Photoemission study of the metal-insulator transition in $VO_2/TiO_2(001)$: Evidence for strong electron-electron and electron-phonon interaction

K. Okazaki,[1,*] H. Wadati,[1] A. Fujimori,[1,2] M. Onoda,[3] Y. Muraoka,[4] and Z. Hiroi[4]

[1]*Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan*
[2]*Department of Complexity Science and Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan*
[3]*Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*
[4]*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*

We have made a detailed temperature-dependent photoemission study of $VO_2/TiO_2(001)$ thin films, which show a metal-insulator transition at ∼300 K. Clean surfaces were obtained by annealing the films in an oxygen atmosphere. Spectral weight transfer between the coherent and incoherent parts accompanying the metal-insulator transition was clearly observed. We also observed a hysteretic behavior of the spectra for heating-cooling cycles. We have derived the "bulk" spectrum of the metallic phase and found that it has a strong incoherent part. The width of the coherent part is comparable to that given by band-structure calculation in spite of its reduced spectral weight, indicating that the momentum dependence of the self-energy is significant. This is attributed to by ferromagnetic fluctuation arising from Hund's rule coupling between different d orbitals as originally proposed by Zylbersztejn and Mott. In the insulating phase, the width of the V $3d$ band shows strong temperature dependence. We attribute this to electron-phonon interaction and have reproduced it using the independent boson model with a very large coupling constant.

I. INTRODUCTION

To elucidate the physical properties of Mott-Hubbard systems has been one of the most challenging subjects in condensed matter physics and has continued to pose controversial theoretical as well as experimental issues. In this respect, the single-particle spectral function of transition-metal oxides, particularly of early transition-metal oxides, is of fundamental importance in the physics of Mott-Hubbard systems. In fact, the coexistence of the coherent part [the quasiparticle (QP) band] and the incoherent part (a remnant of the upper and lower Hubbard bands) in the spectral function and spectral weight transfer between them as a function of electron correlation strength U/W, where U is the Coulomb repulsion energy and W is the bandwidth, are a remarkable manifestation of electron correlation as identified in the photoemission spectra of V and Ti oxides.[1,2] Theoretically, dynamical mean-field theory (DMFT) applied to the Hubbard model has successfully reproduced these characteristic features.[3] Comparison between experiment and theory, however, has not been straightforward. In DMFT, the self-energy is necessarily local, and therefore the density of states (DOS) at the Fermi level (E_F), namely, the spectral intensity at E_F remains the same as that of the noninteracting system and electron correlation effect manifests itself as the narrowing of the coherent QP band. Experimentally, the reduction of the DOS at E_F rather than the narrowing of the coherent part was observed in the photoemission spectra of $Ca_{1-x}Sr_xVO_3$, suggesting the importance of the momentum dependence of the self-energy.[1,2] However, a recent "bulk-sensitive" photoemission study of the same compounds has shown that the QP band is indeed narrowed and the DOS at E_F remains unchanged from that predicted by band-structure calculation, indicating that the self-energy is nearly momentum indepen-

dent as assumed in DMFT.[4] In the present work, we have studied another typical Mott-Hubbard system VO_2, which undergoes a metal-insulator transition as a function of temperature, and examined the spectral function of the "bulk" to see whether the self-energy is momentum independent or not. Our results have shown that the self-energy is *momentum dependent*, probably due to ferromagnetic fluctuations arising from the multiorbital nature of the V $3d$ band of the rutile structure.

VO_2 is well known for its first-order metal-insulator transition (MIT) at 340 K.[5] The transition is accompanied by a structural transition. In the high-temperature metallic phase it has a rutile structure while in the low temperature insulating phase (M_1 phase) the V atoms dimerize along the c axis and the dimers twist, resulting in a monoclinic structure. The magnetic susceptibility changes from paramagnetic to nonmagnetic in going from the metallic to the insulating phases. Hence, this transition is analogous to a Peierls transition and in fact the importance of electron-phonon interaction has been demonstrated by Raman scattering[6] and x-ray diffraction[7] studies. On the basis of local-density approximation (LDA) band-structure calculation, Wentzcovitch *et al.*[8] concluded that the insulating phase of VO_2 is an ordinary band (Peierls) insulator. On the other hand, the magnetic susceptibility of the high-temperature metallic phase is unusually high and temperature dependent, indicating the importance of electron-electron correlation. Furthermore, Cr-doped VO_2 or pure VO_2 under uniaxial pressure in the [110] direction of the rutile structure has another monoclinic insulating phase called the M_2 phase. In the M_2 phase, half of the V atoms form pairs and the other half form zig-zag chains.[9] While the V atoms in the pairs are nonmagnetic, those in the zig-zag chains have local moment and are regarded as one-dimensional Heisenberg chains according to

an NMR study.[10] Based on these observations for the M_2 phase, Rice *et al.*[11] objected to the argument of Wentzcovitch *et al.* Thus it still remains highly controversial whether the MIT of VO_2 is driven by electron-phonon interaction (resulting in a Peierls insulator) or electron-electron interaction (resulting in a Mott insulator forming a spin-Peierls-like state).

To deal with the above problems, photoemission spectroscopy is a powerful technique and, in fact, has been extensively applied to this material.[12–18] However, detailed photoemission studies of the MIT has been hampered because the transition temperature of bulk VO_2 is rather high and therefore it is difficult to keep the surface clean in an ultrahigh vacuum for the high-temperature metallic phase. Also, because the transition is strongly first order with the structural change, the sample is destroyed when it crosses the MIT and one can go through the transition only once for one sample.

In this work, we have avoided those experimental difficulties by using thin film samples epitaxially grown on $TiO_2(001)$ surfaces using the pulsed laser deposition technique.[19] After having obtained a clean surface by oxygen annealing, the surface remained fairly stable for several hours even in the high-temperature metallic phase and allowed us to study detailed temperature-induced changes both in the metallic and insulating phases including the hysteretic behavior across the MIT. Spectral weight transfer between the coherent and incoherent parts of the V $3d$ spectral function accompanying the metal-insulator transition was clearly observed. We have attempted to deduce the "bulk" photoemission spectrum by subtracting surface contributions from the measured spectra. We compare the "bulk" spectrum with the band-structure calculation to discuss electron correlation in the metallic phase, particularly possible momentum dependence of the self-energy. We have also found a strong temperature dependence in the spectra of the insulating phase and attributed it to strong electron-phonon interaction.

II. EXPERIMENTAL

$VO_2/TiO_2(001)$ thin films were prepared using the pulsed laser deposition technique as described in Ref. 19. A V_2O_3 pellet was used as a target. During the deposition, the substrate temperature was kept at 733 K and oxygen pressure was maintained at 1.0 Pa. The film thickness was about 10 nm. The epitaxial growth was confirmed by four-cycle x-ray diffraction (XRD) measurements and the MIT was confirmed by electrical resistivity measurements showing a jump of about thee orders of magnitude. The transition temperature in the films was 295 K on heating cycle and 285 K on cooling cycle, while the MIT occurs at 340 K in bulk samples.[5] The reduced MIT temperature of the films is due to the compressive strain from the TiO_2 substrate.[19] Bulk VO_2 single crystals were prepared by the chemical vapor transport method and measured as described in Ref. 18.

X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) measurements were performed using the Mg $K\alpha$ line ($h\nu = 1253.6$ eV) for XPS and the He I resonance line ($h\nu = 21.2$ eV) for UPS with a VSW hemispherical analyzer. Estimation of the instrumental resolution and binding energy calibration were made by measur-
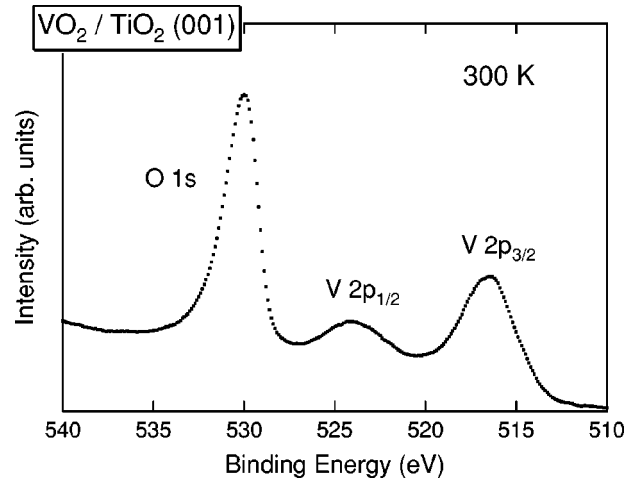

FIG. 1. O $1s$ and V $2p$ core-level XPS spectra of $VO_2/TiO_2(001)$ thin film.

ing gold spectra. The total energy resolution was ~0.8 eV for XPS and ~30 meV for UPS. Clean surfaces were obtained by annealing the films in a preparation chamber connected to the spectrometer at 643 K under ~1 Pa oxygen atmosphere for 1 h prior to the photoemission measurements.

III. RESULTS

Figure 1 shows the O $1s$ and V $2p$ core-level XPS spectra of a $VO_2/TiO_2(001)$ film taken at room temperature. Contributions from the Mg $K\alpha_3$ and $K\alpha_4$ satellites have been subtracted. The O $1s$ peak shows a single peak without any contamination signals at higher binding energies, indicating that the surface became sufficiently clean by the above procedure.

Figure 2 shows the valence-band UPS spectra of $VO_2/TiO_2(001)$ taken at 300 and 280 K. The secondary electron background has been subtracted following the procedure of Li and Henrich.[20] The structures from binding en-
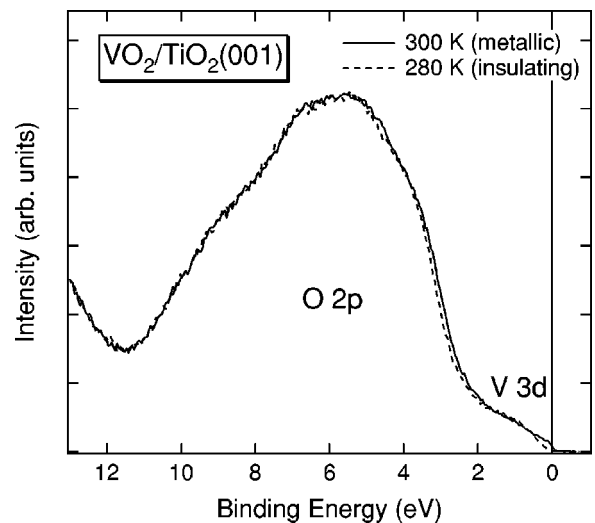

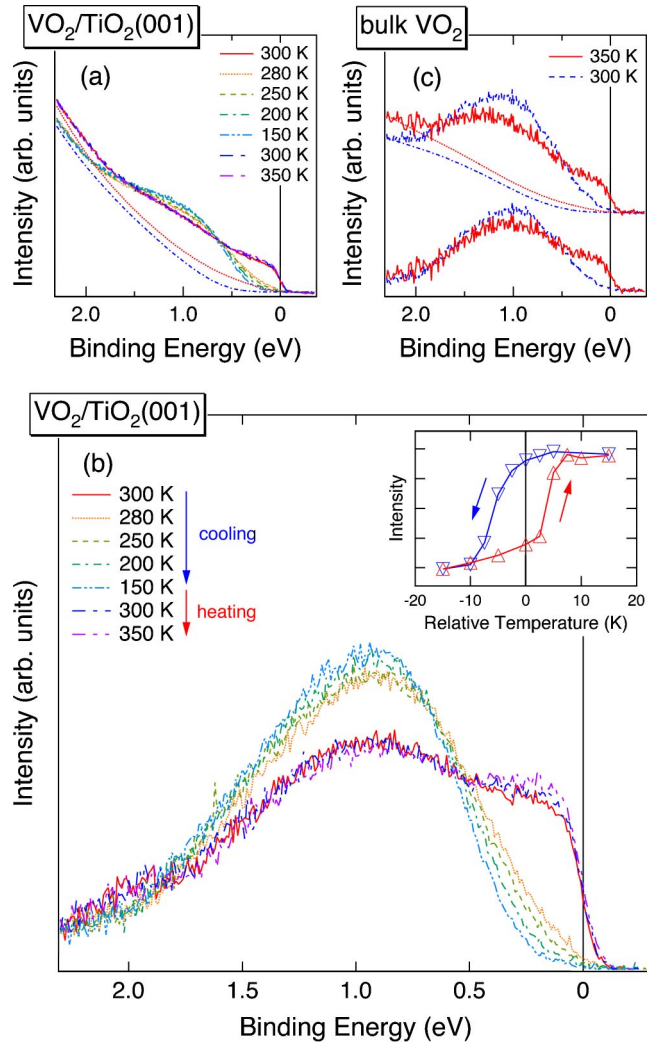FIG. 2. Valence-band photoemission spectra of $VO_2/TiO_2(001)$ thin film. Secondary electron background has been subtracted.

FIG. 3. Photoemission spectra of $VO_2/TiO_2(001)$ thin film in the V $3d$ band region. (a) Raw data. Dotted and dot-dashed lines indicate estimated contributions from the tail the O $2p$ band. (b) V $3d$ band with the O $2p$ contributions being subtracted. The inset shows a hysteretic behavior of the spectral intensity around E_F across the MIT. (c) Photoemission spectra of a bulk single crystal VO_2. Top: raw data; bottom: background being subtracted.

ergies $E_B \simeq 2$ to 12 eV are due to the O $2p$ band. The region from $E_B \simeq 2$ eV to E_F is the V $3d$ band. While the O $2p$ band shows no clear temperature dependence, the V $3d$ band shows a temperature dependence, indicating that the MIT occurred between 280 and 300 K.

Figures 3(a) and 3(b) show the UPS spectra of $VO_2/TiO_2(001)$ in the V $3d$ band region taken at various temperatures. First the temperature was decreased from 300 to 150 K, then it was increased again to above 300 K. The spectra showed good reproducibility within this temperature cycle. The tail of the O $2p$ band has been subtracted as shown in Fig. 3(a) and the resulting spectra have been normalized to the integrated intensity from $E_B = -0.3$ to 2.3 eV, as shown in Fig. 3(b). The MIT is clearly seen as the change in the spectral intensity at E_F accompanied by the spectral weight transfer between the low binding-energy region $E_B = 0 - 0.5$ eV (coherent part) and the high binding-energy re-

gion $E_B = 0.5 - 2$ eV (incoherent part). The spectra of the films [Fig. 3(b)] are almost identical to that of the bulk sample [Fig. 3(c)] except for the somewhat stronger temperature dependence of the film spectra. Because of the much higher stability of the film surface in vacuum, we could obtain the spectra with much higher signal-to-noise ratio at much smaller temperature intervals in the whole temperature range. Also, the film retained the original spectra after several temperature cycles whereas the bulk single crystal broke into pieces once it crossed the MIT. In the previous study of bulk single crystals,[18] detailed temperature-dependent studies were therefore limited to the low-temperature insulating phase, where the crystal did not break. The present temperature dependence in the insulating phase has reproduced the bulk crystal results.

Here, we have observed a hysteretic behavior in the spectra with temperature across the MIT, as demonstrated by the temperature dependence of the intensity around E_F (integrated from $E_B = -0.2$ to 0.5 eV) shown in the inset of Fig. 3(b). The hysteretic behavior is seen over the temperature range of ~ 10 K. This may indicate the coexistence of metallic and insulating regions with changing volume fractions in this temperature range. Photoemission spectra of another system which shows a first-order temperature-induced metal-insulator transition, $R\mathrm{NiO_3}$, also shows a similarly gradual temperature dependence.[21,22] In the case of $R\mathrm{NiO_3}$, the hysteretic behavior in the transport and thermodynamic properties extends over a wide temperature range of several tens K,[23] and correspondingly the photoemission spectra show a more gradual temperature dependence over the wider temperature range.

Recently, it has been demonstrated that photoemission spectra of transition-metal oxides are strongly influenced by surface contributions. In particular, the incoherent part centered around $E_B = 1 - 1.5$ eV contains more surface contributions than the coherent part.[4,24] Since the surface layer tends to have a smaller bandwidth W and hence a larger U/W, the surface layer tends to have a stronger incoherent part and a weaker coherent part than in the bulk.[24,25] In order to remove such surface contributions and to analyze the electronic structure of bulk materials, we attempted to deduce the "bulk" spectrum in the metallic phase under several assumptions. If the thickness of the surface layer is d and the photoelectron escape depth is λ, the observed spectrum $F(\omega)$ is given by

$$F(\omega) = F^s(\omega)(1 - e^{-d/\lambda}) + F^b(\omega)e^{-d/\lambda},$$

where $F^s(\omega)$ and $F^b(\omega)$ are the "surface" and the "bulk" spectra, respectively. As the electronic properties of the surface layer of VO_2 are not precisely known, in the following analyses, we consider the extreme case where the photoemission spectra of the surface layer largely consists of the incoherent part. Therefore, the intensity of the incoherent part in the "bulk" spectrum deduced below should be regarded as the lower bound for the actual bulk one.

Assuming that the spectrum at 280 K ($<T_{MI}$) represents the "surface" spectrum, because the photoelectron escape depth λ is not precisely known, we subtracted the "surface"
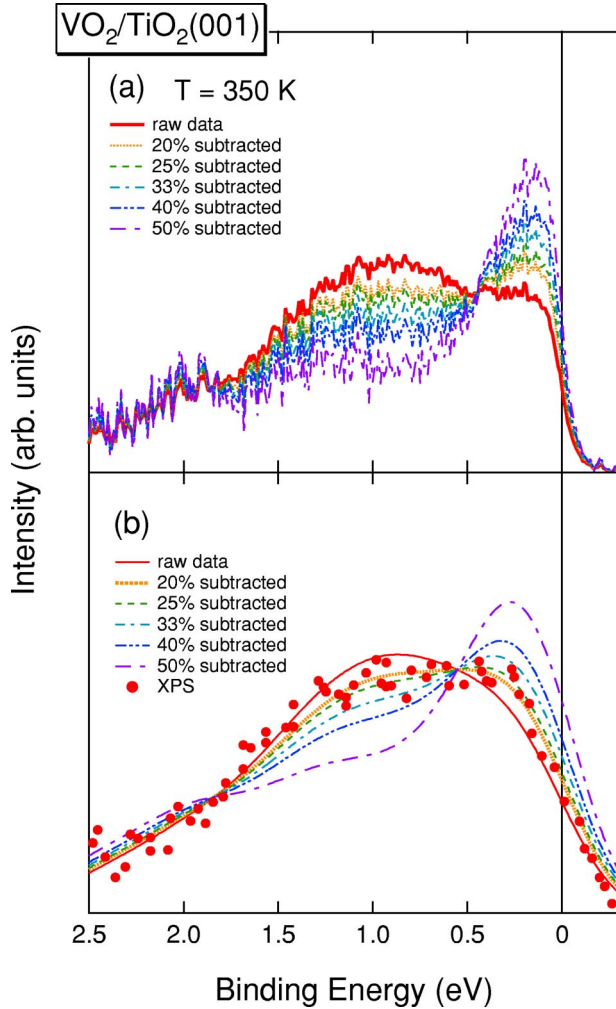
FIG. 4. (a) Subtraction of "surface" contributions with various ratios from the photoemission spectrum of the metallic phase. (b) Comparison of the spectra in (a) with the XPS spectrum from Ref. 12. Here, the curves in (a) have been broadened with a Gaussian to account for the lower energy resolution of XPS.

FIG. 5. "Bulk" spectrum is compared with the LDA band-structure calculation from Ref. 27.

contribution with various ratios as shown in Fig. 4(a). Here, "20% subtracted" means that the intensity of the subtracted insulatorlike spectrum was 20% of the total intensity. In Fig. 4(b), we compare the "bulk sensitive" XPS spectrum in the literature[12] with those spectra in (a) after having broadened them with a Gaussian function corresponding to the lower experimental energy resolution of XPS (~ 0.55 eV). One can see that the XPS spectrum is in best agreement with "20% subtracted" spectrum. According to the "universal curve" of the photoelectron escape depth,[26] the escape depth is ~ 10 Å for $h\nu = 21.2$ eV and ~ 15 Å for XPS ($h\nu = 1486.6$ eV), respectively. Using the surface layer thickness of $2c$ ($= 5.7$ Å) on the (001) surface of the rutile structure, where c is the c-axis lattice constant, the surface contribution is $\sim 44\%$ for $h\nu = 21.2$ eV and $\sim 32\%$ for $h\nu = 1486.6$ eV, respectively. Hence, the "20% subtracted" spectrum should have 30% surface contribution and therefore it is reasonable that the "20% subtracted" spectrum is in agreement with the XPS spectrum. After all, we consider that the "bulk" spectrum is given by the "40% subtracted" spectrum.
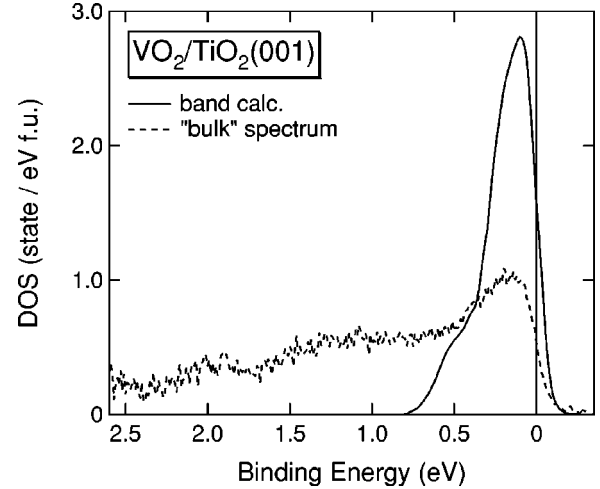
IV. DISCUSSION

A. Metallic phase

In Fig. 5, we compare the "bulk" spectrum thus deduced with the LDA band-structure calculation.[27] The calculated density of states (DOS) is multiplied by the Fermi-Dirac distribution function at 350 K and broadened with a Gaussian corresponding to the instrumental energy resolution. The width of the coherent part ~ 0.5 eV is similar to that given by the band-structure calculation. This means that m^*/m_b is ~ 1, where m^* is the average effective mass of the QP and m_b is the average bare band mass of the V $3d$ band. From the spectral weight ratio of the coherent part to the incoherent part 1:2, the renormalization factor becomes $Z \sim 1/3$. From the ratio of the intensity at E_F of the spectra to the DOS given by the band-structure calculation, one can estimate the average k mass defined by $m_k/m_b = |\partial\varepsilon_k/\partial k|_{k=k_F}/|\partial\varepsilon_k/\partial k|_{k=k_F} + \partial\operatorname{Re}\Sigma(k,\omega)/\partial k|_{k=k_F}|$, as $m_k/m_b \sim 0.3$. Thus, we again obtain $m^*/m_b = (1/Z)(m_k/m_b) \sim 1$. Note that we have assumed that the surface layer is without the coherent part around E_F. If the surface spectrum has a finite coherent part, the coherent part of the "bulk" spectrum would be further reduced and the deduced k mass would be even smaller. Hence, $m_k/m_b \sim 0.3$ deduced here should be taken as the upper limit for m_k/m_b, and therefore on can safely conclude the m_k/m_b is smaller than unity. That is, the momentum dependence of the self-energy is not negligible in the metallic phase of VO$_2$.

Our finding $m_k/m_b < 1$ is contrasted with the "bulk" spectra of Sr$_{1-x}$Ca$_x$VO$_3$ reported by Sekiyama *et al.*[4] In their result, the width of the coherent part of the V $3d$ band of SrVO$_3$ is reduced by a factor of $\sim 40\%$ compared with the LDA result, and the spectral weight of the coherent part is also reduced by $\sim 40\%$ due to the transfer of spectral weight to the incoherent part, resulting in almost the same spectral intensity at E_F as that of the LDA value, that is, the self-energy has negligible momentum dependence in Sr$_{1-x}$Ca$_x$VO$_3$. The origin of the momentum dependence of the self-energy in VO$_2$ is not known at this moment. One
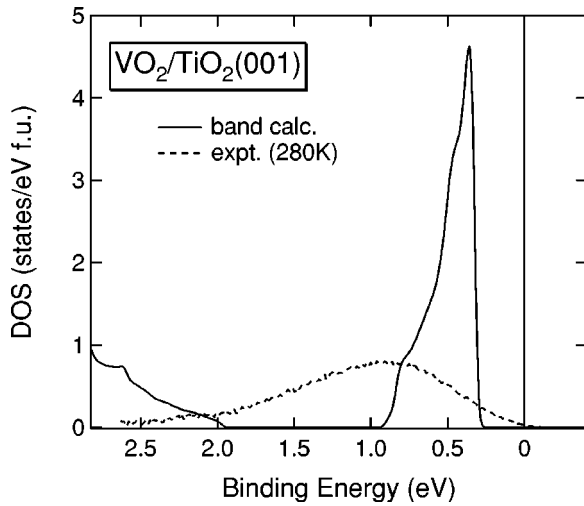
FIG. 6. UPS spectrum in the insulating phase (280 K) compared with the LDA$+U$ band-structure calculation ($U=4.0$ eV) (Ref. 32).

FIG. 7. Comparison of the spectral function of the independent boson model with the photoemission spectra of $VO_2/TiO_2(001)$ in the insulating phase. (a) Spectrum at 150 K and its Gaussian-broadened (FWHM$=200$ meV) spectrum, (b) independent boson model calculation, (c) measured photoemission spectra (the same as Fig. 3).

possibility is poor screening of long-range Coulomb interaction, but it is unlikely that the screening effect is so different between VO_2 and $Sr_{1-x}Ca_xVO_3$. Another possible origin of the momentum dependence is ferromagnetic fluctuations in VO_2 considering the enhanced magnetic susceptibility in the metallic phase, corresponding to $m^*/m_b \sim 6$ (Ref. 28). Recently, Liebsch and Ishida[29] proposed that the multiorbital nature of the V $3d$ band is important to describe the metallic phase of VO_2 (Refs. 29, 30), following the idea originally proposed by Zylbersztejn and Mott.[31] According to these works, the occupancy of the t_{2g} orbitals is very different between the metallic and the insulating phases due to lattice distortion in the insulating phase and this affects the role of local Coulomb interaction in each phase. If many orbitals contribute to the metallic conductivity, ferromagnetic correlation may arise from Hund's coupling between those orbitals. Further studies are necessary to confirm this scenario.

B. Insulating phase

As stated in Sec. I, it has been controversial whether the insulating band gap is primarily caused by the lattice distortion or the electron-electron interaction. In order address this issue, it is useful to examine the photoemission spectral line shape of the V $3d$ band in the insulating phase.

In Fig. 6, we compare the UPS spectrum of the insulating phase with the DOS given by the LDA$+U$ band-structure calculation ($U=4.0$ eV) by Huang *et al.*,[32] where the effect of electron-electron interaction is taken into account on the mean-field (i.e., Hartree-Fock) level. The figure shows that, although the insulating gap can be produced by the LDA$+U$ method, the Gaussian-like broad spectrum of V $3d$ band cannot be reproduced. This disagreement between theory and experiment cannot be explained by a surface effect because since the bulk component should have finite contribution ($\sim 60\%$) even for this low photon energy and therefore the sharp feature should be clearly visible overlapping the surface signals. This means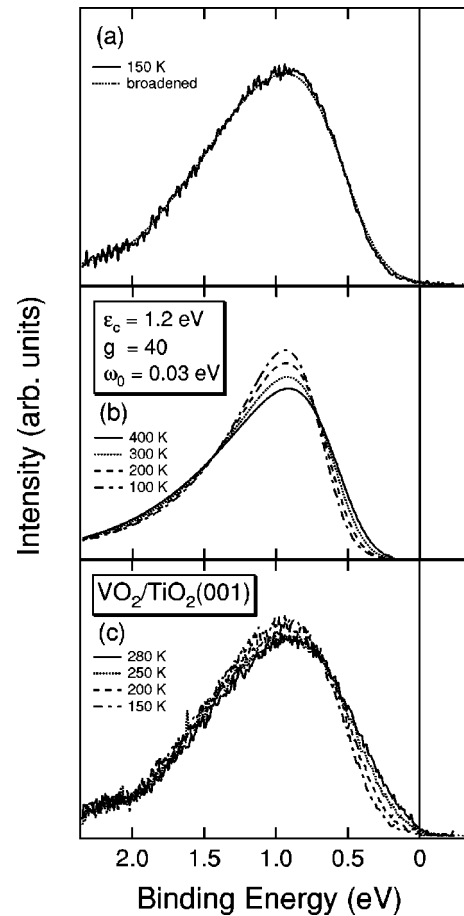 that electron-electron interaction on the mean-field level is not sufficient to understand the photoemission spectrum of the insulating VO_2. Here, we point out that the photoemission spectra of a double-layer manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ also show a broad Gaussian-like line shape in striking contrast with LDA band-structure calculation, and this discrepancy has been attributed to the strong electron-phonon coupling.[33] Furthermore, one can recognize that the spectra of VO_2 show very strong temperature dependence in the insulating phase as shown in Fig. 3. The same temperature dependence was observed in the spectra of bulk single crystal and was attributed to electron-phonon interaction, because the core-level spectra also show a similarly strong temperature dependence.[18]

Simple thermal broadening cannot explain the observed temperature dependence as shown in Fig. 7(a), where the photoemission spectrum taken at 150 K and the same spectrum broadened with a Gaussian, whose FWHM is 200 meV ($\sim 8k_BT$ at 300 K) are compared. In order to simulate the temperature-dependence based on the electron-phonon interaction mechanism, we introduce the spectral function of the independent boson model at finite temperature given by[34]

$$A(\omega) = e^{-g(2N+1)} \sum_l \frac{g^l}{l!} \sum_{m=0}^{l} {}_lC_m N^m (N+1)^{l-m}$$

$$\times \delta[\omega - \varepsilon_c + \Delta - (l-2m)\omega_0],$$

where N is the phonon occupation number, g is the electron-phonon coupling constant, ω_0 is the average phonon energy, the $\Delta = g\omega_0$ is the electron self-energy shift due to coupling to phonons, and ε_c gives the peak position of the spectra. This spectral function describes the situation where spectral weight is transfered from the zero-phonon line at the lowest binding energy $\varepsilon_c - \Delta$ to $\varepsilon_c - \Delta + (l-2m)\omega_0$ by emitting $(l-m)$ phonons or absorbing m phonons. Because this spectral function consists of a series of delta functions, one has to broaden this function to compare with the photoemission spectra. For this purpose, we use a simplified model self-energy $\Sigma(\omega) = G\omega/(\omega + i\gamma)^2$, which simulates the "lifetime" broadening which increases with increasing binding energy.[35] In Figs. 7(b) and 7(c), we compare the spectral function of the independent boson model with the photoemission spectra of $VO_2/TiO_2(001)$ in the insulating phase. We have chosen the parameters as $\varepsilon_c = 1.2$ eV, $g = 40$, and $\omega_0 = 0.03$ eV (Ref. 36) for the independent boson model and $G = 1.5$ eV^2 and $\gamma = 2$ eV for the broadening. Because the tail of the lower binding energy side of the photoemission spectrum reaches the vicinity of E_F, we have chosen the coupling constant g so that $\varepsilon_c - \Delta \sim 0$. Hence, $g = \varepsilon_c/\omega_0 \approx 40$. One can see that the temperature-dependent spectral function of the independent boson model qualitatively reproduces the photoemission spectra.

The extremely large coupling constant $g = 40$ may appear unphysical at first sight. However, Citrin *et al.*[37] have shown that in ionic crystals the coupling constant can be large and reported $g = 55$ for KI based on their analysis of temperature-dependent core-level photoemission spectra. They have estimated the value of g using the expression $g = e^2(6/\pi V)^{1/3}(1/\varepsilon_\infty - 1/\varepsilon_0)/\omega_0$, where V is the volume of a primitive unite cell, ε_∞ and ε_0 are the high- and low-frequency limits of the dielectric constant. For VO_2, $V \sim 29.5$ Å^3, ε_∞ and ε_0 have been given as 5 and 30 in Ref. 31, respectively. From these values, g is calculated as ~ 32. On the other hand, Egdell *et al.*[38] have used $1/2R$ in stead of $(6/\pi V)^{1/3}$ for perovskite-type V oxides, where R is the ionic radius of the transition-metal ion. In this case, g becomes as large as 47. (R is 0.82 Å for VO_2.[36]) Hence, we can say that $g = 30 - 50$ is a reasonable value for the electron-phonon coupling constant for VO_2.

Finally, we comment on how the strong electron-electron interaction and the strong electron-phonon coupling are related with each other in VO_2 (and probably in other transition-metal oxides as well). In ionic crystals, the on-site Coulomb repulsion energy U is given by $U = e^2/2\varepsilon_\infty R$. Therefore, according to the expression of Egdell *et al.*,[38] the large U and the large g is related with each other though ε_∞. This means that the strong electron-phonon interaction is a consequence of strong electron-electron interaction.

V. CONCLUSION

We have studied the electronic structure of VO_2 by measuring the photoemission spectra of $VO_2/TiO_2(001)$ thin films. The metal-insulator transition was clearly observed as a change in the spectral intensity at E_F accompanied by spectral weight transfer between the coherent and incoherent parts of the spectral function. From comparison of the "bulk" spectrum in the metallic phase and the band-structure calculation, we have concluded that, while the mass enhancement factor m^*/m_b is almost unity, the momentum dependence of the self-energy is important in the metallic phase, possibly due to ferromagnetic fluctuations arising from the multiorbital character of the V $3d$ band. In the insulating phase, the V $3d$ band is strongly broadened as the temperature is increased. We attribute this temperature dependence to the electron-phonon interaction and reproduced it using the independent boson model with a very large coupling constant. This indicates that, while electron-electron interaction is necessary to produce the band gap in the insulating phase, electron-phonon interaction is important to fully understand the electronic structure and charge transport in VO_2.

*Present address: Department of Physics, Nagoya University, Nagoya 464-8602, Japan. Electronic address: okazaki@cc.nagoya-u.ac.jp

[1] A. Fujimori, I. Hase, H. Namatame, Y. Fujishima, Y. Tokura, H. Eisaki, S. Uchida, K. Takegahara, and F. M. F. de Groot, Phys. Rev. Lett. **69**, 1796 (1992).

[2] I. H. Inoue, I. Hase, Y. Aiura, A. Fujimori, Y. Haruyama, T. Maruyama, and Y. Nishihara, Phys. Rev. Lett. **74**, 2539 (1995).

[3] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).

[4] A. Sekiyama, H. Fujisawa, S. Imada, H. Eisaki, S. I. Uchida, K. Takegahara, H. Harima, Y. Saitoh, and S. Suga, cond-mat/0206471 (unpublished).

[5] F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).

[6] R. Srivastava and L. L. Chase, Phys. Rev. Lett. **27**, 727 (1971).

[7] D. B. McWhan, M. Marezio, J. P. Remeika, and P. D. Dernier, Phys. Rev. B **10**, 490 (1974).

[8] R. M. Wentzcovitch, W. W. Schulz, and P. B. Allen, Phys. Rev. Lett. **72**, 3389 (1994).

[9] M. Marezio, D. B. McWhan, J. P. Remeika, and P. D. Dernier, Phys. Rev. B **5**, 2541 (1971).

[10] J. P. Pouget, H. Lauois, T. M. Rice, P. Dernier, A. Gossard, G. Villeneuve, and P. Hagenmuller, Phys. Rev. B **10**, 1801 (1974).

[11] T. M. Rice, H. Launois, and J. P. Pouget, Phys. Rev. Lett. **73**, 3042 (1994).

[12] G. K. Wertheim, M. Capagna, H. J. Guggenheim, J. P. Remeika,

and D. N. E. Buchanan, AIP Conf. Proc. **24,** 235 (1975).

[13] C. Blaauw, F. Leenhouts, F. van der Woude, and G. A. Sawatzky, J. Phys. C **8**, 459 (1979).

[14] G. A. Sawatzky and D. Post, Phys. Rev. B **20**, 1546 (1979).

[15] S. Shin, S. Suga, M. Taniguchi, M. Fujisawa, H. Kanzaki, A. Fujimori, H. Daimon, Y. Ueda, K. Kosuge, and S. Kachi, Phys. Rev. B **41**, 4993 (1990).

[16] V. M. Bermudez, R. T. Williams, J. P. Long, R. K. Reed, and P. H. Klein, Phys. Rev. B **45**, 9266 (1992).

[17] E. Goering, M. Schramme, O. Müller, R. Barth, H. Paulin, M. Klemm, M. L. denBoer, and S. Horn, Phys. Rev. B **55**, 4225 (1997).

[18] K. Okazaki, A. Fujimori, and M. Onoda, J. Phys. Soc. Jpn. **71**, 822 (2002).

[19] Y. Muraoka, Y. Ueda, and Z. Hiroi, J. Phys. Chem. Solids **63**, 965 (2002).

[20] X. Li and V. E. Henrich, J. Electron Spectrosc. Relat. Phenom. **63**, 253 (1993).

[21] I. Vobornik, L. Perfetti, M. Zacchigna, M. Grioni, G. Margaritondo, J. Mesot, M. Medarde, and P. Lacorre, Phys. Rev. B **60**, R8426 (1999).

[22] K. Okazaki, T. Mizokawa, A. Fujimori, E. V. Sampathkumaran, M. J. Martinez-Lope, and J. A. Alonso, Phys. Rev. B **67**, 073101 (2003).

[23] J. Blasco and J. Garcia, J. Phys.: Condens. Matter **6**, 10759 (1994).

[24] K. Maiti, P. Mahadevan, and D. D. Sarma, Phys. Rev. Lett. **80**, 2885 (1998).

[25] A. Liebsch, Phys. Rev. Lett. **90**, 096401 (2003).

[26] C. R. Brundle, J. Vac. Sci. Technol. **11**, 212 (1974).

[27] A. V. Nikolaev, Yu. N. Kostrubov, and B. V. Andreev, Sov. Phys. Solid State **34**, 1614 (1992).

[28] G. Villeneuve, A. Bordet, A. Casalot, and P. Hagenmuller, Mater. Res. Bull. **6**, 119 (1971); J. P. Pouget, P. Lederer, D. S. Schreiber, H. Launois, D. Wohlleben, A. Casalot, and G. Villenueve, J. Phys. Chem. Solids **33**, 1961 (1972).

[29] A. Liebsch and H. Ishida, cond-mat/0310216 (unpublished).

[30] M. S. Laad, L. Craco, and E. Müller-Hartmann, cond-mat/0305081 (unpublished).

[31] A. Zylbersztejn and N. F. Mott, Phys. Rev. B **11**, 4383 (1975).

[32] X. Huang, W. Yang, and U. Eckern, cond-mat/9808137 (unpublished).

[33] D. S. Dessau, T. Saitoh, C.-H. Park, Z.-X. Shen, P. Villella, N. Hamada, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **81**, 192 (1998).

[34] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1981), Sec. 4.3.

[35] T. Saitoh, A. Sekiyama, T. Mizokawa, A. Fujimori, K. Ito, H. Nakamura, and M. Shiga, Solid State Commun. **95**, 307 (1995).

[36] F. Gervais and W. Kress, Phys. Rev. B **31**, 4809 (1985).

[37] P. H. Citrin, P. Eisenberger, and D. R. Hamann, Phys. Rev. Lett. **33**, 965 (1974).

[38] R. G. Egdell, M. R. Harrison, M. D. Hill, L. Porte, and G. Wall, J. Phys. C **17**, 2889 (1984).