"Devil's Staircase"-Type Phase Transition in NaV_2O_5 under High Pressure

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(Received 18 April 2001; published 7 August 2001)

The "devil's staircase"-type phase transition in the quarter-filled spin-ladder compound NaV_2O_5 has been discovered at low temperature and high pressure by synchrotron radiation x-ray diffraction. A large number of transitions are found to successively take place among higher-order commensurate phases with $2a \times 2b \times zc$ type superstructures. The observed temperature and pressure dependence of modulation wave number q_c, defined by $1/z$, is well reproduced by the axial next nearest neighbor Ising model. The q_c is suggested to reflect atomic displacements presumably coupled with charge ordering in this system.

DOI: 10.1103/PhysRevLett.87.086402 PACS numbers: 71.27.+a, 61.10.Eq, 62.50.+p

Since discovery of spin-Peierls-like behavior in NaV_2O_5 by Isobe and Ueda [1], a wide variety of experimental and theoretical studies have been carried out. The recent structure analysis [2,3], NMR [4], and convergent-beam electron diffraction [5] experiments have confirmed that NaV_2O_5 has an orthorhombic unit cell (P phase called hereafter) with the space group of centrosymmetric D_{2h}^{13}-$Pmmn$ and lattice constants $a = 11.325$ Å, $b = 3.611 =$ Å, $c = 4.806$ Å under ambient conditions. Na atoms located between V_2O_5 layers composed of two-dimensionally connected VO_5 pyramids in the ab plane play a role of an electron donor [2,3]. All crystallographically equivalent V atoms are dressed a half of $3d^1$ electron ($V^{4.5+}$) so that spins ($S = 1/2$) form a quarter-filled ladder structure along the b axis. At $T_c = 35$ K, the charge ordering [4,6] ($V^{4.5+}$-$V^{4.5+} \rightarrow V^{4+}$-$V^{5+}$), spin-gap formation ($\Delta = 9.8$ meV) [1,7], and lattice dimerization characterized by the modulation wave vector $\mathbf{q} = (1/2, 1/2, 1/4)$ ($2a \times 2b \times 4c$ in real space; $C_{1/4}$ phase called hereafter) [7], take place cooperatively. Regarding the charge ordering pattern below T_c, a few of the theories [8,9] proposed a two-dimensional zigzag-type charge ordering model in the ab plane by taking both on-site and intersite Coulomb interactions into account and described well the $2a \times 2b$ structure in the ab plane. Mostovoy *et al.* further considered the interactions via the lattice distortions [9]. Recently, Nakao *et al.* [6] carried out anomalous x-ray scattering experiments to selectively identify V^{4+} and V^{5+} ions and directly evidenced for the zigzag-type charge order realized in the ab plane as theoretically proposed. A full structure analysis of both atomic displacement and charge order modulation with $\mathbf{q} = (1/2, 1/2, 1/4)$ in the low-temperature phase is very recently accomplished by x-ray scattering [6,10]. However, any microscopic mechanism to stabilize the quadrupling of its unit cell along the c axis is not yet known. The four equivalent realizations of the zigzag charge ordering in the ab plane may provide a clue to understanding the quadrupling along the c direction [9]. The pressure application will be effective for providing key information to clarify such an origin of the long period lattice and charge modulation. This is one of the purposes of the present high-pressure x-ray diffraction experiments.

Recently, Ohwada *et al.* [11] have discovered a new high pressure phase which has a $2a \times 2b \times 1c$ superlattice (C_0 phase) led by the $C_{1/4}$-to-C_0 phase transition taking place at 0.92 GPa ($T = 8$ K). On the other hand, dielectric measurements precisely performed along the c axis [12] indicated the existence of an intermediate phase in a pressure range of $0.5 < P < 1.0$ GPa at temperature $T = 20$–30 K. The second purpose of the present synchrotron x-ray diffraction experiments at low temperatures and high pressure (LT-HP) is to clarify such

an intermediate phase from microscopic structural points of view.

For an overall survey of superlattice reflection in reciprocal space, an x-ray oscillation photographic method was first employed on the micro powder diffractometer [13] equipped with an imaging plate (IP) and with an x-ray CCD system [14] at Photon Factory BL-1B. The wavelength was tuned to 0.6888 Å (18 keV) with a Si(111) double-crystal monochromator. For high resolution measurement to obtain more detailed information, a detector method was employed on a four-circle diffractometer at BL-4C (PF) and BL02B1 (SPring-8). X-ray wavelength monochromatized in the same way as that of BL-1B (PF) was 0.6888 Å at PF and 0.413 Å (30 keV) at SPring-8. For the LT-HP experiments, a He-gas driven diamond anvil cell (DAC) was mounted on a closed-cycle He-gas refrigerator. Pressure was generated in a DAC using a 4:1 mixture of methanol:ethanol pressure transmitting media and was calibrated from a lattice constant of NaCl [15] enclosed with the specimen in the DAC. The sample temperature was monitored with a Au-0.07%Fe chromel thermocouple at BL-1B (PF) and a Si-diode sensor at BL-4C (PF) and BL02B1 (SPring-8) directly attached to the DAC surface. We used as-grown high quality single crystals of NaV_2O_5 with a typical size of 200 μm $\times$ 400 μm $\times$ 50 μm ($a \times b \times c$) grown by the same method as previously reported [16].

Figure 1 shows the oscillation photographs representing temperature dependence of positions of superlattice reflections along the direction of $[15/2, 1/2, l]$ in selected range of reciprocal space at a fixed pressure of 0.88 GPa. All recorded reflections can be completely indexed as indicated in the figure with the aid of data processing system DENZO [17]. With increasing temperature the superlattice reflection $(15/2, 1/2, 3/4)$ disappears at 19 K while a new reflection $(15/2, 1/2, 4/5)$ appears. Furthermore, another new reflection $(15/2, 1/2, 13/16)$ appears at 20.0 K and gradually shifts to the position $(15/2, 1/2, 9/11)$ between 21.5 and 23.0 K. One can notice that all phases have

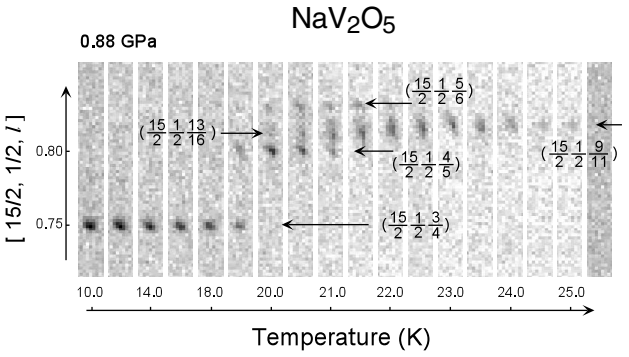

FIG. 1. Temperature dependence of a position of superlattice reflections $(15/2, 1/2, l)$ in the region recorded on IP oscillation photographs at 0.88 GPa. Several intermediate phases with $l = 1/4$, $1/5$, $3/16$, and $2/11$ are systematically observed.

only the $2a \times 2b \times zc$ type superlattices whose modulation wave vector along the c axis can be expressed as $q_c(= 1/z) = 1/4 \rightarrow 1/5 \rightarrow 3/16 \sim 2/11$ in reciprocal lattice units. The superlattice with $q_c = 1/6$ is also observed in a limited temperature range.

Figure 2(a) displays temperature dependence of high-resolution diffraction profiles observed along the $[13/2, 3/2, l]$ direction at 0.92 GPa with the counter-method. In this figure a few more reflections are newly observed and one can clearly see a series of superlattice reflections with $q_c = 1/4$, $1/5$, $1/6$, $2/11$, and $3/17$ which systematically appear and disappear as a function of temperature. Figure 2(b) shows the similar data observed at 1.04 GPa. At the lowest temperature 11 K, three phases with $q_c = 1/4$, $1/6$, and 0 coexist. As temperature increases, two phases with $q_c = 1/4$ and 0 disappear while the other phase with $q_c = 1/5$ emerges in a limited temperature range. At higher temperatures, the phases with $q_c = 2/13$ and $1/7$ show up and the three peaks shift to the more complicated higher-order commensurate position. Some phases are found to coexist at a certain temperature range as seen in Figs. 2(a) and 2(b). Such a coexistence may result from the pressure distribution in the DAC caused by the solidified pressure media. The pressure distribution can be estimated as follows: Fig. 2(c)

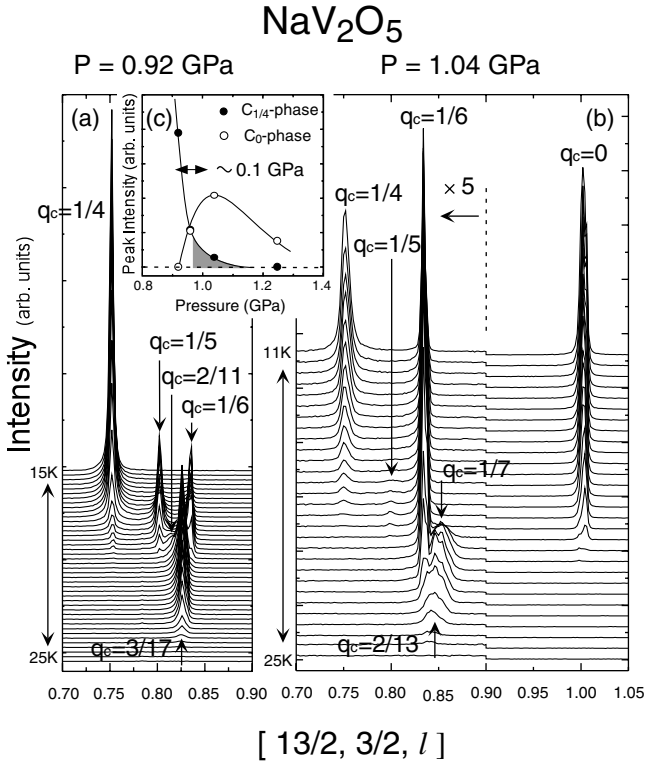

FIG. 2. Temperature dependence of the superlattice reflection experimentally scanned along the $[13/2, 3/2, l]$ direction with high resolution at (a) 0.92 GPa and (b) 1.04 GPa. (c) Peak intensities of both the $C_{1/4}$ and C_0 phases are shown to estimate the pressure distribution.

shows pressure dependence of superlattice peak intensities characteristic of both $C_{1/4}$ and C_0 phases observed at the temperature where the superlattice intensity is saturated. The two phases have a clear phase boundary at 0.95 GPa nearly parallel to the temperature axis. From the pressure range where both phases have finite superlattice peak intensity at about 1.0 GPa, the pressure distribution is estimated as $\Delta P = 0.1$ GPa. Considering thus estimated pressure ($\Delta P = 0.1$ GPa) and temperature ($\Delta T = 0.2$ K) distributions (defined as the *P-T* resolution), we obtain the *P-T* phase diagram of NaV_2O_5 as shown in Fig. 3. All phases are expressed with a characteristic modulation wave number along the *c* axis q_c as C_{q_c}; i.e., the $C_{1/4}$ for $q_c = 1/4$ and the C_0 for $q_c = 0$. We found some more phases whose boundaries could not be determined. Such unidentified phase regions are represented by dotted lines. The hutched area shows the commensurate phases unambiguously identified. The shaded area shows more complicated higher-order commensurate phases or incommensurate phases which we could not identify within the present *P-T* resolution. The intermediate phase is no longer observed below $P = 0.4$ GPa and above 1.25 GPa

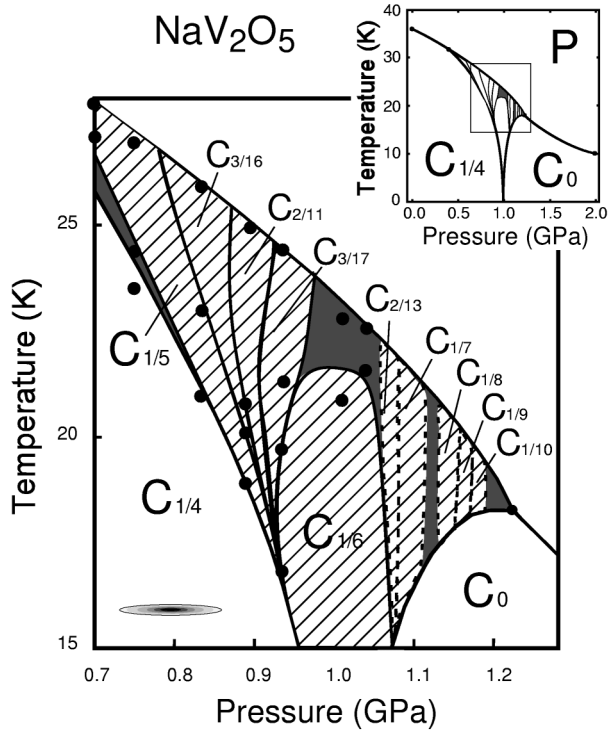

FIG. 3. Experimentally observed *P-T* phase diagram of NaV_2O_5. The hatched area shows commensurate phases unambiguously identified while the shaded area indicates more complicated higher-order commensurate or incommensurate phases unresolved by the present *P-T* resolution, which is represented with an ellipse at the left bottom corner. The phase boundary experimentally not clearly confirmed is drawn with dotted lines. The inset represents the wider range of *P-T* phase diagram.

(see the inset of Fig. 3). At 2.0 GPa the *P*-to-C_0 phase transition temperature decreases to 10 K.

The observed q_c sequences are well understood as the "devil's staircase"-type sequences theoretically obtained from the simple axial next nearest neighbor Ising (ANNNI) model proposed by Bak and von Boehm [18]. They developed theoretical calculations with two competitive interlayer interactions between Ising spins, i.e., the nearest neighbor interaction $J_1 > 0$ (ferro) and the next nearest neighbor interaction $J_2 < 0$ (antiferro). Within a mean field approximation, they obtained a global phase diagram and found extremely complicated phase boundaries separating various kinds of commensurate phases. It is essentially important that there are only two stable ground states as $T \to 0$, i.e., ↑↑↑ ... (ferro, all up configuration, $q = 0$) state for $-J_2/J_1 < 1/2$ and ↑↑↓↓↑↑↓↓ ... (up-up-down-down configuration, $q = 1/4$) state for $-J_2/J_1 > 1/2$. Such a transition between the two ground states as a function of $-J_2/J_1$ was experimentally observed in NaV_2O_5 which undergoes the $C_{1/4}$-to-C_0 phase transition at 0.92 GPa [11]. The other characteristic theoretically proposed for devil's staircase at finite temperature is a systematic existence of modulated phases with the wave numbers $q = 1/5, 1/6, 1/7, 2/11, 3/17, 3/16, 2/13, \ldots$, which is also experimentally observed in a wide range of temperature and pressure in NaV_2O_5 as displayed in Fig. 3. Thus the *P-T* phase diagram observed in NaV_2O_5 resembles extremely well the theoretically obtained devil's staircase with respect to the modulation wave number along the *c* axis. As for the structure in the *ab* plane, the $2a \times 2b$ superstructure is well maintained. The present experiment directly probes the atomic displacements represented by $q = (1/2, 1/2, q_c)$ but does not directly probe the charge ordering. However, the previous x-ray scattering experiments [6,10] evidenced that in the $C_{1/4}$ phase the charge order and atomic displacements are modulated with the same wave vector $q = (1/2, 1/2, 1/4)$. In the present phase diagram, therefore, it is speculated that the charge order is also modulated with the same wave vector in each phase.

By analogy with the ANNNI model, the devil's staircase-type behavior along the *c* axis implies any competitive interlayer interactions, i.e., phenomenologically $J_1 > 0$ and $J_2 < 0$ in NaV_2O_5. The interlayer interactions must relate to the lattice constant *c* which has compressibility as large as $\Delta c/c_0 \sim -0.02$ (GPa^{-1}) [19]. As shown in Fig. 4(a), Ising spins can be defined by the charge disproportionation on the V-O-V rung as $S = 1$ (↑) for the V^{4+}-O-V^{5+} state and $S = -1$(↓) for the V^{5+}-O-V^{4+} state. Local charge arrangement of NaV_2O_5 and Ising spin arrangement of ANNNI model are represented in Fig. 4(b), respectively. A microscopic origin of the interlayer interaction $J_1 > 0$ and $J_2 < 0$ is not yet known. However, it is very surprising that the phase transition of such a very complicated charge-lattice-spin coupled system NaV_2O_5 may be described by the simple ANNNI model.

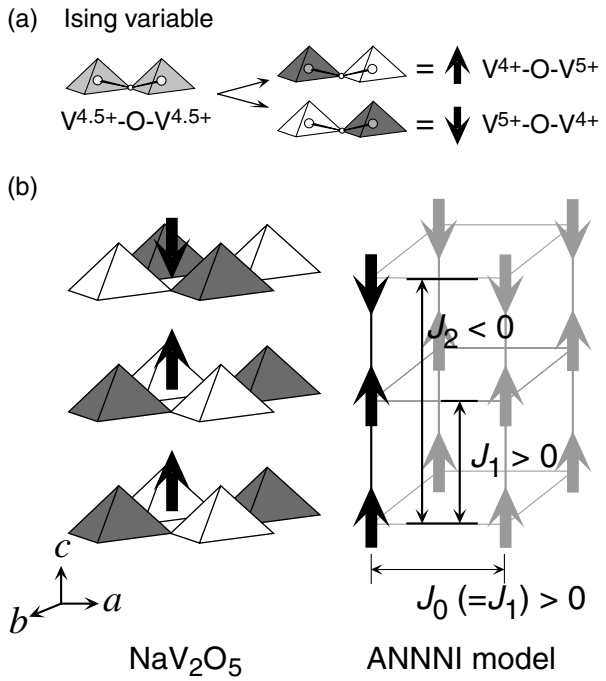

FIG. 4. (a) Ising spins correspond to the charge disproportionation on V-O-V rung defined in the present system. (b) Local charge arrangement of NaV_2O_5 system along the c axis and Ising spin arrangement of ANNNI system.

The instruments for the LT-HP experiments installed at PF/BL-4C were designed by Dr. Yositaka Matsusita. We thank Dr. Akihiko Fujiwara, Dr. Masakazu Nishi, Dr. Hitoshi Seo, and Professor Hiroshi Sawa for their stimulative discussion. Experimental assistance by Mr. Yuya Katsuki and Mr. Hirondo Nakatogawa is also appreciated. One of the authors (K. O.) acknowledges support by the Japan Society for the Promotion of Science for Young Scientist.

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