

XANES study of charge ordering on the spin-Peierls phase transition of α' - NaV_2O_5

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α' - NaV_2O_5 transforms at $T_C = 34\text{K}$, and the origin of the phase transition seems to be caused by the charge order and spin-Peierls mechanism. However the experiments which reveal the existence of charge order are very little. We measured XANES of V atoms which relates to the valence of V. It was found that the valences of V atoms in NaV_2O_5 were $\text{V}^{4.5+}$ in the high temperature phase by comparing pre-edge and XANES of NaV_2O_5 with that of LiV_2O_5 , CaV_2O_5 and V_2O_5 . The analysis of EXAFS also shows the environment of the $\text{V}^{4.5+}$ state. **Keywords:** α' - NaV_2O_5 ;

charge order; spin-Peierls; XANES method.

1. Introduction

Vanadium compounds have various physical properties associated with the valence of V atoms. Among them, Isobe and Ueda successfully synthesized a high-quality inorganic compound α' - NaV_2O_5 (we abbreviate α' - NaV_2O_5 to NaV_2O_5) and discovered a spin-Peierls (SP) behavior in its magnetic susceptibility below $T_C = 34\text{K}$ (Isobe & Ueda, 1996). Both spin-gap and lattice dimerization were also observed by neutron scattering and x-ray scattering, respectively (Fujii *et al.*, 1997). Especially, a structural phase transition was indeed observed by x-ray diffraction (Fujii *et al.*, 1997), ^{23}Na NMR (Ohama *et al.*, 1997) and Raman scattering (Weiden *et al.*, 1997) measurements. Observed superlattice reflections in the x-ray diffraction could not be understood as a consequence of simple dimerization in isolated linear V^{4+} chains, and many other experimental observations question whether this material is an ideal one-dimensional system exhibiting an ordinary SP phase transition. Here, the important key to solve this problem is the structure at room temperature. A previous structural study of this compound at room temperature (Carpy & Galy, 1975) reported that the space group belongs to the nonsymmetric $\text{P2}_1\text{mn}$ and that there are two inequivalent sets of V sites assigned to V^{4+} and V^{5+} , respectively. From the structural point of view, V_2O_5 -layers compose of two-dimensionally connected VO_5 -pyramids in a - b plane, and V^{4+} atom having $s=1/2$ and V^{5+} atom not having spin range linear to b -axis, respectively. Below T_C , it seems that the SP phase transition is generated by V^{4+} atoms in a - b plane causing the dimerization. In the above paper (Fujii *et al.*, 1997), it is reported that the superlattice structure below T_C is $2a \times 2b \times 4c$ structure, as the structure

at room temperature is assumed $a \times b \times c$, and it is not possible to explain the low temperature structure by using the model of SP phase transition. Then, the doubt for the structure of the room temperature phase was produced.

Recent crystal structure analyses indicate that the space group belongs to the centrosymmetric Pmmn and that there is only one set of V site assigned to $\text{V}^{4.5+}$ (Schnering *et al.*, 1998; Smolinski *et al.*, 1998). Then the spins form a quarter-filled ladder structure along the b -axis, and the V^{5+} -O- V^{5+} rung dresses one localized $3d^1$ electron in dynamically fluctuating state $\text{V}^{4.5+}$ -O- $\text{V}^{4.5+}$. Below T_C , the charge orders like V^{4+} -O- V^{5+} . On the basis of this structure at room temperature, the structure below T_C was almost determined (Ludecke *et al.*, 1999). They applied 3+1 dimensional superspace group with a modulated structure. The origin of the phase transition of NaV_2O_5 is not a simple SP phase transition, but seems to be a charge ordering, which was suggested by NMR experiments (Ohama *et al.*, 1999) and predicted by theories (Seo & Fukuyama, 1998). However, there is almost no experiment to observe the charge order directly. Indeed, the experiment which examined the charge state of room temperature is not carried out except by ^{23}Na NMR. The purpose of this study is to examine the valence of V atoms in NaV_2O_5 at room temperature by using the X-ray absorption near-edge structure (XANES) method. In addition, we performed preliminary measurements below T_C .

2. Experimental

The XANES measurements were carried out at the XAFS beamline (BL01B1) of SPring-8. We used double Si 111 monochromators and a double-mirror to reduce the higher order contamination and to converge the vertical X-ray beam. The used energy was about 5.5keV which is near the K-edge of V atom. Energy resolution was about 0.5eV at 5.5keV. The incidence and transmittance monitors were ionization chambers containing He/ N_2 (30%) mixture and N_2 gas, respectively. The samples were the powder of MV_2O_5 ($M = \text{Na}, \text{Li}, \text{Ca}$ and non) holding in mending tape so as not to be absorbed by any other things except sample and settled between two ionization chambers. The cryostat of the He gas-circulative refrigerating type was used for the cooling. In this case, the mending tape entering the sample was hold in an aluminum foil so that heat conduction to the sample may be improved.

3. Results and discussions

3.1. Pre-edge

Fig.1 shows the pre-edge of several V compounds. Opened and closed triangles are the pre-edge of V_2O_5 and CaV_2O_5 , and opened and closed circles are the pre-edge of NaV_2O_5 and LiV_2O_5 , respectively. CaV_2O_5 and V_2O_5 are the reference samples of pure V^{4+} and V^{5+} compounds, respectively. The energy difference of the pre-edge between V^{4+} and V^{5+}

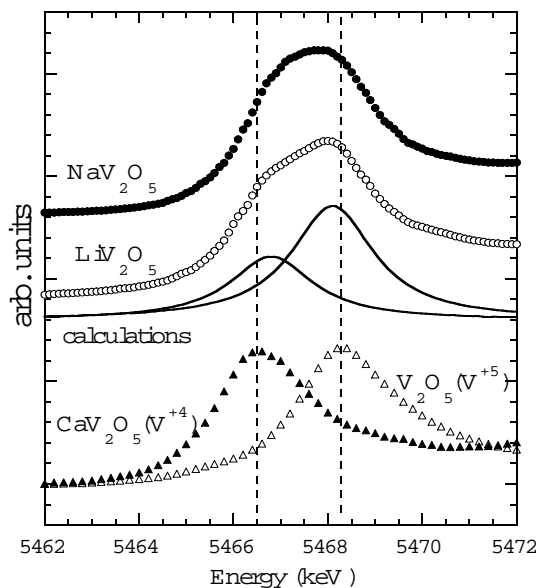


Figure 1

The pre-edge of V compounds. Opened triangles and closed triangles are the pre-edge of V_2O_5 and that of CaV_2O_5 , and opened circles and closed circles are the pre-edge of NaV_2O_5 and that of LiV_2O_5 , respectively.

is observed as about 1.8eV. As the third reference sample, we used LiV_2O_5 . The valences of V atoms in LiV_2O_5 are believed to be coexisting and ordered arrangement of V^{4+} and V^{5+} . The shape of pre-edge of LiV_2O_5 in Fig. 1 shows very characteristic one with two shoulder-like peaks whose positions are 5466.6 and 5468.0eV, respectively. In the figure, we show two components with solid line. The peak positions are closed to those of pre-edges of CaV_2O_5 and V_2O_5 , respectively. This result implies that we successfully decompose the pre-edge peak of LiV_2O_5 with V^{4+} and V^{5+} component, and that V atoms in LiV_2O_5 coexists of V^{4+} and V^{5+} state. Comparison of the pre-edge of LiV_2O_5 with that of NaV_2O_5 is very interesting because these compounds have same stoichiometry, though the structures are not equal. The pre-edge of NaV_2O_5 is located between the pre-edge of CaV_2O_5 and that of V_2O_5 , as well as that of LiV_2O_5 . But the shape of pre-edge of NaV_2O_5 and that of LiV_2O_5 are clearly different. The pre-edge of LiV_2O_5 has two peaks, while the shape of the pre-edge of NaV_2O_5 is broad one peak sitting between V^{4+} and V^{5+} positions. We failed to decompose the peak to two components. This result indicates that the charge state of V atoms in NaV_2O_5 is not ordered state but disordered state in the higher temperature phase.

3.2. XANES

Fig. 2(a) shows XANES of various V compounds. Opened and closed triangles are XANES of V_2O_5 and CaV_2O_5 , and opened and closed circles are XANES of LiV_2O_5 and NaV_2O_5 , respectively. Fig. 2(b) shows the enlarged view of absorption edge, which corresponds to a region surrounded with dotted lines in Fig. 2(a). In Fig. 2(b), the scale is adjusted so that the build-up value of the absorption edge and the highest peak become equal each other. It was found that

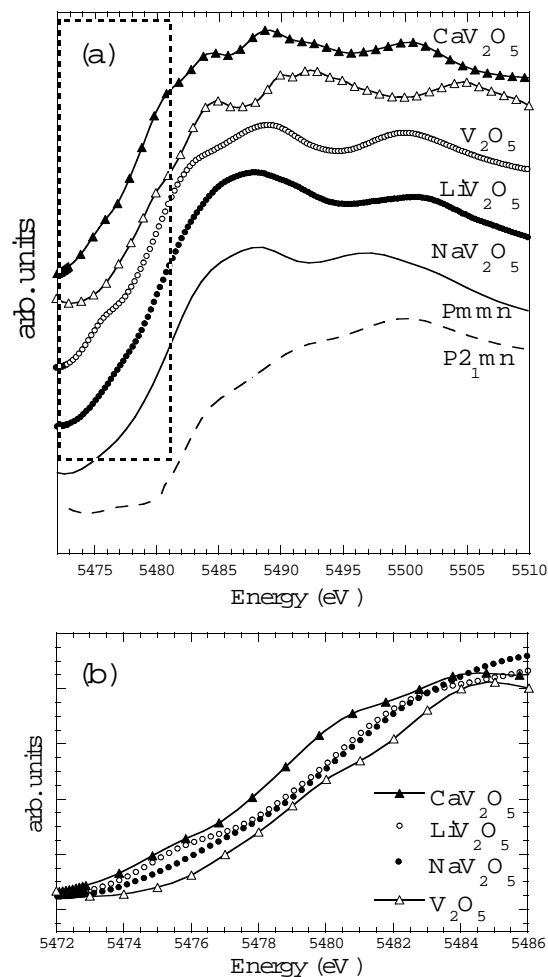


Figure 2

(a) XANES of various V compounds. Opened and closed triangles are XANES of V_2O_5 and CaV_2O_5 , and opened and closed circles are XANES of LiV_2O_5 and NaV_2O_5 , respectively. Lines and dotted lines are calculated ones by FEFF, based on the structure analysis (Pmmn and $P2_1mn$). (b) The enlarged view of absorption edge, which is a region surrounded with dotted lines in Fig. 2(a).

the spectra of LiV_2O_5 and NaV_2O_5 were between that of CaV_2O_5 and V_2O_5 . However the shape of the spectra of LiV_2O_5 and NaV_2O_5 was different each other. The former was the stairlike shape, and the spectra of lower energy side, ranged between 5472 and 5476eV, approached the spectra of CaV_2O_5 , and the spectra of higher energy side approached that of V_2O_5 . Toward this, the later was almost the middle between the spectra of CaV_2O_5 and that of V_2O_5 . This result seems that the valences of LiV_2O_5 are mixed valences with V^{4+} and V^{5+} , and those of NaV_2O_5 are disorder valence with $V^{4.5+}$.

Comparing the higher-energy positions of spectra, the peak positions or peak heights of each spectra are different, respectively. We examined the difference of charged state from the calculation by FEFF (Ankudinov *et al.*, 1998). Line and dotted line in Fig. 2(a) show calculated ones by FEFF, based on the structure analyses (Pmmn and $P2_1mn$). In these calculations, used cluster size was 60 atoms ($<6\text{\AA}$). Comparing the calculated spectra with the observed one, we can clearly conclude that the calculated spectra

using the atomic distances given by the structure analysis with the space group Pmmn resembles the observed spectra. This result implies that the environment of V atom is closed to the $V^{4.5+}$ state rather than the V^{4+} and the V^{5+} states.

Honestly speaking, however, we consider that the comparison of the two structure analyses are not fair, since the quality of the data are quite different. Then, we tried the calculation using the atomic distance given by the structure analysis (Chatterji & Weiden, 1998) with the space group Pmmn and using the mixed valences of V^{4+} and V^{5+} given by the structure analysis with the space group $P2_1mn$. This means that only valence of V atoms is belonging to the lower symmetry. The calculated result was almost the same as the one using the valences of $V^{4.5+}$, except the pre-edge peak. Therefore, we consider that XANES looks the environment of V atoms which is very sensitive to the valence state.

3.3. EXAFS

Fig. 3 shows EXAFS spectra of NaV_2O_5 . Closed circles are corresponding to the observed one, and lines are simulated ones by FEFF, based on the structure analysis (Pmmn and $P2_1mn$). For the simulation by FEFF, the difference of the spectra occurs from the difference of the geometric structure, because the reduction factor, intrinsic loss or thermal factor etc., has not been put in. These two EXAFS spectra simulated are very different. Table 1 shows the atomic distance between vanadium and oxygen atoms. In the space group Pmmn (Chatterji & Weiden, 1998), the distances between V and oxygen atoms exist only four types, and the valence of V is only one site $V^{4.5+}$. Toward this, in the space group $P2_1mn$ (Carpy & Galy 1975), the distances between V and oxygen atoms exist eight types, and the valences of V are V^{4+} and V^{5+} . Comparing two simulations with observed result, we can clearly conclude that the simulated result by using the atomic distances given by the structure analysis with the space group Pmmn resembles the observed result.

3.4. Low temperature experiments

We carried out the measurement of whether the shape of XANES of NaV_2O_5 changes to like that of LiV_2O_5 accompanied with the phase transition as we cooled down. However, such change was not observed down to 9K, in which temperature was measured at the cold-head position of the cryostat. Even in EXAFS measurement, there is no change as a function of the temperature. Though there are various possibilities on the reason why the XANES profile does not change on this experiment, nothing is clear about the low temperature phase at the moment. Details of the study will appear in a future.

4. Conclusions

We performed XANES measurement of NaV_2O_5 at BL01B1 in SPring-8. The shape of pre-edge of NaV_2O_5 is different from that of other V compounds, and the result suggests that the valence of NaV_2O_5 is $V^{4.5+}$ in the room temperature phase. Also the analysis of XANES calculated with FEFF suggests that the V atoms are disordered state in NaV_2O_5 . In addition, the analysis of EXAFS agrees with the structure based on the space group Pmmn at the room temperature phase, in which the charge state of V atoms is $V^{4.5+}$ from the symmetry requirement.

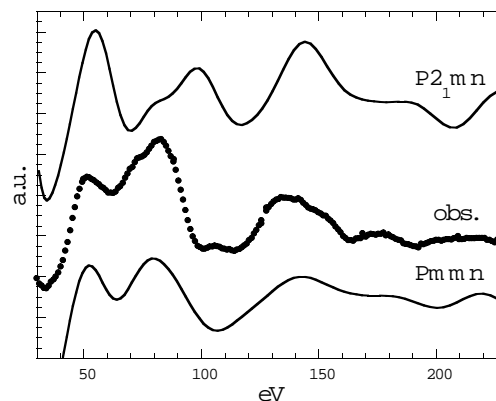


Figure 3
EXAFS spectra of NaV_2O_5 . Dotted ones are corresponding to the observed one, and lines are simulated ones by FEFF, based on the structure analysis (Pmmn and $P2_1mn$)

Table 1
The bond distance between Vanadium and oxygen

	Pmmn		$P2_1mn$
$V^{4.5+}-O1$	1.611(Å)	$V^{4+}-O1$	1.65(Å)
$V^{4.5+}-O2$	1.916(Å)	$V^{4+}-O3$	1.89(Å)
$V^{4.5+}-O3$	1.965(Å)	$V^{4+}-O4$	1.96(Å)
$V^{4.5+}-O4$	1.830(Å)	$V^{4+}-O4'$	1.96(Å)
$V^{4.5+}-O4'$	1.830(Å)	$V^{4+}-O2$	1.98(Å)
		$V^{5+}-O5$	1.53(Å)
		$V^{5+}-O3$	1.76(Å)
		$V^{5+}-O2$	1.87(Å)
		$V^{5+}-O2'$	1.87(Å)
		$V^{5+}-O4$	1.98(Å)

References

- Isobe, M. & Ueda, Y. (1996). *J. Phys. Soc. Jpn.* **65**, 1178–1181.
 Fujii, Y., Nakao, H., Yoshihama, T., Nishi, M., Nakajima, K., Kakurai, K., Isobe, M., Ueda, Y. & Sawa, H. (1997). *J. Phys. Soc. Jpn.* **66**, 326–329.
 Ohama, T., Isobe, M., Yasuoka, H., & Ueda, Y. *J. Phys. Soc. Jpn.* **65**, 545–548.
 Weiden, M., Hauptmann, R., Geibel, C., Steglich, F., Fischer, M., Lemmens, P. & Guntherodt, G. (1997). *Z. Phys. B* **103**, 1–3.
 Carpy, A. & Galy, J. (1975). *Acta Crystallogr. B* **31**, 1481–1482.
 von Schnering, H., G., Grin, Yu., Kaupp, M., Somer, M., Kremer, R., K., Jepsen, O., Chatterji, T. & Weiden, M. (1998). *Z. Kristallogr.* **213**, 246.
 Smolinski, H., Gros, C., Weber, W., Peuchert, U., Roth, G., Weiden, M. & Geibel, C. (1998). *Phys. Rev. Lett.* **80**, 5164–5167.
 Ludecke, J., Jobst, A., van Smaalen, S., Morre, E., Geibel, E. & Krane, H.-G. (1999). *Phys. Rev. Lett.* **82**, 3633–3636.
 Ohama, T., Yasuoka, H., Isobe, M. & Ueda, Y. (1999). *Phys. Rev. B* **59**, 3299–3302.
 Seo, H. & Fukuyama, H. (1998). *J. Phys. Soc. Jpn.* **67**, 2602–2605.
 Ankudinov, A., L., Ravel, B., Rehr, J., J. and Conradson, S., D. (1998) *Phys. Rev. B* **58**, 7565–7576.
 Murata, T., Matsukawa, T., Naoe, S., Horigome, T., Matsudo, O. & Watanabe, M. (1992). *Rev. Sci. Instrum.* **63**(1), 1309–1312.
 Spiller, J. (1981). *AIP Conf. Proc.* **75**, 124–130.
 Urisu, T. & Kyuragi, H. (1987). *J. Vac. Sci. Technol. B* **5**, 1436–1440.