5. Materials Science

5-1. Zigzag Charge Ordering in α'-NaV_2O_5

The physical properties of condensed matter are subject to four degrees of freedom: 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. The inorganic system α'-NaV_2O_5 has a novel phase transition in which the charge-ordering, spin singlet, and lattice-distortion occur simultaneously.

This compound has been classified as having a spin-Peierls system as follows. The crystal structure has been determined and identified as orthorhombic ($a_p \times b_p \times c_p$) with linear chains of V^{4+} (S = 1/2) ions separated by nonmagnetic V^{5+} chains [1]. The 1D Heisenberg spin susceptibility and the magnetic moment have been determined to vanish below T_C = 34 K independent of the crystal direction [2]. However, many later experimental and theoretical investigations have found that the degree of charge freedom remains in the high-temperature (HT) state, and that this material has a quarter-filled two-leg ladder structure consisting of only one vanadium site as $V^{4.5+}$. It should be noted that ^{51}V NMR measurements indicate that the single V site above T_C split into two groups of V^{4+} and V^{5+} states and that no V sites remain as $V^{4.5+}$ [3]. Therefore, the transition includes not only the spin singlet, but also charge-ordering and lattice-distortion, simultaneously.

Recently, several X-ray diffraction studies of the low-temperature (LT) structure have been reported [4,5]. The results of these studies have given qualitatively the same structure as $2a_p \times 2b_p \times 4c_p$ with space group (SG) F*mm2*. The structure includes three different electronic states of the V sites (V^{4+}, V^{5+} and $V^{4.5+}$). This charge distribution is incompatible not only with the V-NMR results [3], but also with resonant X-ray measurements [6].

In this study, we have determined by the synchrotron radiation X-ray diffraction at KEK that the α'-NaV_2O_5 is in the LT state [7].

In order to determine the lattice system below T_C, high-resolution scattering measurements were performed by a Huber four-circle diffractometer at BL-4C. The temperature dependence of typical several reflections shows that the b^* reflection was split along the a^*-axis below T_C; splitting along the other directions was not observed. This b^* splitting disappeared above T_C again. The width of the splitting increased with decreasing temperature, and saturated to $\Delta\gamma$ = 0.07 degrees at the lowest temperature. Consequently, we conclude that the correct LT symmetry is monoclinic (SG: A112), with the unit cell being revised as (a_m, b_m, c_m)=(a_p–b_p, $2b_p$, $4c_p$), and the crystal would include a domain as (b_p–a_p, $2b_p$, $4c_p$).

In order to determine the crystal structure, we used a two-dimensional (2D) cylindrical imaging-plate detector of an MPD system on BL-1B. The

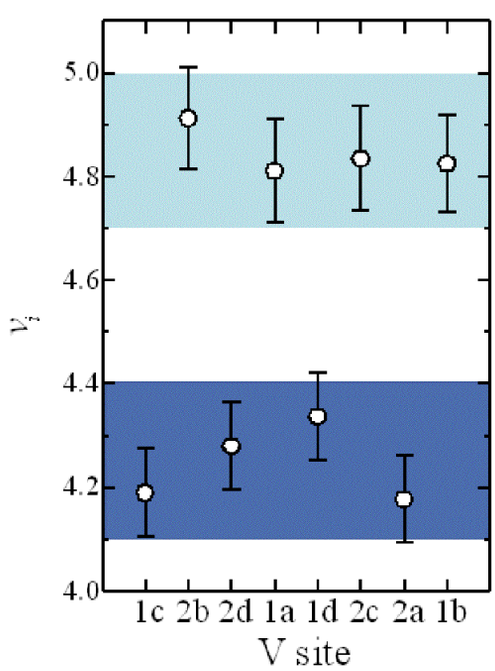

Figure 1.
The estimated valences v_i for eight V sites by the BVS calculation. Colored areas are guide for eyes. These sites are clearly separated into two regions in the range of errors.

intensities of the 2072 ($I > 3\sigma(I)$) Bragg reflections were measured at 10.0 K. The DENZO program was used for 2D image processing. The Shelx98 program was used for refinements. No peak splitting was observed below T_C because of less resolution of BL-1B than BL-4C.

Without any assumption concerning the domain, the full refinement used by all reflections gave essentially the same as results as in ref. [4, 5]. However, the resulting structure with the domain is different from that with F*mm2*, and the *R*-factor being 0.037. The crystal structure consists of 8 independent vanadium sites. A BVS calculation clearly indicates that the valence ordering ratio of vanadium is V^{4+}:V^{5+} = 4:4 (Fig. 1). This result showing the two separated V sites is in good agreement with those of the V-NMR [3]. In this result, the intra-ladder charge ordering shows a V^{4+} and V^{5+} zigzag pattern along the *b* axis, as in Fig. 2. This intra-ladder pattern is in good agreement with the results of a theoretical calculation including a long-range order Coulomb repulsion [8]. In the $a_p \times b_p$ plane, the charge ordering pattern shows a stripe in which the same valence V ions stand in the $a_p/3 + b_p$ direction. The 4*c* period structure involves two factors: primarily, the solid-crossing structure consists of two neighboring $a_p \times b_p$ planes with different direction stripe patterns caused by minimization of the lattice distortion. A secondary pair of these two planes stacks along the c axis in out-of-phase of charge ordering, with each site being caused by a long-range Coulomb interaction.

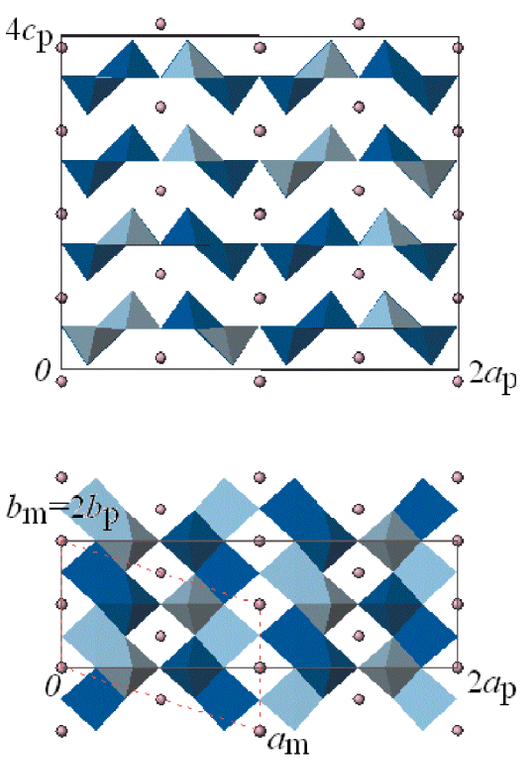

Figure 2.
Crystal structure in LT state. Pink circle shows Na atom. Navy blue and light blue pyramids show $V^{4+}O_5$ and $V^{5+}O_5$, respectively. Lower figure shows z~1/8 plane.

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5-2. White X-Ray Magnetic Diffraction of Ferromagnets at BL-3C3

White X-ray magnetic diffraction [1] (WXMD) is a unique method that can measure spin- and/or orbital-magnetic form factors of ferromagnets independently. This method utilizes white X-rays of elliptically polarized synchrotron radiation emitted from a bending magnet out of the electron orbit plane of a storage ring. The accuracy of the measurements is dependent on the emittance and stability of the electron beam in the storage ring. A second-generation low-emittance ring may be suitable for this experiment because of a good balance of adequately low emittance and high stability of the electron beam; one such ring is that of the Photon Factory. The advantage of the white X-ray method over a monochromatic X-ray method is that the magnetic form factors at plural reciprocal-lattice points are measured simultaneously in a measurement. The disadvantage is that the measurements are affected by fluorescent radiation from a specimen and multiple scattering at the specimen.

Beamline BL-3C3 is equipped with a five-circle diffractometer that is optimized to the WXMD experiment and minimizes the above disadvantageous effects. An electromagnet and a refrigerator are installed in the diffractometer. We have some choices of the magnetic-field strength and the temperature of the specimen. Typical cases are: (1) 1.0 tesla and room temperature, (2) 0.4 tesla and temperatures as low as 20 K (using a refrigerator of the He gas circulating type), and (3) 0.3 tesla and temperatures as low as 5 K (using a refrigerator of liquid He flowing type). We have three choices for the magnetic field directions: (a) parallel to the incident beam, (b) parallel to the diffracted beam, and (c) parallel to the scattering vector. Configurations (a), (b) and (c) give us the magnetic form factors of the orbital moment only (that is, the orbital-magnetic form factor), those of the total (spin+orbital) moment (that is, the total magnetic form factor), and those of the spin moment only (that is, the spin-magnetic form factor), respectively, with the 90 degree scattering angle.

In the present study we applied the WXMD method to measure the spin-magnetic form factor of ferromagnetic $YTiO_3$. $YTiO_3$ has a crystal structure of the perovskite type and exhibits orbital ordering of the 3d electrons of Ti atoms [2, 3]. This compound is ferromagnetic below 28 K. Polarized neutron diffraction [4] and the resonant X-ray scattering [5] were performed and provided models of the ordered orbitals. The spin- and/or orbital- magnetic form factors measured by the WXMD experiment will give us complementary information about the ordered orbitals.

The specimen crystal was provided by Dr. Y. Taguchi and Prof. Y. Tokura. Preliminary measure-

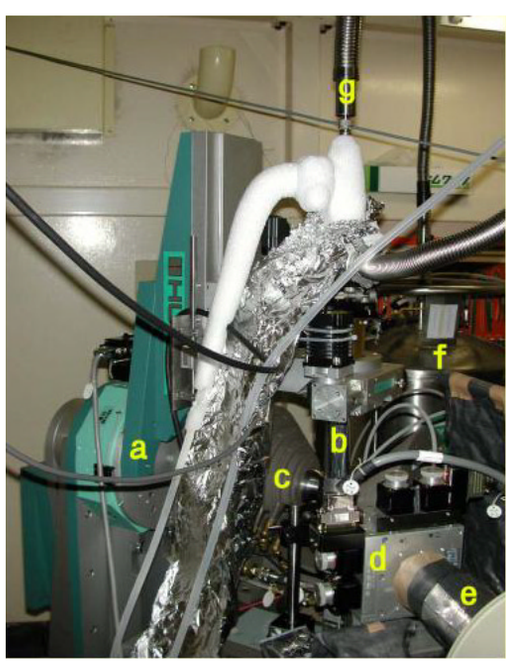

Figure 3.
Experimental setup of the white X-ray magnetic diffraction of $YTiO_3$: a, five-circles diffractometer; b, refrigerator of liquid He-flowing type to keep the temperature of the specimen at 5 K; c, electromagnet producing 0.3 tesla at a gap length of 50 mm; d, slit for receiving diffraction beam and minimizing fluorescent radiation from the specimen; e, pure Ge solid state detector; f, vessel of liquid He; g, transfer tube of liquid He.

ments of the magnetization of the specimen crystal showed that 0.3 tesla is sufficient to saturate the magnetization when the magnetic field is applied along the easy axis of [001]. Because the magnetization was aligned along the [001] axis and the reflection plane was (001) with a scattering angle of 90 degrees (the above (c) configuration), the spin-magnetic form factor was selectively measured. The experimental setup is shown in Fig. 3. We measured the change in the diffraction intensity accompanied by reversing the magnetization direction, so-called the flipping ratio, and obtained the spin-magnetic form factor (μ_S(k)) of the reciprocal lattice points of 0 0 6, 0 0 8, 0 0 10, and 0 0 12. The results are shown in Fig. 4. The observed spin-magnetic form factor shows almost negative values. This result is different from those of other 3d transition metal elements of Fe, Ni and Co which show almost positive values of the magnetic form factors for the magnitude of the scattering vectors in Fig. 4. The obtained spin-magnetic form factor should be related to the ordered orbital of the 3d electrons of Ti atoms. Further analyses and experiments are needed to elucidate the ordered orbital through the observed spin-magnetic form factors. The present experiment will be detailed elsewhere [6].

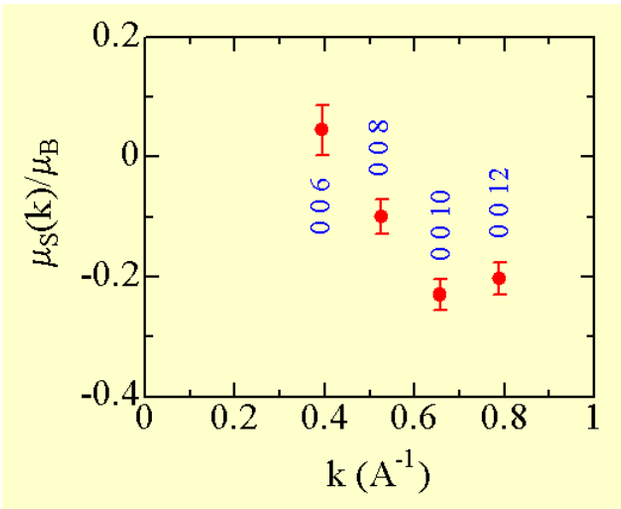

Figure 4.
Observed spin-magnetic form factor (μ_S(k)) of $YTiO_3$ at 5 K for reciprocal lattice points of 0 0 6, 0 0 8, 0 0 10 and 0 0 12. k = sin θ/λ where θ is the Bragg angle and λ is the X-ray wavelength. μ_B is the Bohr magneton.

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