattice peak was performed independently along the H and K directions. As shown in Fig. 3, the data taken along the two directions were extremely consistent with each other, which indicates that the integration of the intensity was successful.

### B. X-ray diffuse scattering measurement

Diffuse scattering was also measured. Since the diffuse scattering intensity of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  is very weak, we chose three spots on the three-directional tail of the  $(10, 11/6, -2)$  superlattice Bragg reflection and the intensities at the three spots were counted for 1000 s at each temperature. The three spots were  $(10, 11/6, -2) + (0.122, 0, 0)$  (the H direction),  $(10, 11/6, -2) + (0, -0.075, 0)$  (the K direction), and  $(10, 11/6, -2) + (0, 0, -0.073)$  (the L direction), where the diffuse scattering is strong and unaffected by the tail of the intense superlattice Bragg peak. The results are shown in Fig. 4. It is clear that the diffuse scattering exhibits a strong anomaly along the L direction, while no anomaly is observed along the K direction.

### C. Critical exponent $\beta$

Figure 5 shows the integrated intensity data for  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  as a function of reduced temperature with  $T_{\text{MI}} = 130.0 \text{ K}$  on a log-log scale. The value of  $T_{\text{MI}}$  and the critical exponent  $\beta = 0.226(3)$  are obtained from a least-squares fit to the data of from  $8 \times 10^{-3}$  to  $\sim 6 \times 10^{-2}$  using the power-law function in such a way that the data lie on the power-law function in the widest reduced-temperature range below  $T_{\text{MI}}$ . The deviation close to the critical point below  $8 \times 10^{-3}$  originates from the contribution of the diffuse scattering, which is a dynamic contribution. We thus eliminated this region in the fitting.

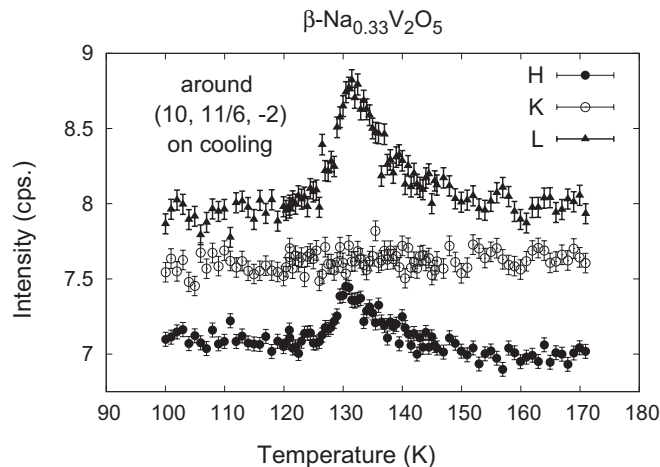


FIG. 4. Temperature dependence of the diffuse scattering intensities of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  measured at the three-directional tail of  $(10, 11/6, -2)$  Bragg position.

The same type of experiment was also performed using another experimental setup with synchrotron radiation x-rays and the reproducibility of the results was confirmed.

### III. DISCUSSION

#### A. Quasi-two dimensionality and non-Ising-like order parameter

As shown in Fig. 4, the diffuse intensity exhibits a large anomaly along the L direction but no anomaly along the K direction. This is due to the magnitude of the correlation, i.e., the correlation is weak along the L direction and strong along the K direction. The short correlation length results in broad diffuse scattering in the reciprocal space, which is easily detectable at the off-Bragg position, while the long correlation length results in the opposite situation. This means that the correlation concerning charge ordering is robust along the  $b$ -axis, moderate along the  $a$ -axis and weak along the  $c$ -axis.

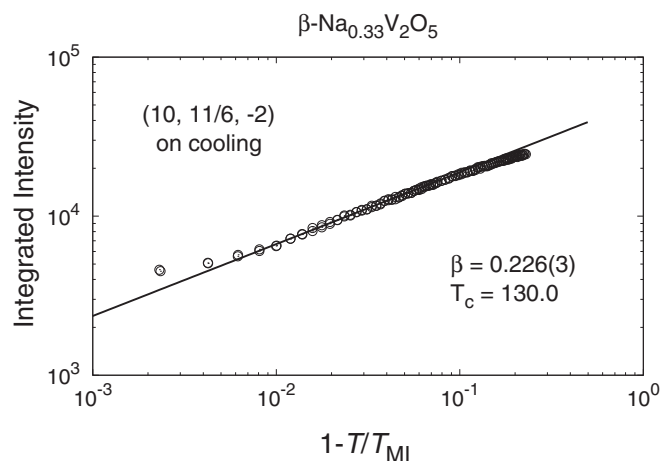


FIG. 5. Log-log plot of the integrated intensity vs reduced temperature. The background has been subtracted. The solid line drawn through the data is the fitting result by using the power law with  $\beta = 0.226(3)$ .

Thus the charge ordering of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  is considered to be basically 2D in nature.

We briefly review the critical exponent  $\beta$  for typical cases. A theoretical estimation based on the standard three-dimensional (3D) model (Ising,  $XY$ , and Heisenberg) gives  $\beta \sim 0.34 \pm 0.02$ ,<sup>22</sup> while the exact solution of the 2D Ising model gives  $\beta = 0.125$ .<sup>15</sup> It has also been reported that a finite size effect gives rise to an effective  $\beta$  value of 0.23 in the case of the 2D- $XY$  model.<sup>23,24</sup>

It is well known that the 2D system does not undergo a conventional phase transition except for the Ising system, although strongly 2D correlated systems (so-called quasi-2D or 2D-like systems) ultimately exhibit 3D order with a low  $\beta$  value close to 0.2.<sup>24</sup> Of course, the 2D-to-3D crossover should take place very close to the critical points. For example, the 2D Heisenberg-like ferromagnet  $\text{K}_2\text{CuF}_4$  is reported to undergo the crossover from  $\beta = 0.22$  for  $t = 2 \times 10^{-2} - 3 \times 10^{-1}$  to  $\beta = 0.33(3)$  for  $t = 1 \times 10^{-3} - 2 \times 10^{-2}$ .<sup>25</sup> However, not every quasi-2D system has been reported to show such a clear dimensional cross over.

We therefore conclude that the anisotropy of the diffuse scattering and the low  $\beta$  value close to the 2D- $XY$  limit (0.23) suggest that the MI transition of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  is basically 2D in nature and that the dimension of the order parameter is not Ising like.

#### B. Relation between $\beta$ value and structure

The non-Ising-like order parameter indicates that the MI transition of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  is not a simple order-disorder type such as that of  $\alpha'$ - $\text{NaV}_2\text{O}_5$ , i.e., the valence at each V site of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  is allowed to be noninteger ( $d^{0-1}$ ) similarly to a charge-density wave. We next discuss the MI transition of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  by considering its structure.

We first revisit  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . As stated in the introduction,  $\alpha'$ - $\text{NaV}_2\text{O}_5$  has Ising-like character owing to the two equivalent charge-ordering patterns in the  $ab$  plane (2D plane) as shown in Fig. 2.<sup>16-20</sup> This results in the simple situation that each V site should take two discrete states ( $d^0$  or  $d^1$ ). This closely corresponds to the classification using the critical exponent as described in the introduction.

For  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ , we also concentrate on the 2D  $ab$  plane as shown in Fig. 6. As given in the introduction, the unit cell of the insulator phase is  $a \times 6b$ . The charge arrangement pattern in the  $a \times 6b$  unit cell has already been predicted by neutron diffraction<sup>9</sup> and NMR<sup>10</sup> measurements. The  $6b$ -lattice modulation along the  $b$  axis is given by a combination of the noninteger valence arrangement with a period of  $3b$  and the preexisting cation arrangement with the  $2b$ -lattice modulation. The valence is also shared disproportionately among the V1, V2, and V3 sites (see yellow circles in Fig. 6). Both neutron diffraction<sup>9</sup> and NMR<sup>10</sup> measurements also predicted the existence of no  $d$ -electron sites with a period of  $3b$  (see arrows in Fig. 6).

As is well known, to realize such a charge-density-wave-like arrangement, two degrees of freedom, *phase* and *amplitude*, are needed. This corresponds to our result that the order parameter should be non-Ising like. The freedom of the phase and amplitude potentially gives an infinite number of energetically equivalent charge-modulation patterns along the

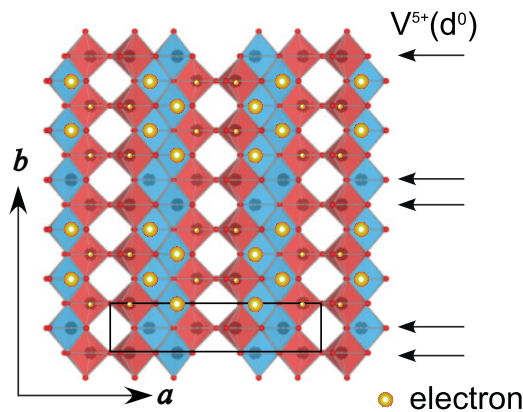


FIG. 6. (Color online) 2D framework of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  ( $ab$  plane). Only the V1 and V2 sites are shown. The valence predicted by NMR measurements<sup>10</sup> is shown, where the radius is proportional to the valence. The crystal structure is drawn by VESTA (see Ref. 3).

$b$  axis in the  $a \times 6b$  unit cell. The fluctuation among the charge-modulation patterns should result in conduction above  $T_{\text{MI}}$ . The pattern obtained by the neutron diffraction<sup>9</sup> and NMR<sup>10</sup> measurements is just one of the possible charge-modulation patterns. This is considerably different from the case of  $\alpha'$ - $\text{NaV}_2\text{O}_5$ , which is insulating in the whole temperature range, and only two charge-ordering patterns, as seen in Fig. 2, are strongly related by a phase shift by  $\pi$  along the  $b$  axis.

The conductivity of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  shows that the system is quasi-1D;<sup>1,2</sup> however, our present results suggest that the correlation among the electrons via the lattice is basically 2D. We believe that the two-dimensionality is related to the SC state under high pressure.<sup>1</sup>

#### IV. SUMMARY

We have investigated the critical phenomena of the MI transition of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ . The critical exponent  $\beta$  of 0.226(3) and the anisotropic diffuse scattering suggest that the MI transition of  $\beta$ - $\text{Na}_{0.33}\text{V}_2\text{O}_5$  is 2D in nature and that the dimension of the order parameter is non-Ising like. The non-Ising-like order parameter indicates that the MI transition is not a simple order-disorder type such as that of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  but charge-density-wave like, where the valence at each V site is continuous and the arrangement is modulated. This closely corresponds to the situation predicted by neutron diffraction<sup>9</sup> and NMR<sup>10</sup> measurements.

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