Angle-resolved photoemission study of the quasi-one-dimensional superconductor β-Na$_{0.33}$V$_2$O$_5$

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We have studied the electronic structure of β-Na$_{0.33}$V$_2$O$_5$, which becomes a superconductor under pressure, by angle-resolved photoemission spectroscopy. Clear band dispersions are observed only along the chain direction, indicating the quasi-one-dimensional (1D) electronic structure. The spectra of the V 3d band are dominated by a Gaussian-like broad feature at ~ 1 eV below the Fermi level (E_F) with negligible intensity at E_F, which we attribute to strong electron-phonon coupling as in other 1D polaronic metals. In the momentum space, the spectra show a maximum intensity at $k \sim \pm \pi/4b$, where b is the V-V distance along the b axis, reflecting the band filling of the chain and/or ladder.

The recent discovery of superconductivity ($T_C = 8$ K) under high pressure (8 GPa) in β-Na$_{0.33}$V$_2$O$_5$ attracted considerable interest[1] because this is the first observation of superconductivity in vanadium oxides and because the superconductivity occurs in a quasi-one-dimensional conductor analogous to organic superconductors. β-Na$_{0.33}$V$_2$O$_5$ belongs to a class of β-vanadium bronzes which have highly anisotropic crystal structures as shown in Fig. 1. There are three kinds of V sites denoted by V1, V2, V3. The V1O$_6$ octahedra form a zigzag chain along the b axis, the V2O$_6$ octahedra form a two-leg ladder, and the V3O$_5$ pyramids form a zigzag chain. Previously, this compound had been studied from the view point of a bipolaron conductor.[2] Recently, Yamada *et al.*[3] found that a metal-insulator transition (MIT) occurs at $T_{MI} = 135$ K and that above T_{MI} it shows metallic conductivity along the chain direction (the b axis). Itoh *et al.*[4] found by a NMR study that this metal-insulator transition is accompanied by a charge ordering below T_{MI}. They also discussed the population of d electrons at each vanadium site and concluded that the V3 is V^{5+}-like while the V1 and/or V2 are in a mixed-valence state. Nishimoto and Ohta studied charge ordering by Mardelung potential calculations and found that electrons enter the V1 zigzag chain in the most stable charge distribution.[5] The superconductivity in this material invoked considerable interest also because of possible roles of polarons or electron-phonon interaction in the superconductivity. The electronic structure is also interesting from the viewpoint of one dimensionality.[6,7]

In this Rapid Communication, we report on an electronic structure study of β-Na$_{0.33}$V$_2$O$_5$ using angle-resolved photoemission spectroscopy (ARPES). We have found that the V 3d band has a Gaussian-like broad line shape and its peak does not cross E_F even in the metallic phase. In the momentum space, on the other hand, the maximum intensity of the V 3d band occurs at $k \sim \pm \pi/4b$ although in the vicinity of E_F, the intensity is suppressed. We shall discuss the origins of these unusual spectral behaviors in the context of one-dimensional (1D) metal under the strong influence of polaronic effect.

Single crystals of β-Na$_{0.33}$V$_2$O$_5$ were grown by the rf heating Czochralski method as described in Ref. 1. Photoemission measurements were performed using a Gammadata-Scienta SES-100 electron analyzer and a Gammadata-Scienta VUV-5000 He discharge lamp with a toroidal grating monochromator. The energy calibration and the estimation of the energy resolution were made by measuring gold spectra. The energy resolution and the momentum resolution were set at ~ 25 meV and $\pm 0.2°$ near E_F and ~ 40 meV and $\pm 0.4°$ otherwise. The base pressure of the
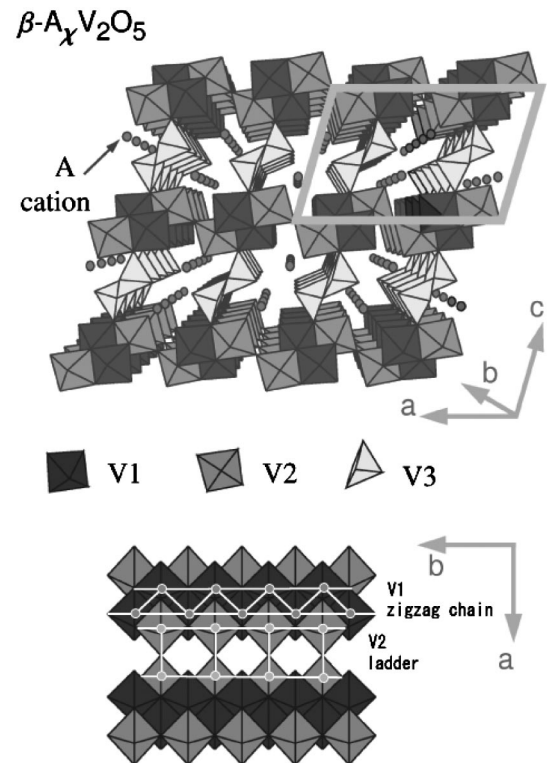

FIG. 1. Crystal structure of β-vanadium bronze A_xV$_2$O$_5$. Schematic drawing of the V1 zigzag chain and the V2 ladder is also shown.
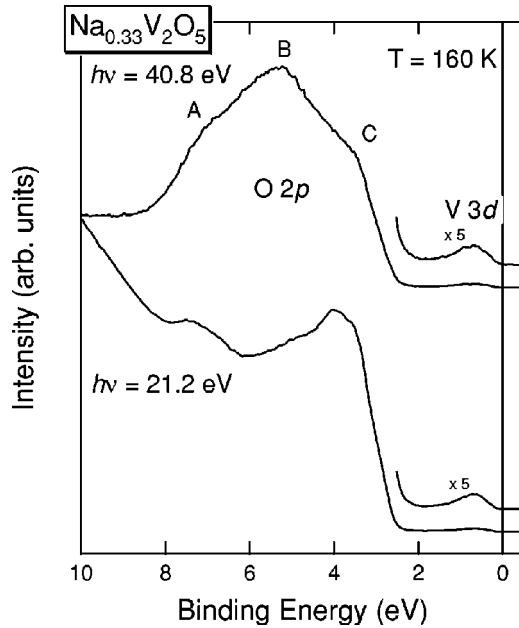
FIG. 2. Normal emission spectra of β-$Na_{0.33}V_2O_5$ taken at 160 K.

analyzer chamber was 5×10^{-10} Torr. Clean surfaces were obtained by cleaving the sample *in situ*. We have collected ARPES data within 2 h after cleaving and confirmed that the spectra did not change from that measured right after cleaving. The reproducibility was checked by repeated cleaving and measurements.

Figure 2 shows the spectra in the entire valence-band region taken with He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) at normal emission. Because no structure was observed around 9–10 eV, where surface contamination signal emerges in transition-metal oxides, we can say that the cleaved surface was sufficiently clean. The structures at 2.5–8 eV binding energies (E_B's) are originated from the O $2p$ band while the weak feature at $E_B \simeq 1$ eV is originated from the V $3d$ states. Because there is only one V $3d$ electron per six vanadium atoms, the intensity of the V $3d$ band is extremely weak. The relative intensity of the V $3d$ band to the O $2p$ band is reduced to $\sim 1/3$ compared to that of NaV_2O_5 (Ref. 8) and LiV_2O_5 (Ref. 9). This indicates that surface stoichiometry is nearly the same as that in the bulk. Among the three structures in the O $2p$ band, A, B, and C, structure B is enhanced in the He II spectrum compared to He I, indicating that this structure is strongly hybridized with the V $3d$ states since the relative photoionization cross section of the V $3d$ states to the O $2p$ states is larger for the He II spectra than for the He I spectra.[10]

Figure 3 shows the angular dependence of the spectra taken at 160 K. The left panels (a) and (c) show the spectra with momentum along the chain (b axis) while the right panels (b) and (d) show the spectra with momentum perpendicular to the chain (i.e., along the c axis). The vertical lines in the O $2p$ band indicate local minimum positions in the second derivative of the spectra while those in the V $3d$ band indicate peak positions and the inflection points determined by the first and second derivatives, respectively. Clear dis-
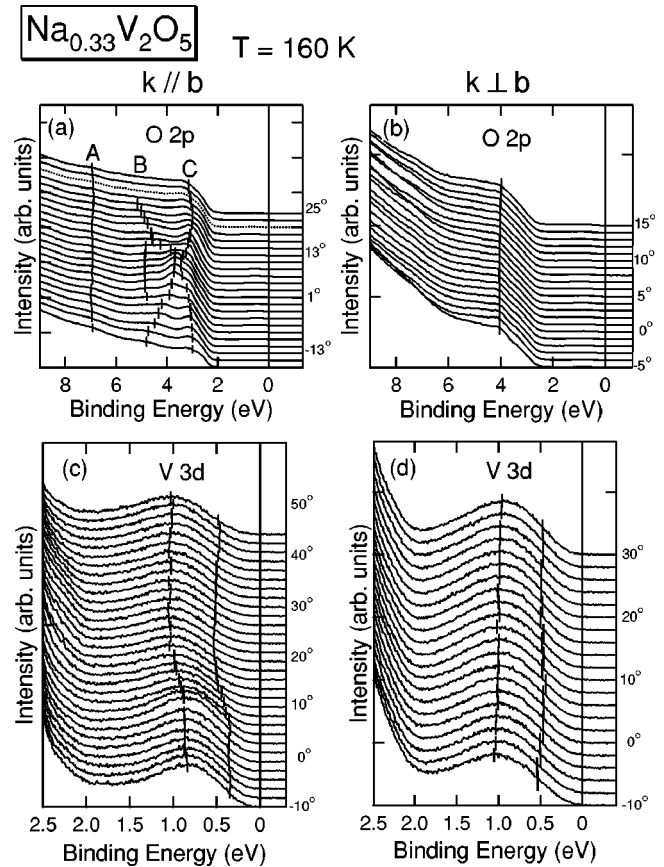

FIG. 3. ARPES spectra of β-$Na_{0.33}V_2O_5$ taken at 160 K. The vertical lines indicate peak positions or inflection points.

persion can be seen only along the chain direction both for the O $2p$ and the V $3d$ bands. Structure B is the most strongly dispersive in the O $2p$ band probably because this structure is most strongly hybridized with the V $3d$ states as mentioned above. The V $3d$ band has a broad line shape and the peak position is located at $E_B \sim 0.9$ eV. The dispersional width is ~ 0.25 eV.

The peak position of the V $3d$ band in β-$Na_{0.33}V_2O_5$ is closer to E_F than that in the related insulating vanadates NaV_2O_5 ($E_B \sim 1.5$ eV, Ref. 8) and LiV_2O_5 ($E_B \sim 1.3$ eV, Ref. 9) with d^1 electronic configuration, reflecting the smaller band filling or the lower E_F in the present compound. However, the intensity is suppressed near E_F and the peak does not disperse sufficiently to allow the band crossing E_F. The ARPES spectra of a quasi-1D conductor $(TaSe_4)_2I$, which shows a charge-density wave (CDW) transition at 160 K, as reported by Perfetti *et al.*[11] also show a similar behavior in its metallic phase and only the tail of the Ta $5d$ band reaches E_F. They interpreted this characteristic spectral feature of $(TaSe_4)_2I$ in terms of a polaron picture[12] because electron-phonon interactions are obviously important in CDW systems such as $(TaSe_4)_2I$. In fact, for β-$Na_{0.33}V_2O_5$ strong electron-phonon coupling had been proposed.[2] The Gaussian-like broad feature of the V $3d$ band and the small spectral weight at E_F may therefore be attributed to strong electron-phonon coupling. The high resistivity ($\sim 10^{-2}$ Ω cm) for a metal may indicate that electron-
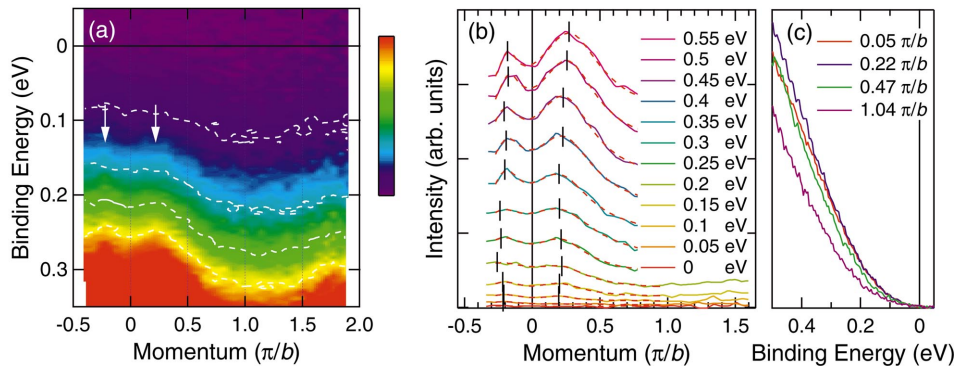
FIG. 4. (Color) (a) Intensity plot of ARPES spectra near E_F in the E-k plane. The vertical arrows indicate $k = \pm \pi/4b$. (b) Momentum distribution curves. Dashed curves are fitted Lorentzians and the vertical lines indicate their peak positions. (c) Energy distribution curves.

phonon interaction is very strong and that the charge carriers are mobile small polarons.[13] In a recent optical study, too, it has been proposed that the charge carriers in β-$Na_{0.33}V_2O_5$ should be regarded as small polarons.[14]

In order to make the above argument precise, we should take into account the effects of surface contribution because it has been known that the electronic states around 1 eV of vanadium oxides are strongly effected by the surface for low-photon energies used here.[15–17] However, if only the bulk electronic structure had sharp structures, it should be visible overlapping the broad surface feature because the bulk component should have finite contribution even for this low-photon energy. Hence, one can conclude that the bulk electronic states also have the broad feature. In the following, we discuss the electronic structure near E_F. The discussions will not be altered even if we take into account the surface effects because the surface states tend to be insulating and spectral features near E_F arise mainly from bulk states.[15,18]

The intensity plot of the ARPES spectra near E_F in the E-k plane is shown in Fig. 4(a). One can see that the contour lines become closest to the E_F at $k \sim \pm \pi/4b$. From the fitting of the momentum distribution curves (MDC's) to two Lorentzians, as shown in Fig. 4(b), their peak positions indicated by the vertical bars are $\pm (0.22 \pm 0.02) \pi/b$ ($\sim \pm \pi/4b$), where b is the V-V distance along the b axis of the zigzag chains or of the ladder [see Fig. 1(b)], and depend on E_B only very weakly (corresponding to the Fermi velocity of > 10 eV Å). This means that although most of the spectral weight of the V $3d$ band is confined in the Gaussian-like broad peak centered at $E_B \sim 0.9$ eV and the Gaussian peak does not cross E_F, there are underlying strongly dispersive features and their Fermi surface crossings at $k \simeq \pm \pi/4b$. Strongly dispersive weak feature crossing E_F has been observed in a double-layer metallic manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ (Refs. 19 and 20), where the spectra are also dominated by a broad Gaussian-like peak at higher binding energy and a very weak feature reaches and crosses E_F. To explain this unusual spectral behavior, a polaron model has been proposed.[19,20]

The occurrence of the maximum intensities at $k \simeq \pm \pi/4b$ is contrasted to the corresponding feature in the insulating NaV_2O_5 (Ref. 8) and LiV_2O_5 (Ref. 9), whose band maxi-

mum and hence the maximum intensity near E_F occurs at $k \simeq \pm \pi/2b$. The smaller value $k \simeq \pm \pi/4b$ in the present compound should be related to the smaller band filling of the chains and/or ladders in β-$Na_{0.33}V_2O_5$. Based on this observation, in the following we discuss possible band filling of the V1 zigzag chain and the V2 ladder for several cases depending on the relative strength of the nearest-neighbor and next-nearest-neighbor V-V hopping in the chain and the relative strength of the V-V hopping within the rung and within the leg of the ladder. First, we consider the case where the bonding within the rung and the nearest-neighbor hopping in the zigzag chain are strong. If the doped electrons enter the V $3d$ orbitals only of the ladder, the ladder would become quarter filled (1/2 electron per V2 site) and the band filling would be similar to NaV_2O_5. In the high-temperature phase of NaV_2O_5, because the bonding orbital of the rung is occupied and the antibonding orbital is empty, the quarter-filled ladder effectively behaves as a half-filled 1D chain, and the ARPES spectra are well reproduced by the half-filled 1D t-J model or Hubbard model,[21] resulting in the band maximum at $k = \pm \pi/2b$. We expect the same situation for the quarter-filled ladder in β-$Na_{0.33}V_2O_5$. If the doped electrons enter only the zigzag chain, the chain would be quarter filled and the Fermi-level crossing (and hence the intensity maximum) would occur again at $k = \pm \pi/2b$. (Note that there are two V1 atoms per b.) If $\sim 50\%$ of doped electrons go into the zigzag chain (resulting in the 1/8-filled zigzag chain) and the remaining $\sim 50\%$ go into the ladder (the 1/8-filled ladder), Fermi-level crossing would occur at $k = \pm \pi/4b$, consistent with experiment. In this case, the band filling of the chain and ladder is determined by a subtle balance between the energy levels of the chain and the ladder and therefore may vary sensitively under high pressure. Electrons may be transferred between the zigzag chain and the ladder under high pressure as in the hole-doped ladder system $Sr_{14-x}Ca_xCu_{24}O_{41}$ (Ref. 22), which also shows a pressure-induced superconductivity.

Second, we consider the case where the bonding within the rung of the ladder is weak or the nearest-neighbor hopping in the zigzag chain is weak compared to the next-nearest-neighbor hopping in the chain. Indeed, the bonding within the rung of the ladder in β-$Na_{0.33}V_2O_5$ may be weaker than that of NaV_2O_5, because the V-V distance is

longer: 3.6 Å for β-$Na_{0.33}V_2O_5$ versus 3.45 Å for NaV_2O_5. In that case, the ladder or the zigzag chain can be regarded as two independent single chains. Therefore, if $\sim$50% of doped electrons go into one of the two independent chains and the remaining $\sim$50% go into another chain, these chains become quarter-filled single chains and the intensity maximum would occur at $k = \pm\pi/4b$ near E_F. Hence, electrons may enter both of the ladder and the zigzag chain, or may enter either the ladder or the chain, because that ladder or zigzag chain consists of two quarter-filled chains. The existence of quarter-filled single chains is analogous to the quarter-filled quasi-1D band in organic superconductors such as Bechgaard salts.[23]

Since β-$Na_{0.33}V_2O_5$ is shown to be a 1D metal above T_{MI} ($= 135$ K), we have attempted to analyze the photoemission spectra within the Tomonaga-Luttinger (TL) liquid framework. In Fig. 4(c), energy distribution curves (EDC's) near E_F are shown for the metallic phase. As mentioned above, the intensity is suppressed near E_F, which is a characteristic of a TL liquid. The line shape is approximately parabolic for all momenta. Therefore, the anomalous exponent α is at least $\sim$ 2 in the present system,[7,24] extremely large compared to other 1D conductors ($\alpha \lesssim 1$).[25–27] Note that the Hubbard model predicts $\alpha < 1/8$ (Ref. 28). One possible origin of the large α is that electron-phonon interaction is strong compared to other systems. Another possibility is that the long-range Coulomb interaction is unscreened because there are few conducting carriers. Theoretically, it has been shown that

if long-range interaction exists, the exponent α can be any large value.[29]

Finally, we briefly comment on the temperature dependence of the spectra across T_{MI}. The leading edge of the V $3d$ band is shifted toward higher binding energies by $\sim$15 meV in going from the metallic to insulating phases, taken at 160 K and 100 K, respectively. We have also studied changes in the band dispersion from the peak positions and the inflection points [Fig. 3(c)]. We could not, however, observe clear change from those plots across T_{MI}.

In conclusion, we have studied the electronic structure of β-$Na_{0.33}V_2O_5$. The band dispersion is finite only along the chain direction, indicating the quasi-1D electronic structure. In spite of the metallic conductivity, the V $3d$ band has a Gaussian-like broad feature whose peak does not cross the Fermi level. We attributed this to the strong electron-phonon coupling in the quasi-1D metal. In the momentum space, the V $3d$ band shows maximum intensities at $k \sim \pm\pi/4b$, due to a Fermi-level crossing or a valence-band maximum. Based on this observation, we have discussed possible band filling of the zigzag chain and the ladder in β-$Na_{0.33}V_2O_5$.

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