



High-energy spectroscopy of NaV_2O_5

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Abstract

Oxygen K-edge X-ray absorption spectroscopy of NaV_2O_5 at various temperatures both above and below $T_c = 34$ K for $E\parallel a$ and $E\parallel b$ was carried out. The spectra taken above T_c showed little temperature dependence whereas significant change was observed between the spectra taken at 70 and 25 K. This change in the electronic structure through T_c may be due to the phase transition from the V–O–V molecular orbital state to the charge disproportionated ground state. © 2000 Elsevier Science B.V. All rights reserved.

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Recently, NaV_2O_5 was found to be a quasi-one-dimensional spin system which exhibits a spin-Peierls (SP) transition at 34 K [1]. Its crystal structure was reported to be noncentrosymmetric structure ($P2_1mn$) characterized by the charge ordered V^{4+} ($S = \frac{1}{2}$) and V^{5+} ($S = 0$) chains along the b -axis [2]. This discovery has invoked strong interest in NaV_2O_5 and joined many theoretical and experimental efforts. However, those experimental results were not always explained in terms of a SP transition. As for the crystal symmetry at room temperature, a new X-ray diffraction experiment revealed a centrosymmetric ($Pm\bar{m}n$) crystal structure with only one type of V site, indicating it to be a quarter-filled ladder compound with the spins carried by V–O–V molecular orbitals on the rungs [3]. Therefore, the crystal symmetry as well as the spin state of NaV_2O_5 both above and below T_c is still a controversial issue. In this work, we performed oxygen K-edge X-ray absorption spectroscopy (XAS) of NaV_2O_5 at temperatures above and below T_c . O K-edge XAS is a very useful tool in the study of this phase transition because it maps the unoccupied states of the V 3d band through O 2p–V 3d covalent mixing.

The XAS measurements were carried out at the BL-19B at the Photon Factory, using the varied-line space-grating monochromator. The XAS spectra were measured by fluorescence yield to avoid surface contribution in an ultrahigh vacuum chamber where the base pressure was approximately 5×10^{-10} Torr. The single crystal of NaV_2O_5 was cleaved in situ parallel to the ab -plane. The single crystal growth and sample characterization are described elsewhere [1].

Fig. 1(a) shows the O K-edge XAS spectra of NaV_2O_5 taken at several temperatures for $E\parallel b$. The spectra have structures up to about 536 eV due to V 3d character in the unoccupied states. Note that little temperature dependence was observed above 70 K, whereas significant change was observed between the spectra taken at 25 and 70 K. This means the change of the electronic structure of the V 3d band accompanies this transition. The spectra taken above 70 K have a strong peaked structure at 530.6 eV and a broad structure around 533 eV. Roughly speaking, the former structure corresponds to d_{xy} , d_{yz} , and d_{zx} orbitals and the latter one to the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states, respectively. At 25 K, the intensity just above the absorption edge is strongly suppressed. According to the calculated energy bands within density-functional theory [3], this suppressed structure corresponds to the bonding-type V–O–V molecular orbitals made up of the d_{xy} orbitals which consist the rung of the V ladder. That is to say the electronic structure of the bonding molecular orbitals undergoes significant change at 34 K. Furthermore, the higher-lying bands of the 70

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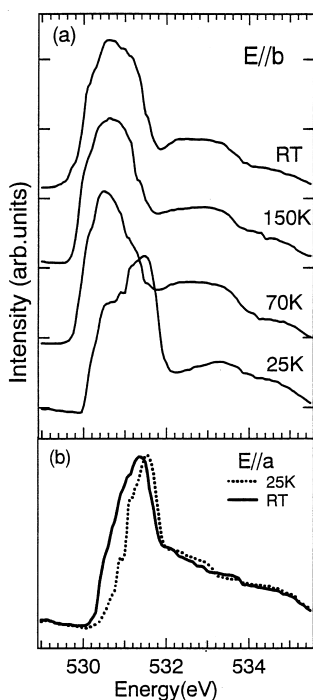


Fig. 1. (a) Temperature dependence of oxygen K-edge XAS spectra of NaV_2O_5 for $E//b$ taken at 25, 70, 150 K, and room temperature. (b) Temperature dependence for $E//a$ taken at 25 K and room temperature.

and 25 K spectra also show difference in their shapes and peak positions, which is indicative of the existence of other transformation derived from the transition.

The temperature dependence for $E//a$ XAS spectra is shown in Fig. 1(b). As compared with the $E//b$ spectra, less temperature dependence was observed. They both exhibit a single peak structure around 531.4 eV and little difference were observed in the higher-lying bands. The only difference was the spectral intensity at lower-energy side of the peak around 530–532 eV. It can also be attributed to the change in the bonding V d_{xy} orbital. Aside from the d_{xy} orbitals, the electronic structure along the a -axis hardly changed contrary to that along the b -axis. Here, we compared our XAS results with the reported optical conductivity spectra. In the optical conductivity experiment [4], two spectral features ascribed to charge transfer excitations from the occupied V 3d to the empty 3d site (d - d transition) and that from O p_x or p_y to V d_{xy} orbitals were observed. The former feature is unable to observe in XAS. The latter structure, on the other hand, roughly corresponds to a XAS spectrum that reflects an excitation from O 1s to V 3d orbitals. However, those two structures in the optical spectra scarcely changed over a wide temperature range above and below T_c , which contradicts our XAS results. Nishimoto et al.

[5] explained this result by assuming the system to be in a charge disproportionated state both above and below T_c , and attributed the conflict with the recent X-ray structural analysis [3] and NMR measurement [6] to an issue of time scale of measurement. If this assumption works, no temperature dependence should be observed in the XAS spectra because the frequency of the electric field of X-ray is incomparably faster than the charge fluctuation of V ions. Although we cannot definitely conclude this, there should occur significant change in the electronic state such as the molecular orbital state to the localized charge disproportionated one to explain this temperature dependence.

In addition to the temperature dependence, a polarization dependence of the XAS spectra of NaV_2O_5 is worthy of note. First, we compared the $E//a$ and the $E//b$ spectra taken at room temperature. The $E//b$ spectrum arises around 529.5 eV whereas no intensity is observed in the $E//a$ spectrum in this energy region. This result is consistent with the calculations which revealed that the bands which disperse around the Fermi level are only seen in the Γ - Y direction or b -axis. Here again, we compared the XAS results with the optical conductivity experiment. The excitation feature from O to V d_{xy} orbitals was reported to be anisotropic between $E//a$ and $E//b$ [4]. The onset energy of this feature is different by about 0.5 eV, which is quantitatively consistent with our XAS spectra. This is the evidence of strong one-dimensionality in NaV_2O_5 . Next, we focused our attention to the polarization dependence below T_c . Similarly, strong difference was observed between the $E//a$ and $E//b$ spectra. Especially, the intensity just above the threshold is quite different, but the both curves reach maximum at 531.6 eV and the onset energy is not so different as that of room temperature.

In conclusion, the temperature dependence and the polarization dependence of O K-edge XAS was reported. We observed that significant changes in electronic state occur along the b -axis at 34 K. We must conclude that the crystal symmetry of NaV_2O_5 of the higher- and the lower-temperature phase are different, but this contradicts with the analysis of the optical conductivity experiment. To the further understanding of the phase transition of NaV_2O_5 , we must wait for detailed experimental and theoretical studies.

References

- [1] M. Isobe, Y. Ueda, J. Phys. Soc. Japan 65 (1996) 1178.
- [2] P.A. Carpy, J. Galy, Acta Crystallogr. B 31 (1975) 1481.
- [3] H. Smolinski et al., Phys. Rev. Lett. 80 (1998) 5164.
- [4] S.A. Golubchik et al., J. Phys. Soc. Japan 66 (1997) 4042.
- [5] S. Nishimoto, Y. Ohta, J. Phys. Soc. Japan 67 (1998) 3679.
- [6] T. Ohma et al., Phys. Rev. B 59 (1999) 3299.