~8 keV photoemission of the metal–insulator transition system VO₂

S Suga¹, A Sekiyama¹, S Imada¹, 6, T Miyamachi¹, H Fujiwara¹, A Yamasaki¹, 7, K Yoshimura², K Okada³, M Yabashi⁴, K Tamasaku⁴, A Higashiya⁴ and T Ishikawa⁴

¹ Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
² Graduate School of Science, Kyoto University, Kitashirakawa, Sakyoku, Kyoto 606-8224, Japan
³ Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan
⁴ SPring-8/Riken 1-1-1 Kouto, Mikazuki, Sayo, Hyogo 679-8148, Japan

E-mail: ssmsuga@gmail.com

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Abstract. Hard and soft x-ray photoelectron spectroscopies (called HAXPES and SXPES) were performed at ~8 and ~1.25 keV for the metal–insulator transitions (MIT) system VO₂. From the sharp difference between HAXPES and SXPES in the O 1s spectra, it was found that the clean surface of the metal VO₂ is covered with a less itinerant surface layer. Clear changes of the spectral shapes were observed in HAXPES on MIT for the V 1s, 2p, 3s, 3p and O 1s core levels. The enhanced intensity of these core levels in the low-binding-energy (E_B) region of the main peak in the metal phase is due to the non-local or long range screening effects. The V 3d valence band in the metal phase is composed of coherent and incoherent parts. The prominent peak near 0.9 eV in the insulator phase has an incoherent tail in the high-E_B region and the peak and its lower E_B components are understood to have a noticeable coherent component. It is experimentally confirmed that both electron correlation and band changes induced by lattice distortion are responsible for the spectral changes on MIT in VO₂.

⁵ Author to whom any correspondence should be addressed.
⁶ Present address: Faculty of Science and Engineering, Ritsumeikan University, Shiga 525-0055, Japan.
⁷ Present address: Faculty of Science and Engineering, Konan University, Kobe 658-8501, Japan.
1. Introduction

Studies of phase transitions including metal–insulator transitions (MIT) [1, 2] provide essential clues to understanding intriguing static and dynamic phenomena in strongly correlated electron systems such as superconductivity, colossal magneto-resistance and spin/charge/orbital orderings. The importance of electron correlation effects for the case of transition metal oxides, which show a variety of phase transitions including MIT, has been discussed extensively. Electron–phonon interactions have also been pointed out to be playing essential roles in some systems [3]–[5].

Among many strongly correlated electron systems, VO$_2$ is attracting wide interest as a 3d$^1$ system with MIT from a metallic rutile (R) structure to an insulating monoclinic (M1) structure near $T_V \sim 340$ K, where the dimerization of V atoms into pairs and their tilting take place in the bulk insulator (I) phase. Although VO$_2$ has extensively been studied for many decades, the origin of MIT is not yet fully settled [6]–[12], [13]$^8$, [14, 15].

Photoelectron spectroscopy (PES) [16] is one of the most powerful experimental techniques to study the changes of electronic structures on MIT. Valence-band PES can easily reveal changes in their spectral functions across MIT. It is, however, difficult to fully establish the physics of MIT solely from the valence-band information. Chemical information should also be obtained through PES measurements at the core levels. However, the change in surface sensitivity [17, 18] of PES with the photoelectron kinetic energy $E_k$ has induced many debates on strongly correlated electron systems. Gradually the bulk sensitivity of soft x-ray PES (SXPES) [19]–[22] with high resolution and accuracy was recognized to be essential for studying 4f and 3d systems. The bulk sensitivity can be further improved by hard x-ray PES (HAXPES) [23, 24].

PES of VO$_2$ has so far been performed under different conditions [11]–[13], [25, 26], [27]$^9$. [28] and the importance of the electron correlation and lattice distortion is discussed in [13]–[15], [26]. For example, SXPES spectra [25]–[27] have shown a prominent coherent peak and a much weaker incoherent peak in the metal (M) phase compared with the so-far reported surface-sensitive low-energy PES below 120 eV. The spectra in [26] are interpreted based on the theory of the correlation-assisted Peierls transition model [14]. In order to probe MIT changes of VO$_2$ with a greater probing depth, HAXPES was first performed at 7.937 keV.

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$^8$ The measurement was done on a VO$_2$ thin film on (001) TiO$_2$, which shows the transition at 295 K on heating and at 285 K on cooling.

$^9$ The measurement was done on a VO$_2$ thin film on (001) TiO$_2$. Its $T_V$ was $\sim 292$ K. The spectral shift of the low-$E_B$ threshold of the ‘O 2p’ peak on IMT is inconsistent between HAXPES and SXPES within this reference.
on a 10 nm thin VO$_2$ film grown on a (001) TiO$_2$ substrate [28] by grazing incidence excitation with $\theta \sim 89^\circ$ in order to obtain the count rate. Then the extensive results were interpreted in the Mott–Hubbard transition scenario in contrast to several other previous studies [14, 15, 26]. Since the electronic structures may be changed by the tensile stress effects in such a thin film, as seen, for example, from the much lower $T_V$ of $\sim 292$ K [28] compared with the bulk value of 340 K, we have performed HAXPES at $h\nu = 7.932$ keV and SXPES at 1.25 keV on single-crystalline bulk samples to reveal genuine bulk electronic structures of VO$_2$ and also discuss possible surface and stress effects. We have found noticeable differences between our bulk results and those on the thin film sample [28]. The present genuine bulk results are interpreted by considering both the crystal distortion and the electron correlation effects in the I phase. The results in the M phase are interpreted by considering the non-local or long range screening effect. In order to interpret the spectral changes on the MIT of core states, a simplified theoretical model is proposed and the calculated result is compared with the O 1s spectral changes.

2. Experimental

The HAXPES experiment was performed at BL19LXU of SPring-8 with a 27 m long 781 period in-vacuum planar undulator using horizontally polarized light. A newly developed MBS A1-HE hemispherical analyzer withstanding up to 14 kV with a long-term stability of $\pm 8$ meV was employed. The possible ambiguity of the evaluation of the electron binding energy $E_B$ is less than 27 meV. The total resolution of the PES system was checked at $h\nu = 7.932$ keV to be better than 70 meV, whereas the resolution was set to 250 meV (FWHM) to have enough counts for the V 3d state with a very low photoionization cross section [29]. The single crystal sample was fractured in situ in ultra-high vacuum at 260 K and O 1s, V 1s, 2p, 3s, 3p, O 2s, O 2p and V 3d spectra were measured in the I phase. After $E_B$ calibration by the Au Fermi edge, the sample temperature was increased and the same series of measurements was repeated in the M phase at 350 K. Nearly normal emission was measured for the light incidence angle of $\theta \sim 60^\circ$ from the surface normal. SXPES was performed at BL25SU of SPring-8 at 1.25 keV using circularly polarized light. The clean surface of a single-crystal sample was likewise prepared and SXPES was measured with the resolution of 400 meV. The $E_B$ calibration was done in the same way by the Au Fermi edge. In both HAXPES and SXPES, the accuracy and reproducibility of the $E_B$ were better than 30 meV.

3. Results and discussion

The O 1s and V 2p core spectra after subtracting the Shirley-type background and normalized at the O 1s peak height are shown in figure 1(a). In the I phase, a rather symmetrical and sharp O 1s structure was observed near $E_B = 530$ eV. A broad charge transfer (CT) satellite is observed around 540 eV. In the metal (M) phase, however, the O 1s main peak is shifted by $\sim 0.4$ eV toward smaller (lower) $E_B$ and the asymmetry toward larger (higher) $E_B$ becomes noticeable, as a result of which a clear difference from the spectral shape in the I phase is observed 1–5 eV above the main peak in the M phase. Powder diffraction studies have revealed a single O site in the rutile M phase and two non-equivalent O sites in the I phase [30]. The highly symmetrical and sharp (FWHM = 0.8 eV) O 1s spectrum in the I phase suggests, however, that the site-dependent difference in charge density is marginal and the structure in the M phase is due to other mechanisms.
Figure 1. HAXPES of a fractured single-crystal VO$_2$ measured at $h\nu = 7.932$ keV with a resolution of 250 meV at 260 and 350 K, corresponding to the insulator (I) and metal (M) phases. (a) O 1s and V 2p spectra. Spectra are normalized by the peak height of the O 1s main peak. (b) V 1s spectra, normalized by the integrated peak intensity. (c) V 3s, 3p and O 2s, 2p spectra. The O 2s spectrum is expanded in the inset.

In the case of V 2p spectra, the $2p_{3/2}$ state shows a sharp peak in the I phase, whereas this intensity decreases and a prominent low $E_B$ shoulder is observed at 514 eV in the M phase. The intensity in the latter region is close to 80–90% of the intensity at the peak left at the original $E_B$. The peak height of the V 2p$_{1/2}$ component is likewise suppressed. The V 1s core spectra probed with high enough bulk sensitivity (kinetic energy $E_K \sim 2460$ eV) are shown in figure 1(b) after normalization by the integrated area. Although one sharp peak is observed at around 5467.5 eV in the I phase together with a CT satellite near 5480 eV, the V 1s peak is broadened toward lower $E_B$ and the CT satellite is slightly suppressed in the M phase. The V 1s peak in the M phase has thus a very broad top. If compared with the HAXPES on a thin film VO$_2$ [28], the transfer of the
spectral weight toward low $E_B$ is more prominent in the present HAXPES on the fractured bulk sample for all peaks of O 1s, V 2p$_{3/2}$ and V 1s states. Figure 1(c) shows the wide $E_B$ spectrum covering the V 3s ($E_B \sim 68$ eV), V 3p ($\sim 40$ eV) and O 2s ($\sim 21$ eV) core levels together with ‘O 2p’ (10–2 eV) and V 3d (2–0 eV) valence bands after normalization by the integral area of the O 2s peak. The V 3s and 3p spectra show a similar behaviour as the V 1s spectrum in the insulator-to-metal transition (IMT). Namely, the intensity in the lower $E_B$ region is noticeably enhanced in the M phase and the height of the main peaks is suppressed. In the inset is shown the expanded spectra of the O 2s state, where the centre of gravity is also shifted to smaller $E_B$ by $\sim 0.1$ eV in the M phase beyond the experimental errors. The very small energy shift of the main peaks in the V 2p, 3s and 3p core spectra on MIT and the sharp single-peak structure in the V 1s and O 1s core spectra in the I phase confirm that the spectral changes across MIT are not caused by a trivial charging-up effect in the I phase but are due to intrinsic effects.

Details of the ‘O 2p’ and V 3d valence bands not resolved in figure 1(c) are reproduced in figure 2(a), where very clear spectral changes are revealed on MIT. The ‘O 2p’ valence band in the I phase is composed of a prominent peak near 7.3 eV and another peak near 5.2 eV. In the M phase, the former structure shifts toward lower $E_B$ by around 0.3–0.4 eV and the latter structure near 5.2 eV becomes less prominent on the IMT. The low-energy threshold of the ‘O 2p’ band ranging from 5 to 2.7 eV in the I phase is also shifted toward lower $E_B$ by about 0.3 eV in the M phase. These shifts are again in strong contrast to the HAXPES results on a thin film sample [27, 28], where such shifts are very small. In contrast to these obvious shifts toward lower $E_B$ on IMT, however, the spectral weight around $E_B = 9.0$ eV is increased in the M phase.

Figure 2(b) compares the detailed V 3d spectra, which show a clear change on MIT. The main peak observed at $E_B = 0.25$ eV in the M phase corresponds to the coherent peak or the quasi-particle (QP) state. The intensity at the Fermi level $E_F$ is nearly 1/2 of the coherent peak height. A rather flat region expanding in the range of $E_B = 0.9–2.2$ eV can be interpreted as an incoherent component or the lower Hubbard band. In the I phase, a prominent peak is observed at 0.90 eV. Judging from the non-bonding character of the shallow $E_B$ part of the ‘O 2p’ band, we extend the lower $E_B$ tail of ‘O 2p’ band as the dashed curve and can evaluate the V 3d spectral weight as the difference between the solid and dashed curves in figure 2(b). Then a noticeable tail is observed in the higher $E_B$ region of the main V 3d peak even in the I phase.

We compare these spectral changes on MIT with unpublished results for Wadley phase $V_6O_{13}$ [31] and Magneli phase $V_5O_9$ [32] by HAXPES. These materials are also known to show clear MIT at $\sim 150$ and $\sim 135$ K, respectively. In the case of $V_6O_{13}$, MIT is accompanied by a structural distortion [33] and both $V^{5+}$-like and $V^{4+}$-like sites are induced in the I phase. Half of the $V^{4+}$ ions are thought to form the spin singlet state in the I phase. However, no anomalously short V–V separations are observed in the I phase in direct contrast to the paired V sites observed in the I phase of VO$_2$. The dimerization effect is fully negligible in the I phase of $V_5O_9$ [34]. In $V_6O_{13}$, for example, the spectral changes are much less prominent than VO$_2$ in all cases of the O 1s, V 2p$_{3/2}$, V 1s, V 3s, V 3p, O 2s and ‘O 2p’ bands. Still one can see a finite shift of the lower $E_B$ threshold of the O 1s and V 1s peaks by about 0.1 eV on MIT (not shown). The shifts of the reflectance peaks on MIT observed in the photon energy region of 3–25 eV are likewise much smaller for $V_6O_{13}$ than for VO$_2$ [12]. These results suggest that the very clear spectral changes observed in VO$_2$ by HAXPES on MIT are mostly caused by the

10 Magneli phase $V_5O_9$ and $V_6O_{11}$ are discussed.
V–V dimerization effect in the I phase, even though the presence or absence of the long-range metallic screening plays an essential role in the two phases. In contrast to the thus confirmed V–V dimerization effect in VO$_2$ in the I phase, there is no dimerization effect in V$_5$O$_9$ in the I phase. A small but finite shift of the lower $E_B$ threshold toward smaller $E_B$ is observed as V$_6$O$_{13}$ for the O 1s state on IMT and the long-range metallic screening feature appears in the M phase on the lower $E_B$ threshold of the V 1s and V 2p main peaks. Thus, it is clear that the spectral shapes of both V and O core states change on MIT even without such crystal distortion as dimerization but the prominent changes in spectral shapes on MIT in VO$_2$ are surely due to the additional dimerization effects.

O 1s spectra are reproduced in figures 3(a) and (c) for the M and I phases, respectively, where the results of SXPES measured on the same sample by using a different PES setup are included. The resolution in this experiment for the 7.93 keV HAXPES and 1.25 keV SXPES is
250 and 400 meV, respectively. It is noticed that the centre of gravity of the single O 1s peak is almost degenerate in the I phase between HAXPES and SXPES (figure 3(c)), although the spectral width is much different, reflecting the employed instrumental resolution. On the other hand, the centre of gravity of the O 1s spectra in the M phase is noticeably shifted toward lower $E_B$ for HAXPES compared with the SXPES, although the low $E_B$ threshold overlaps well with each other. Consequently, there is a large intensity difference between HAXPES and SXPES in the region of $E_B = 529.5–532$ eV for the M phase in figure 3(a), which cannot be explained by the difference in resolution. There seem to be more than two components in the HAXPES spectrum in the M phase. Judging from the high bulk sensitivity of HAXPES at $E_K \sim 7.4$ keV, this HAXPES shape must be reflecting the bulk electronic structures. In contrast to this, the $E_K$
is only slightly above 700 eV for the present O 1s SXPES spectrum and the surface spectral weight can never be negligible. So the HAXPES is broadened to the Gaussian resolution of 400 meV to be directly compared with SXPES as shown in figure 3(b). By subtracting this broadened bulk spectrum from the SXPES, one can evaluate the surface contribution as shown by the dashed curve in figure 3(b). Since the inelastic mean free path of the photoelectron ($\lambda$) is evaluated as 13.5 Å in VO$_2$ under the present condition [35], the thickness of the surface ($s$) is evaluated as 6.6 Å from the relative bulk spectral weight represented by $\exp(-s/\lambda)$. This value of $s$ is twice larger than the unit cell length along the c-axis. It is also noticed that the spectral shape of the thus derived surface component is not much different from the SXPES spectrum of the I phase shown in figure 3(c) except for the slight energy shift.

Thus it is revealed from the combined studies of HAXPES and SXPES that even the clean surface of the metal VO$_2$ is covered by a clear surface layer with less itinerant electronic structures. A very similar result is also obtained in the case of the heavy fermion material LiV$_2$O$_4$ [36]. The presence of such a surface layer is already confirmed by the spectral analysis of the Cu 2p state in a high-$T_c$ cuprate, Nd$_{2-x}$Ce$_x$CuO$_4$ [37]. There are thus many cases of the presence of a less itinerant surface layer on the clean surfaces of metallic transition metal oxides besides several rare earth compounds [38, 39]. Therefore conventional PES in the $h\nu$ region of 20–120 eV with less bulk sensitivity is not an appropriate PES approach, and HAXPES combined with SXPES is necessary to investigate strongly correlated electron systems such as transition metal oxides and rare earth compounds.

Now we discuss the spectral shape of the O 1s core HAXPES. In order to interpret the essential features of the unusual behaviour of the O 1s HAXPES, a simplified model with a direct product of local and non-local CT degrees of freedom is considered. The local CT satellite is treated by a single-site dp cluster model, where one d orbital and one p orbital are considered. The non-local CT degrees of freedom are treated by two finite-size Hubbard-cluster models, representing the electron–hole pair excitations near $E_F$. This model including both dp and Hubbard clusters is called a double-cluster model (DCM) in this paper. Two Hubbard models are employed to handle both the $d_\parallel (a_{1g})$ and the $d_\pi (e_g^\pi \text{ or } \pi^\ast)$ bands [7, 14]. Our model is an extension of the attempt to simulate the non-local screening in Mn and Ru compounds by using the Hubbard models [40]. The change of the band structures across MIT, namely, the effect of the lattice distortion, is simulated in our paper by the energy difference $\delta$ between the centres of gravity of the $d_\parallel$ and the $d_\pi$ bands. Our Lanczos calculation performed for this DCM shows that the spectrum first gives the main peak and the CT satellite by the dp single-cluster model. Then each peak is accompanied by electron–hole pair excitations through the Hubbard-cluster models. In the M phase, both $d_\parallel$ and $d_\pi$ bands are quarter-filled. With increasing $\delta$, the $d_\pi$ band becomes empty and the $d_\parallel$ band becomes half-filled, resulting in the I phase. This treatment is analogous to that in [15], which takes the orbital switching in the 3d states on MIT into account.

In the I phase with $\delta = 1.2$ eV, a symmetric single peak is predicted as in figure 4. In the M phase with $\delta = 0.9$ eV, the peak is shifted toward lower $E_B$ with a noticeable tail on the higher $E_B$ side of the main peak, where a noticeable difference is observed 0.8–4 eV above the main peak. A slight change of the spectral shape of the CT satellite is also predicted on IMT. The general behaviour of the calculated spectra is consistent with our observation. The essence of the unusual shift of the O 1s peak toward lower $E_B$ on IMT is thus consistent with the model of orbital switching-assisted collaborative Peierls transition resulting from the lattice distortion-induced changes of band structures under the influence of the electron correlation.
A DCM calculation has been performed under the following conditions: for the dp cluster, one d orbital and one p orbital are considered. The d–d correlation energy $U$ and the p–d CT energy $\Delta_1$ are fixed ($U = 4$ eV, $\Delta_1 = 2$ eV). The core hole potential $Q$ and the effective hybridization $V_{\text{eff}}$ for the V 3d–O 2p states is taken as $Q = 5$ eV and $V_{\text{eff}} = 3.5$ eV. The Lorentz broadening width $\Gamma(E_B)$ is approximated as $0.3 + 0.03 \times (E_B - E_0)$, where $E_0$ is the energy of the main peak. For each Hubbard model, we considered a one-dimensional eight-site cluster, where the on-site d–d correlation energy $U_1$ is assumed to be different, depending on whether the system is metallic or not. The core hole potential is taken as $Q_1 = 1.5$ eV. The transfer energy is assumed to be $t = 0.2$ eV for $d_\parallel$ and $t = 1$ eV for $d_\pi$ band, where the effect of the $d(e_g)$ bands is renormalized. The typical calculated results for the O 1s core spectrum is shown with $\delta = 1.2$ and $U_1 = 3$ eV for the I phase and $\delta = 0.9$ and $U_1 = 2$ eV for the M phase, respectively. The CT region is expanded in the inset.

The clear shift of $E_B$ toward lower $E_B$ and the noticeable tail toward higher $E_B$ are also clearly recognized for the ‘O 2p’ valence band features on IMT in figure 2(a) and are interpreted in a similar way. A slight shift due to the same mechanism is also observed for the O 2s state as shown in the inset of figure 1(c). The spectral change of the V 1s core state with the appearance of the lower $E_B$ metallic screening structure and a tail on the higher $E_B$ side is likewise interpreted by employing a slightly different parameter set, reflecting the difference in the V 3d and O 2p characters in the valence and conduction bands. All V core states have shown the appearance of the lower $E_B$ metallic screening structure due to an equivalent mechanism as that for the O 1s state.

Now the valence band spectra are discussed. In comparison with the low-energy PES [12, 27], the enhancement of the so-called ‘O 2p band’ near $E_B = 7–8$ eV is prominent in HAXPES. It is known that the photoionization cross section of the transition metal 4s orbital is relatively much increased compared with the 3d orbital with increasing $h\nu$ in the hard x-ray region [29].

Although it has not explicitly been taken into account in many band structure calculations, the transition metal 4s state is in reality noticeably hybridized with the O 2p orbital in the deep
$E_B$ region ($E_B = 7\text{-}8\text{ eV}$ region) of the ‘O 2p’ band [41]. With increasing $h\nu$, this component becomes relatively enhanced in the ‘O 2p’ band as seen in various V and Cr oxides. Although the d component was proposed to be responsible for the resonance enhancement of the 7.5 eV peak for the V 2p–3d excitation [28], the V 4s component is more plausible for such a resonance enhancement. The V 3d component is more hybridized in the region of $E_B \sim 5\text{ eV}$ in the form of the O 2p–V 3d bonding state, where the resonance enhancement for the V 2p–3d excitation is also seen in their experimental results. As for the ‘O 2p’ band spectral shapes in the bulk, we have observed clear changes on MIT in the whole spectral region in contrast to the less obvious change in a thin film sample [28]. This difference revealed that the electronic structures in such a thin film sample (10 nm) probed by HAXPES down to the interface region with the TiO$_2$ substrate are much different from those in the real bulk sample, since the stress effect induced from the substrate may have changed the electronic structures in the whole region of the thin film. This scenario may be validated by the fact that the MIT temperature in this thin film sample is much different from that in bulk samples. Namely, such a thermal behaviour reflects the average properties in the whole film, and its deviation from the bulk properties is a proof of the deviation of the lattice and electronic properties in such a thin film. The observed shift of the whole ‘O 2p’ band toward lower $E_B$ on IMT is very similar to the result of the O 1s peak and can be understood in the same way. In addition, the broadening of the ‘O 2p’ peaks on IMT including the enhancement of the high-$E_B$ tail in the region of $E_B \sim 9\text{ eV}$ may suggest that the hybridization between the O 2p and V 3d, 4s states is increased in the M phase. The coherent peak and the lower Hubbard band in the M phase have already been discussed. Here the relative intensity at $E_F$ in regard to the coherent peak height in the M phase is much higher in VO$_2$ than in V$_5$O$_9$ and V$_4$O$_7$ (not shown). It is also found in the M phase that the intensity of the incoherent peak relative to the coherent peak increases in this order. These results suggest that the electron correlation effect is weaker in VO$_2$ than in the others. The weakness of the incoherent part or the lower Hubbard band located at around 1.8 eV is theoretically predicted by the correlation-assisted Peierls transition model [14]. The VO$_6$ cluster model calculation in [28], however, predicts a too strong intensity for the incoherent part in the M phase and a too weak intensity for the higher $E_B$ tail of the 0.9 eV peak in the I phase in contrast with our genuine bulk results. In the I phase, the prominent peak at $\sim 0.9\text{ eV}$ is located between this coherent peak and the incoherent part or the lower Hubbard band in the M phase. If we extend the lower energy tail of the 0.9 eV peak in the I phase down to zero intensity, it crosses the zero line at 0.28 eV, yielding the gap energy between the top of this band and $E_F$ as 0.28 eV. This gap is also found to get decreased when one moves to V$_5$O$_9$ and V$_4$O$_7$. All these unusual tendencies of the valence band in VO$_2$ in both M and I phases reinforce the scenario that the gap opening in VO$_2$ is not solely due to the electron correlation effects [14, 15, 26].

Since the low-$E_B$ threshold of the O 2p non-bonding state in the I phase HAXPES is delayed by 0.3 eV in the bulk toward the larger $E_B$ side compared with that in the M phase, there is still a noticeable tail left in $E_B = 2.4\text{-}1.6\text{ eV}$ in the HAXPES in the I phase as recognized in the lower panel of figure 2(b). This region can be ascribed to the incoherent part or the lower Hubbard band in the I phase when compared with the result in the I phase of V$_5$O$_9$ with a noticeable intensity of the incoherent part [32].

The excitation in the I phase from the top of this band (0.28 eV) to the conduction band edge located about 0.50 eV above $E_F$ [12] is expected to be beyond 0.78 eV. On the other hand, a simple summation of the present peak energy (0.9 eV) and the band edge energy (0.5 eV) [12] below and above $E_F$ in the I phase results in 1.4 eV. Meanwhile, the gap threshold energy
estimated from the infrared absorption is 0.68 eV at 260 K and the lowest-energy broad absorption peak is reported in the I phase near 0.85 eV. The possible excitonic binding energy for valence excitons in these narrow gap semiconductors or insulators can be at most 0.1 eV. So, even the possible excitonic effect for the excitation predicted at 1.4 eV cannot explain the experimental absorption structure at 0.68–0.84 eV. Thus the lowest absorption threshold is most probably ascribed to the interband excitation from the dispersing part of the band (up to $E_B = 0.28$ eV) to the lowest conduction band. In this way, the dispersing character of the band centred at $E_B = 0.9$ eV is clear, even though the incoherent component may be overlapping in the region of this main peak. Therefore an interpretation such as that the V 3d main peak at 0.90 eV in the I phase has a strong coherent character with a dispersion up to 0.28 eV below $E_F$ is validated, supporting the calculation based on the cluster extension of the dynamical mean-field theory (C-DMFT) [14], where the system is interpreted to be a renormalized (by correlation effects) Peierls insulator. Although there are several possible explanations for MIT mechanisms when only the spectral changes in the valence band region are considered, the mechanism based on the lattice distortion with a strong electron correlation can only explain the experimentally observed changes of both core and valence band spectra on MIT in the case of bulk VO$_2$.

4. Conclusions

It is revealed by combined HAXPES and SXPES studies that the surface of the metal VO$_2$ is covered by a surface layer with electronic structures of less itinerancy than the bulk. By utilizing the HAXPES at ~8 keV, however, the bulk electronic structures are revealed. Spectral changes are observed for all core levels and valence bands on MIT. The long-range or non-local metallic screening is found to play an important role in the M phase. The V 3d peak near 0.9 eV in the I phase is experimentally confirmed to be caused by the coherent peak and not caused by the lower Hubbard band in contrast with the recently reported HAXPES study on a thin film sample. Spectral shapes of the present results on a fractured bulk sample are noticeably different from those reported for a thin film sample, suggesting the effects of stress from the substrate in the case of thin films. In this way, the scenario that both the lattice distortion accompanied by changes of band structures and the electron correlation effects are responsible for MIT in VO$_2$ is fully clarified. These results demonstrate the importance of really bulk-sensitive measurements for studying correlated electron systems.

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