Single-Particle Excitations in One-Dimensional Mott-Hubbard Insulator NaV_2O_5

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(Received 2 September 1997)

We have made an angle-resolved photoemission study of NaV_2O_5 at room temperature, i.e., in the paramagnetic phase well above the spin-Peierls transition temperature. The obtained results reflect the one dimensionality of the electronic structure. The lower binding energy side of the V $3d$ band shows a clear momentum-dependent modulation with the periodicity of π, indicating the existence of antiferromagnetic correlations or holon excitations in the one-dimensional Mott insulator. We compare the results with recent theoretical works on the one-dimensional Hubbard and t-J models and discuss consistency between model parameters. [S0031-9007(98)05765-2]

PACS numbers: 71.10.Pm, 71.27.+a, 75.20.Ck, 79.60.−i

Recently, quantum-spin systems in low dimensional compounds such as spin-Peierls [1,2], spin-ladder, Haldane, and frustrated Heisenberg systems have attracted considerable interest. The most basic but far from trivial among them is the one-dimensional (1D) antiferromagnetic (AF) Heisenberg chain and its excitation spectra. Theoretical works on its excitation spectra based on the Hubbard model or t-J model have shown signs of spin-charge separation: as a result of one dimensionality, the degrees of freedom of an electron are decoupled into spinlike and chargelike elementary excitations called "spinon" and "holon," respectively [3]. Parameters appearing in those models are the transfer integral t between nearest neighbors, the exchange coupling constant J (> 0) and the on-site Coulomb energy U. Exact diagonalization and analytical studies [3–7] have shown that the single-particle spectral function has spinon and holon dispersions for momentum $k < \pi/2$. The energy scale of the holon excitation is given by t, while that of the spinon excitation is given by J. In the photoemission spectra, from $k = 0$ to $\pi/2$ the holon excitations disperse towards the chemical potential and beyond $k = \pi/2$ disperse back. In the case of the $U \to \infty$ ($J \to 0$) 1D Hubbard model [3], which can be solved analytically, the holon dispersion has two branch cuts at $E(k) = E_0 + 2|t| \sin k$ and $E_0 - 2|t| \sin k$, between which there exist continuum excitations. The spinon band is located at $E(k) = E_0$ ($k < \pi/2$) and has no dispersion because $J \to 0$. Observation of a dispersional width of $\sim t$ is therefore an indication of spin-charge separation. Experimentally, an angle-resolved photoemission spectroscopy (ARPES) study has been performed for a 1D charge-transfer type insulator $SrCuO_2$ [8], and the spectra agree well with calculations on the 1D t-J model with parameters appropriate for this compound, exhibiting such spinon and holon excitations. Because the t-J model is an effective low-energy Hamiltonian of the more realistic but complicated p-d model for the Cu-O chain, it is natural to ask whether simpler Mott-Hubbard (MH) systems [9] can be described by the Hubbard model.

In this Letter, we report on an ARPES study of α'-NaV_2O_5, typical 1D MH-type insulators in the paramagnetic phase. We focus on a dispersive feature of V $3d$ character in the lower Hubbard band. We compare our results with the theoretical results on the 1D Hubbard [3,4] and t-J [6] models. α'-NaV_2O_5 is the second example of inorganic spin-Peierls (SP) compounds [10] discovered following $CuGeO_3$ [1]. As shown in Fig. 1 [11], it consists of layers (ab planes) of VO_5 square pyramids isolated by interlayer Na ions. The V atoms are in a mixed valent state of V^{4+}:V^{5+} = 1:1 and are charge ordered in one-dimensional rows: V^{4+} (d^1, $S = 1/2$) and V^{5+} (d^0) chains are alternatingly running along the b axis. The VO_5 pyramids are sharing corners along the chain direction. As a result, this compound is expected to behave as an ideal 1D-AF system (1D half-filled MH system) with nearest-neighbor exchange interaction, being much simpler than $CuGeO_3$ [12]. Indeed, the magnetic susceptibility $\chi(T)$ is well fitted to the characteristic curve for the 1D-AF Heisenberg chain (the Bonner-Fischer curve [13]) with $J \sim 560$ K above the SP transition temperature $T_{SP} = 34$ K [10]. Below T_{SP}, $\chi(T)$ decreases rapidly. Here, we restrict ourselves to the paramagnetic phase at

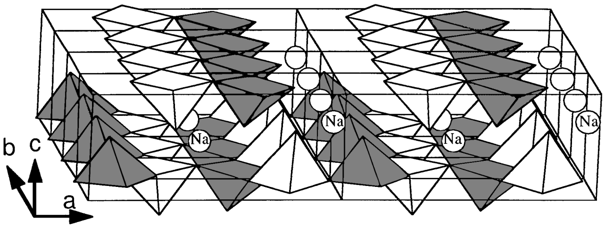

FIG. 1. Crystal structure of α'-NaV_2O_5. The $V^{4+}O_5$ and $V^{5+}O_5$ pyramids running along the b axis are shown by the white and shaded square pyramids, respectively.

room temperature. In fact, severe charging effect prohibited us from doing measurements at lower temperatures.

Single crystals of NaV_2O_5 with typical sizes $\sim 1 \times 0.5 \times 4\ \text{mm}^3$ were prepared by the melt growth method using $NaVO_3$ as a flux [14]. The crystals could be cleaved parallel to the ab plane. ARPES measurements were made using the He I resonance line ($h\nu = 21.2$ eV) and a hemispherical analyzer. The angular resolution was ±1° and the energy resolution was set 80–100 meV. Measurements were done for several cleaves to confirm the reproducibility. Here, we present reproducible results on "good cleaves" as judged from laser reflection. The base pressure in the spectrometer was below 1×10^{-10} Torr.

Figure 2 shows ARPES spectra in the entire valence-band region. The upper panel shows spectra with momentum parallel to the b axis ($k \parallel b$), and the bottom panel those with momentum parallel to the a axis ($k \perp b$). The prominent features at binding energies (E_B) from 3 to 8 eV are the O $2p$ band, while the weaker structures between 0.5 and 3 eV are the V $3d$ band. The spectra are normalized to the area of the O $2p$ band. The $k \parallel b$ spectra in the upper panel clearly show dispersive O $2p$ features as marked by the dashed curves. Around $k = 0$ (take-off angle $\theta = 0°$) the spectra have three distinct peaks. The top of the O $2p$ band appears to be located around $k = \pi$. In contrast, the $k \perp b$ spectra in the bottom panel are nearly independent of angles. This supports the view that NaV_2O_5 has a highly anisotropic electronic structure with sizable dispersions only along the b axis. This is not obvious from the crystal structure alone, however, because it has a two-dimensional V-O network in the ab plane (see Fig. 1). Presumably, the dispersions of the O $2p$ bands are predominantly caused by hybridization with V $3d$ states, which are arranged in the one-dimensional way.

The V $3d$ band located between $E_B = 0.5$ and 3 eV is broad and shows no spectral weight at the Fermi level (E_F), reflecting its insulating behavior. The broad peak centered at $E_B \sim 1.5$ eV, which has also been observed in other vanadium oxides such as insulating $LaVO_3$ [15], metallic $SrVO_3$, and $CaVO_3$ [16,17], would be attributed to the lower Hubbard band or its remnant feature separated from the upper Hubbard band by the Coulomb repulsion energy U. Looking at both the $k \parallel b$ and $k \perp b$ spectra in Fig. 2, we notice that the intensity of this peak takes a minimum around the normal emission ($\theta = 0°$). If the occupied V $3d$ orbital has xy symmetry lying in the ab plane [18], normal emission from this orbital is forbidden due to a selection rule [19]. The weak but finite intensity for the normal emission can be explained by the tilting of the VO_5 pyramid from the ab plane [11].

In Fig. 3, we show the spectra of the V $3d$ band normalized to the peak height at $E_B \sim 1.5$ eV. For the $k \parallel b$ spectra shown in Fig. 3(a), θ was varied from $-19°$ to $53°$, corresponding to $k = -0.7\pi$ to 1.8π

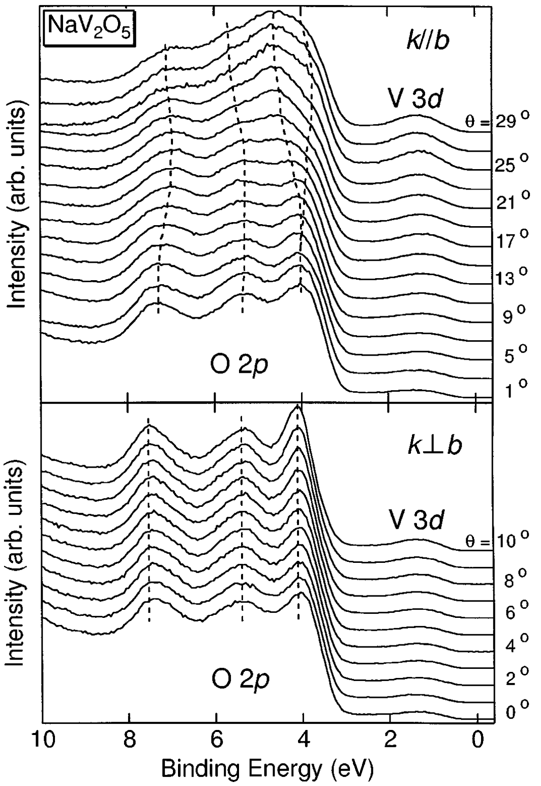

FIG. 2. ARPES spectra of NaV_2O_5 for various take-off angles θ. Upper panel: $k \parallel b$ axis. Lower panel: $k \perp b$ axis. The dashed lines indicate the dispersions of the O $2p$ bands.

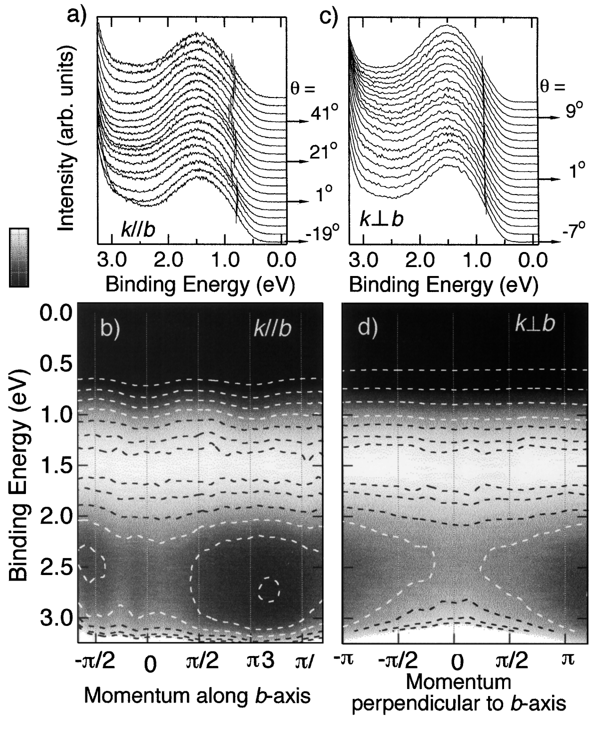

FIG. 3. (a) $k \parallel b$ spectra in the V $3d$ band region. They are normalized to the peak height around $E_B = 1.5$ eV. The vertical lines indicate the inflection points. (b) The intensity plot. The dashed lines are contours. (c) $k \perp b$ spectra in the V $3d$ band region and (d) the intensity plot.

along the b axis. The line shape of the lower binding energy side ($E_B = 0.5-1.2$ eV) shows a weak but clear k dependence. The inflection points obtained from the second derivative of the spectra are marked with vertical bars in the same figure while this dispersion seems to overlap the stronger feature centered at $E_B = 1.5$ eV. The intensity plot in the E-k plane on the grey scale shown in Fig. 3(b) indicates that the lower binding energy side of the lower Hubbard band disperses with the periodicity of π, half of the reciprocal lattice vector $k = 2\pi$. In fact, the spectra at $k = -\pi/2$, $\pi/2$, and $3/2\pi$ have shoulders around $E_B = 0.5-1.2$ eV. It thus appears that the spatial periodicity is effectively doubled for the electronic structure of the V $3d$ states. On the contrary, the higher binding energy side ($E_B = 1.8-2.5$ eV) shows no sign of periodicity π, and the result seems consistent with the periodicity of 2π as in the O $2p$ band, reflecting the periodicity of the crystal structure (although we could not check the 2π periodicity within our k range $\sim 2\pi$). The structure centered at $E_B \sim 1.5$ eV itself does not seem to disperse. We show the $k \perp b$ spectra in Fig. 3(c) with their inflection points marked by vertical lines, which signs no dispersive feature. The intensity plot in Fig. 3(d) also does not show any detectable k modulation on the lower binding energy side of the lower Hubbard band.

To perform more quantitative analysis, we have made a line-shape analysis between $E_B = -0.1$ and 2.1 eV on the assumption that each spectrum I can be decomposed into two components and an appropriate background as $I = I_A + I_B + I_{\mathrm{bg}}$ [see Fig. 4(a)]. Here, I_A and I_B are assumed to be Gaussian and represent the dispersive feature on the lower binding energy side of the ~ 1.5 eV peak and that of the nondispersive feature at ~ 1.5 eV, respectively, although actual line shapes may be more complicated [3,4,6,7]. I_{bg} is assumed to be $\propto E_B^2$. The peak position and the width of Gaussian A were treated as fitting parameters, while those of B were assumed to be k independent. (The B peak position may be weakly dependent on k, but when it was allowed to vary with k, we could not obtain reasonable convergence in the least-squares fitting. The origin of B shall be discussed below.) In Fig. 4(b), we have plotted the peak position of A as well as the inflection points. The figure shows that the momentum dependence of the peak position of A, which is consistent with that of the inflection point, seems to have the periodicity of π, fully supporting our observation discussed above. In Fig. 4(c), we show the result of the analysis of the $k \perp b$ spectra, indicating no detectable k dependence.

Now, we consider two possible causes for the observation of the doubled periodicity along the b axis: short-range order and spin-charge separation in the 1D system. Possible short-range order in NaV_2O_5 is due to SP fluctuations or due to AF fluctuations. Such fluctuations would cause a weak "shadow band" at $k > \pi/2$ in the excitation spectra. The observed shadow band is, however, strong. On the other hand, the one dimensionality may lead to a spin-charge separation which gives rise to the appearance of the spinon and holon bands in the excitation spectra [20]. A similar interpretation to that performed for $SrCuO_2$ [8] would be possible for NaV_2O_5. Concerning the SP versus AF fluctuations, Augier *et al.* [6] have shown by exact diagonalization of the t-J model that the ARPES spectra of NaV_2O_5 calculated for the SP chain is quite similar to the results for the undimerized chain because of sizable AF correlations.

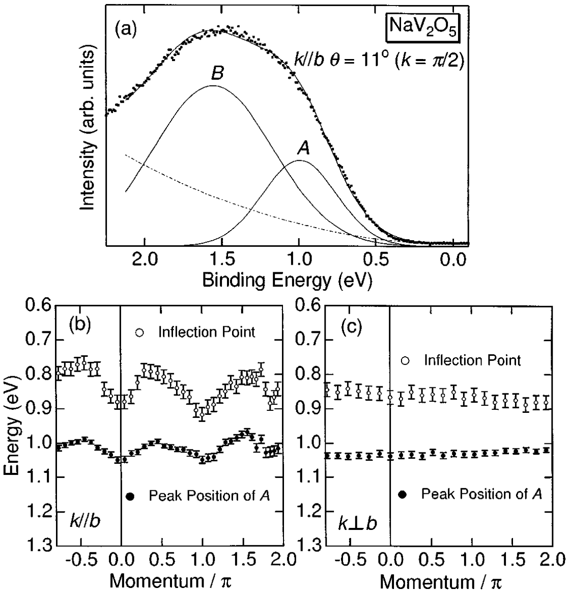

FIG. 4. (a) Line-shape analysis of an ARPES spectrum. The measured spectrum is plotted with dots, I, I_A, and I_B with solid curves, and I_{bg} with a dot-dashed curve. (b) Peak positions for the $k \parallel b$ spectra obtained from the line-shape analysis (closed circles and the inflection points) and the inflection points (open circles). (c) Peak positions for the $k \perp b$ spectra.

Now we compare our results with the prediction of the Hubbard model. J for NaV_2O_5 has been estimated to be 560 K (~ 0.05 eV) from the Bonner-Fischer type magnetic susceptibility [10]. On the other hand, U is known to be $2-4$ eV for vanadium oxides [17,21,22]. With relationship $J = 4t^2/U$, t is estimated to be 0.15–0.25 eV, which should give the dispersional width $2t = 0.3-0.5$ eV of the upper holon band (with the total holon band width being $\sim 4t$) [4]. In fact, the experimental dispersional width of the V $3d$ band $0.06-0.12$ eV is smaller but still in the same range as that $2t$ value. In this sense, our result well reflects the nature of the 1D AF quantum system and indicates spin-charge separation realized in this system. On the other hand, the spinon band, whose spectral weight should remain large, is not identified in the present spectra. In addition, the holon band should consist of two branch cuts while in our spectra the higher binding energy part seems to be buried under the intense feature (B) around $E_B \sim 1.5$ eV. A possible reason for the discrepancy is that the finite temperature effect may result in the weight redistribution and the broadening of the holon band. In fact, our measurements have been done at $T \sim 300$ K, which is as large as $\sim J/2$. As to the weight redistribution, Tohyama and Maekawa [4] have calculated the excitation spectra of the t-J model at finite temperatures by exact diagonalization and found that at $T \sim J/2$ the spectra become broader and look more symmetric with respect to $k = \pi/2$ with the holon band being smeared out and at the same time the spinon band being obscured in going from $k < \pi/2$ to $k > \pi/2$. Similarly, Penc and Serhan [23] have shown that in such a strongly correlated 1D system finite temperature causes a transfer of spectral weight from the spinon band to the holon band over a wide energy range of t ($\gg T$) rather than of T. On the other hand, in regard to the broadening of the holon band, Tsunetsugu [24] have obtained the temperature dependence of the spin correlation length (ξ_s) for the 1D Hubbard model and estimated ξ_s to be a few lattice spacings at $T/t \sim 0.2$. This short correlation length causes broadening of the band by $\sim 1/\xi_s$ along the k direction, which may have obscured the k dispersion and lead to the reduction of the apparent dispersional width $2t$. Besides these two possibilities, t might be effectively reduced from ~ 0.2 eV estimated above by a polaronic effect caused by the strong electron-phonon coupling neglected in the Hubbard model. If t is effectively as small as ~ 0.05 eV, which means that $t \sim J$, the excitation spectra should again look symmetric with respect to $k = \pi/2$ [6], making the spinon band hardly identifiable.

So far we have focused on the k-dispersive feature (A) of the V $3d$ band, which appears relevant to the upper binding energy part of the holon branch cuts. As for the intense feature (B) around $E_B \sim 1.5$ eV, a very similar feature has been observed in the spectra of 3D vanadium and titanium oxides with $3d^1$ configuration and has been interpreted as the "incoherent part" of the spectral function accompanying the quasiparticle excitation at lower binding energies [16,17,25]. The position of structure B is almost independent of k and has almost the same width as that of the 3D compounds [16,17,21]. The origin of this incoherent part is not known at present but is presumably due to effects which are not included in the Hubbard model such as electron-phonon interaction and long-range Coulomb interaction [26]. This remains to be clarified in future studies.

In summary, we have performed an ARPES study of the 1D MH-type insulator NaV_2O_5. The lower Hubbard band in the $k \parallel b$ spectra has a k-modulated feature with the periodicity of $k = \pi$, implying an effective doubling of the unit cell while the higher binding energy part of the V $3d$ band rather reflects the lattice periodicity. While the feature with periodicity π might be qualitatively explainable as a shadow band due to short-range AF or SP order, we have analyzed the experimental results based on theoretical works on the 1D Hubbard and t-J models. Possible causes of the discrepancies between theory and experiment, namely, the smearing out of the spinon band and the existence of the large incoherent part, have also been discussed. Those possibilities may be tested by performing ARPES measurements by changing temperature. Further ARPES studies on other dimerized and undimerized 1D systems as well as 2D quantum-spin systems will shed more light on the properties of the low dimensional quantum-spin systems.

We would like to thank T. Tohyama and S. Maekawa for providing the results of exact diagonalization studies prior to publication and for fruitful discussion and H. Shiba, C. Kim, and H. Suzuura for informative discussions. One of us (K. K.) acknowledges support by the Japan Society for the Promotion of Science for Young Scientists. This work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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