V-V dimerization effects on bulk-sensitive hard x-ray photoemission spectra for Magnéli phase vanadium oxides

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Highly bulk-sensitive hard x-ray photoemission has been performed for the Magnéli phase V_5O_9 and V_6O_{11}, which are composed of V_2O_3 and VO_2 from chemical point of view. The valence-band spectra near the Fermi level are rather similar between V_5O_9 and V_6O_{11} in both metallic and insulating phases. Although the core-level spectra in the metallic phase are similar between V_5O_9 and V_6O_{11}, the core-level spectra in the insulating phase are noticeably different. Our results are understood by considering the contribution of the V-V dimerization effects, which are strong in V_6O_{11} and negligible in V_5O_9. Comparison of the core-level spectra of V_5O_9 and V_6O_{11} with those of VO_2 has revealed that the mechanism of the metal-insulator transitions for the former two compounds is different from that for VO_2.

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Among various strongly correlated electron systems, the metal-insulator transition (MIT) of vanadium oxides has been discussed for a very long time. For example, a variety of theoretical and experimental studies have been made for V_2O_3 and VO_2, which show MITs as a function of temperature. In addition, it is known that structural phase transitions are associated with their MIT. Namely, corundum V_2O_3 and rutile VO_2 in the metallic phase show a monoclinic structure in the insulating phases.[1–5] While V_2O_3 is thought as a typical example of the Mott-Hubbard MIT system,[6] the origin of the MIT in VO_2 was controversial.[7–14] In comparison with intensive studies of MITs of V_2O_3 and VO_2, the Magnéli phase vanadium oxides; V_nO_{2n-1} (with $4 \leq n \leq 9$), have been less studied, though most of them show MITs as a function of temperature except for V_7O_{13}.[15] They show similar crystal structures[16,17] and can be understood to be chemically composed of V_2O_3 and VO_2 as $V_nO_{2n-1}=V_2O_3+(n-2)VO_2$.[18] Metallic V_nO_{2n-1} comprises a mixture of rutile (VO_2-like) and corundum (V_2O_3-like) regions. In these V_nO_{2n-1}, crystal structures are preserved in their triclinic space group $P\bar{1}$ across the MIT, but the lattice parameters and interatomic distances change discontinuously. Therefore, it is very important to study various V_nO_{2n-1} to understand the physics of MIT associated with the structural changes of vanadium oxides.

Photoelectron spectroscopy (PES) is a powerful tool to study the electronic structures of materials.[19] In the case of strongly correlated electron systems, however, the importance of bulk sensitivity has gradually been recognized as demonstrated in the soft x-ray PES,[20,21] because their surface electronic structures often deviate from those in the bulk. We have here performed further bulk-sensitive hard x-ray PES (Refs. 22 and 23) (HAXPES) for V_5O_9 and V_6O_{11}.

The crystal structures of V_5O_9 and V_6O_{11} were already described in detail by Marezio *et al.*[24] and Schwingenschlögl *et al.*[25] As schematically shown in Fig. 1, their structures are rather similar. The homologous number $n=5$ or 6 corresponds to the length of the chains of the O octahedra with V atoms inside along the pseudorutile c_{prut} axis in the figure. In the case of rutile structure (VO_2), these chains have infinite length and, therefore, VO_2 is assumed to be the end member of $V_nO_{2n-1}(n=\infty)$. On the chain along the same c_{prut} axis, one can also see 4 or $5(=n-1)$ empty O octahedra without central V atoms. In the bottom panels of Fig. 1, the two adjacent chains along the c_{prut} axis with 5 and 6 filled V atoms are displayed for V_5O_9 (left) and V_6O_{11} (right). There are two different types of layers for both materials. One is the layer formed by only odd-numbered vanadium atoms (V1, V3, and V5) and the other is composed of even-numbered vanadium ions (V2, V4, and V6), whose nomenclature follows Refs. 24 and 25 reflecting the site difference with different effective charges. The two layers alternate along the a_{prut} axis. In order to make connections between the V1 and V2 atoms, the vanadium chains are shifted parallel to the c_{prut} axis.[25] Although V_5O_9 and V_6O_{11} preserve their crystal structures of $P\bar{1}$ type across the MIT, they show a kind of structural transformation. The most significant changes take place for the distances between vanadium ions. Especially in V_6O_{11}, V4-V6 dimers are formed with changing their distances from 2.85 Å in the metallic phase to 2.62 Å in the insulating phase. Such a change is analogous to the V-V dimerization in VO_2 across the MIT. In contrast, there is little change in the V-V distances across the MIT for V_5O_9.[24] Then, we can regard VO_2, V_5O_9, and V_6O_{11} as fully dimerized, nondimerized, and partially dimerized systems, respectively.

The samples employed here were single-crystalline V_5O_9 and V_6O_{11} grown by chemical-vapor transport using $TeCl_4$.[26] HAXPES measurements were performed at BL19LXU of SPring-8.[27] The spectra were measured with the MBS A1-HE

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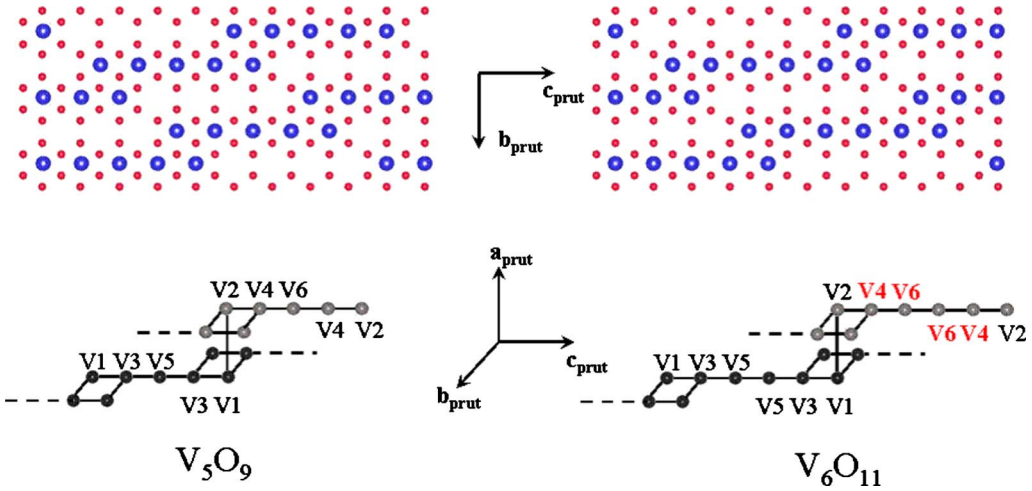

FIG. 1. (Color online). Schematic crystal structure of V_5O_9 (left) and V_6O_{11} (right). Top two panels are viewed along the a_{prut}. Large open and small filled circles mark vanadium and oxygen atoms, respectively. The hexagonal arrangement of O atoms does not show the real position of the O atoms but only stands for the O octahedron. Bottom two panels are schematic views of two adjacent V chains along the a_{prut} axis.

analyzer. The photon energy $h\nu$ was set to ~7945 eV so that enough bulk sensitivity can be realized even in such a deep binding energy (E_B) region as the V 1*s* core level. Clean surfaces were obtained by fracturing *in situ* under ~4.0 $\times 10^{-8}$ Pa. The Fermi energy (E_F) was calibrated by the Fermi edge of Au electrically connected to the sample. The total energy resolution was set to about 180 meV. Because the MIT temperature T_t for V_5O_9 (V_6O_{11}) is about 135 K (Refs. 24, 28, and 29) [170 K (Refs. 25 and 30)], measurements in the metallic phase were first performed at 150 K (200 K). Then, spectra in the insulating phase were measured at 100 K (150 K).

Figure 2 displays valence-band HAXPES spectra of V_5O_9 and V_6O_{11} in both metallic (upper two spectra: M) and insulating (lower two spectra: I) phases. MITs are clearly observed in both V_5O_9 and V_6O_{11} by comparing the spectra in the metallic and insulating phases. It should be noticed that the spectral shapes are rather similar between V_5O_9 and V_6O_{11} in both phases. In the metallic phase a prominent coherent peak (quasiparticle) is clearly observed in both materials, which crosses E_F with noticeable intensity. In addition, incoherent parts corresponding to the lower Hubbard band (LHB) are observed as a tail or weak shoulder in the higher E_B region (labeled L) between ~1 and ~2 eV. The incoherent parts are also observed in the insulating phase between 1.5 and 2.6 eV as a characteristic tail of the peak located at ~0.7(~0.8 eV) in V_5O_9(V_6O_{11}).[31] Note that this strong peak in the insulating phase is located at much lower E_B than that of the LHB in the metallic phase. Therefore the peak at 0.7–0.8 eV in the insulating phase cannot be simply interpreted as LHB but should be interpreted as reflecting coherent spectral weight. Such a situation was suggested from the dynamical mean-field theory for insulating $3d^1$ transition-metal oxides.[13,32] Although the V 3*d* valence band spectrum in the insulating phase of V_2O_3 is interpreted as $3d^2\underline{L}$ single component ($\underline{L}$ is a ligand hole) in Ref. 33, the multiple component structures must be considered for a proper analysis.

While the spectral shape near E_F does not show prominent difference between V_5O_9 and V_6O_{11}, significant changes are observed in the core-level spectra. As the first example, the V 1*s* core-level spectra are shown in Fig. 3(a). After the subtraction of an integral background, each spectrum is normalized by the integrated intensity of the V 1*s* main peak. On the lower E_B side of the main peak, one can recognize in each metallic phase a shoulder structure labeled A. It is ascribed to the well-screened final states where the core holes are screened by conduction electrons. Such a feature is absent in the spectra of the insulating phase. A similar structure in the core-level spectra has been reported not only

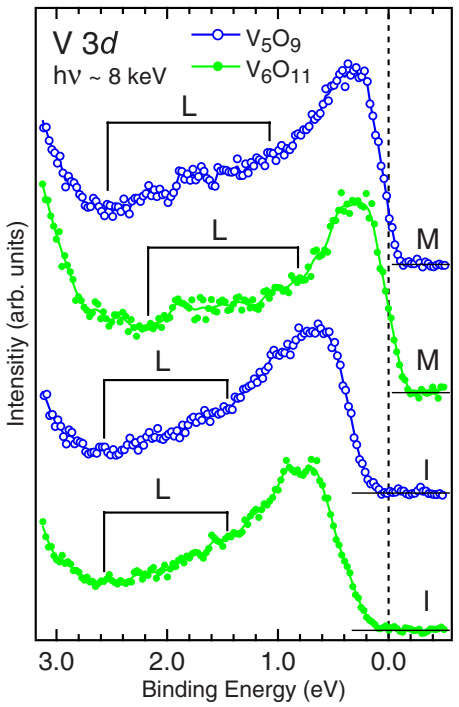

FIG. 2. (Color online). Valence-band spectra of V_5O_9 (spectra with open ○ mark) and V_6O_{11} (spectra with filled ● mark). Upper (lower) two spectra are in the metallic: M (insulating: I) phase. The solid lines show the smoothed data.

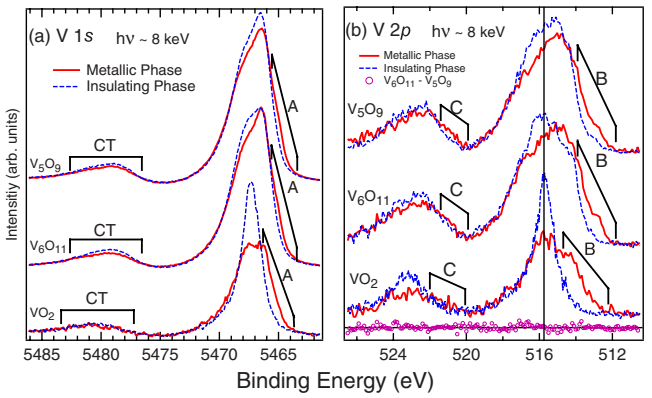

FIG. 3. (Color online). (a) V 1*s* and (b) V 2*p* core-level spectra of V_5O_9, V_6O_{11}, and VO_2. Spectra in the metallic (insulating) phase are indicated by full (dashed) lines in both (a) and (b).

in vanadium oxides[14,34–36] but also in various transition-metal oxides.[37,38] There is a small structure (labeled CT) located at around ~12 eV above the main peak. This structure CT is ascribed to the charge-transfer satellite as clarified by cluster model calculations.[34,35] The V 1*s* main peak in the insulating phase comprises two components in both V_5O_9 and V_6O_{11} in contrast to a single component in the case of VO_2 (Ref. 35) in the insulating phase. Although the relative intensity between the two components does not change much across MIT for V_5O_9, it changes much for V_6O_{11}, where the higher E_B component is noticeably suppressed above T_t.

Figure 3(b) summarizes the V 2*p* core-level spectra. Both spectra in the metallic and insulating phases are normalized to have the same area of the V 2*p* component after subtracting the integral backgrounds. On the lower E_B side of the V $2p_{3/2}$ main peak, the well-screened final states labeled B are recognized in the metallic phase for all materials. The structure C, which is labeled on the lower E_B side of the V $2p_{1/2}$, may have the same origin. When the V_5O_9 spectrum in the metallic phase is subtracted from the spectrum of metallic V_6O_{11}, it is clear that there is only little difference as shown by the empty circles at the bottom of Fig. 3(b). In the VO_2 spectrum[35] in the insulating phase, the component B in the metallic phase is much suppressed and the intensity of the higher E_B component becomes suddenly stronger. A partly similar behavior is seen across MIT for V_6O_{11} while such a behavior is not obvious for V_5O_9. In the insulating phase, both V_5O_9 and V_6O_{11} spectra show at least two components in contrast to a single component in VO_2. Moreover, the difference between the spectra of insulating V_5O_9 and V_6O_{11} is clearly recognized. The spectral weight of the higher E_B component is larger than that of the lower E_B component in V_6O_{11} whereas the situation is opposite in V_5O_9. The vertical line drawn at ~515.8 eV is a guide to the eye for comparison of the peak position in the 2*p* spectra for V_5O_9, V_6O_{11}, and VO_2.

In order to address these spectral behaviors mentioned above, we focus our attention on the difference in the distance between V ions. In the case of VO_2 the V-V dimers are formed across the MIT with changing the value of the V-V distance from 2.85 Å (metallic phase) to 2.62 Å (insulating phase). As summarized in Table I, V_6O_{11} has six inequivalent

TABLE I. Distances between vanadium atoms (in the unit of Å). Values of V_5O_9(V_6O_{11}) are from Marezio *et al.* (Ref. 24) [Schwingenschlögl *et al.* (Ref. 25)].

	V_5O_9		V_6O_{11}	
	Metallic (298 K)	Insulating (110 K)	Metallic (298 K)	Insulating (20 K)
V1-V2	3.50	3.50	2.77	2.77
V1-V3	2.96	2.95	2.95	2.90
V3-V5	2.82	2.81	2.91	2.99
V5-V5			2.80	2.79
V2-V4	3.04	3.00	2.95	3.06
V4-V6	2.89	2.95	2.85	2.62
V6-V6			2.82	3.30

vanadium sites and seven different V-V distances. One of them, namely, the shrinking of the V4-V6 distance in the insulating phase of V_6O_{11} corresponds to the V-V dimerization seen in VO_2, whereas the V-V distances for V_5O_9 do not change so much.[24]

In order to clarify the origin of the different core-level line shapes among V_5O_9, V_6O_{11}, and VO_2 in the insulating phase, we try to reproduce the V 1*s* and V 2*p* core-level spectra of V_6O_{11} by a proper sum of the spectra of nondimerized V_5O_9 and fully dimerized VO_2 in the insulating phase. As shown in Fig. 4, the V 1*s*(2*p*) spectrum of V_6O_{11} is well reproduced by the sum of the spectra of V_5O_9 and VO_2 with

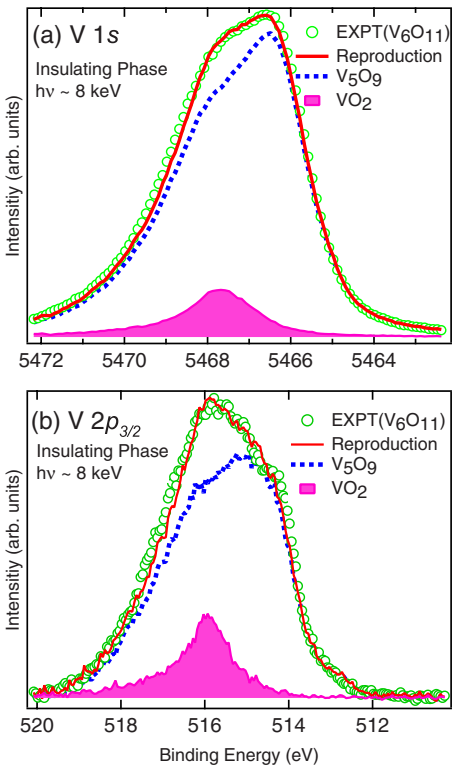

FIG. 4. (Color online). (a) V 1*s* and (b) V $2p_{3/2}$ spectra in the insulating phase of V_6O_{11} (open circles) can be reproduced by the sum of V_5O_9 (dotted line) and VO_2 (hatched area) data.

the ratio of ~90:10 (~85:15). The fraction of the dimerized VO_2 "contribution" in the reproduction process of V $2p_{3/2}$, namely, 15%, is comparable to the ratio of the V4-V6 chains (~17%) in the total V sites in the insulating V_6O_{11}. Therefore, we can conclude that the different core-level line shapes between V_5O_9 and V_6O_{11} originate mainly from the contribution of the V-V dimerization in the insulating phase. Though the V-V dimerization effects cannot be observed clearly in the V $2p_{1/2}$ spectral weight for the insulating V_6O_{11}, we have confirmed that the V $2p_{1/2}$ spectral shape can be reproduced by the same procedure as for the V $2p_{3/2}$ spectra (not shown here).

On the other hand, rather similar spectral shapes are observed between V_5O_9 and V_6O_{11} in the core-level spectra in the metallic phase as well as in the valence-band spectra in both metallic and insulating phases. The resemblance in the valence-band spectral shapes between these two compounds suggests that the strength of the electron correlation is comparable. Although the V-V dimerization effects are not so clear in the valence-band spectra of these materials compared with VO_2,[35] they are explicitly traced in the core-level spectra. The relative spectral weight of the well-screened final states in the V 1*s* and 2*p* core-level spectra in the metallic phase is stronger for VO_2 than for these two materials, suggesting that the electron correlation effect is weaker for VO_2 than for V_5O_9 and V_6O_{11}. The MIT temperature T_t, on the other hand, is much higher for VO_2 (~340 K for the bulk samples[39]). By further considering the facts that the antiferromagnetic ordering is seen at low temperatures in insulating phase of V_5O_9 and V_6O_{11} while VO_2 is nonmagnetic below T_t (Ref. 18) in addition to our spectroscopic results, we conclude that the mechanism of MIT for V_5O_9 and V_6O_{11} is much different from that for VO_2. Still it is unclear whether that for V_5O_9 and V_6O_{11} is similar to V_2O_3.

In conclusion, we have performed HAXPES for the Magnéli phase V_5O_9 and V_6O_{11}. The valence-band spectra show similar spectral shapes for V_5O_9 and V_6O_{11} in both metallic and insulating phases, suggesting comparable electron correlation effects. The core-level spectra in the insulating phase, however, differ clearly between them, reflecting the effects of the partial V-V dimerization effects in V_6O_{11}. The mechanisms of the MIT for V_5O_9 and V_6O_{11} is different from that for VO_2.

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