Cluster model and band structure calculations of V_2O_5: Reduced V^{5+} symmetry and many-body effects

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We studied the electronic structure of the V_2O_5 compound using cluster model calculations. The calculation included the reduced V^{5+} symmetry and the strong V $3d-O\ 2p$ covalence effects. The many-body effects are taken into account using the configuration interaction method. The ground state of V_2O_5 is highly covalent and dominated by the $3d^1\underline{L}$ ($^1A_1$) configuration, where $\underline{L}$ denotes a ligand hole. The V_2O_5 material is in the charge-transfer regime and the band gap is due to *p-d* transitions. The first removal state is given by the $3d^0\underline{L}$ ($^2A_1$) configuration, and the first addition state is formed by the $3d^1$ (^2E) configuration. The results of the cluster model are in good agreement with band structure calculations. The calculation results are also in good agreement with photoemission and x-ray absorption spectra. The V $2p$ core-level spectra exhibit many-body effects despite the nominal $3d^0$ occupancy. These effects and the reduced V^{5+} symmetry are crucial to describe the electronic structure of V_2O_5.

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I. INTRODUCTION

The vanadium oxide family forms many different compounds with a broad range of physical properties. The interest in this kind of materials is often related to the presence of a metal-insulator transition (MIT).[1] Although it does not present a MIT transition, the V_2O_5 compound is one of the most widely studied. The studies on this material are mostly focused in its applications in Li-ion batteries,[2] electrochromic devices,[3] gas sensors,[4] and supported catalysis.[5]

The structure of the V_2O_5 material is orthorhombic with the V^{5+} ions in a square pyramid coordination.[6] The structure consists of layers formed by these square pyramids and presents a strong two-dimensional character. The V_2O_5 compound is a semiconductor with a band gap of approximately 2.2–2.3 eV.[7,8] The electronic structure of V_2O_5 was studied experimentally using photoemission,[9,10] resonant photoemission,[11] x-ray absorption,[12,13] photoemission and Auger,[14] x-ray emission,[15] x-ray appearance near edge structure and extended x-ray absorption fine structure,[16,17] and electron-energy-loss[18] spectroscopy.

The electronic structure of V_2O_5 was studied theoretically using band structure[19,20] and cluster model[21,22] calculations. These calculations showed the crucial relationship between the crystal structure and the electronic structure. The V $2p$ x-ray photoelectron spectrum of V_2O_5 was analyzed using cluster model calculations.[23] This calculation method included explicitly many-body effects and the strong V $3d-O\ 2p$ hybridization, but it did not include the correct local V^{5+} symmetry and it was restricted to the V $2p$ core-level spectrum.

The aim of this work is to study the electronic structure of V_2O_5 using cluster model calculations. The approach includes now the reduced symmetry of the V^{5+} ions and also relevant many-body effects. These two effects are completely necessary to describe the electronic structure of the V_2O_5 compound. The cluster model results are in good agreement with band structure calculations, as well as with the experimental photoemission and x-ray absorption spectra. The calculated band gap mainly has a *p-d* character and is in good agreement with the experimental value.

II. EXPERIMENTAL DETAILS

The samples were V_2O_5 polycrystals with large and highly oriented needlelike grains. These polycrystals were obtained from the melt in air at 650 °C and cooled down at 1 °C/min. The subsequent powder x-ray diffraction analysis showed that the resulting samples were single phase.

The photoemission spectrum was measured at the plane-grating monochromator beamline in CAMD. The photon energy was set to 50 eV, the energy resolution was about 0.4 eV, and the energy scale was calibrated using the Fermi level of a gold foil. The x-ray photoelectron spectrum was measured using Mg $K\alpha$ radiation in a conventional equipment. The energy resolution was about 0.9 eV, and the energy scale was calibrated using the peak positions of a Ag foil.

The x-ray absorption spectra were measured at the spherical-grating monochromator beamline in LNLS. The energy resolution was about 0.5 eV, and the energy scale was calibrated using the known V_2O_5 peak positions. The sample was scrapped with a diamond file in all cases to remove the surface contamination. All the spectra presented here were normalized to the maximum after a constant background subtraction.

III. CALCULATION DETAILS

A. V^{5+} ion symmetry

The transition metal ions in oxides usually appear in MO_6 blocks with an octahedral local symmetry. The resulting O_h

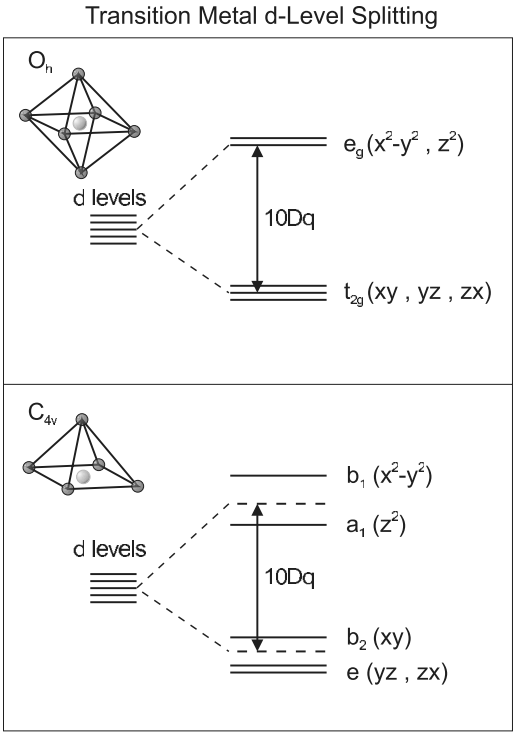

FIG. 1. Splitting of the transition metal d levels in O_h and C_{4v} symmetries.

crystal field, given by the Dq parameter, splits the M d orbitals into the t_{2g} and e_g levels (see Fig. 1). Many transition metal oxides present distortions within the MO_6 octahedra and/or alterations in the way these MO_6 blocks are connected together. These lattice distortions are responsible for changes in the physical properties of these compounds.

The VO_6 block in the V_2O_5 compound presents a rather large deviation from octahedral symmetry. In fact, one of the apical oxygen ions is so far away that the corresponding V-O interaction is much weaker. Thus, it is more appropriate to use a VO_5 square base pyramid as a block to describe the V_2O_5 compound. The resulting C_{4v} crystal field, given by the Dq, Ds, and Dt parameters, produces an additional splitting (see Fig. 1). The relative energy position of the different V $3d$ levels in C_{4v} symmetry is given in Table I.

B. Cluster model

The cluster consisted of a $[VO_5]^{-5}$ square base pyramid structure resulting in a V^{5+} ion with a nominal $3d^0$ occupancy. The model was solved using the configuration interaction method, which includes relevant many-body effects.[24,25] The ground state Φ_i was expanded in the following configurations: $3d^0$, $3d^1\underline{L}$, $3d^2\underline{L}^2$, $3d^3\underline{L}^3$, etc., where $\underline{L}$ denotes a hole in the O $2p$ band. The main parameters of the model were the charge-transfer energy Δ, the Mott-Hubbard repulsion U, the p-d transfer integral $(pd\sigma)$, and the core-hole potential Q $(Q=1.25U)$.[23] The multiplet splitting was obtained in terms of the crystal field parameters Dq, Ds, and Dt, as well as the p-p transfer integral $(pp\pi)$-$(pp\sigma)$.

TABLE I. Energy position of the different V $3d$ levels in C_{4v} symmetry.

Level	Position
b_1 (x^2-y^2)	6 Dq+2 Ds−1 Dt
a_1 (z^2)	6 Dq−2 Ds−6 Dt
b_2 (xy)	−4 Dq+2 Ds−1 Dt
e (yz,zx)	−4 Dq−1 Ds+4 Dt

TABLE II. Model parameters used in the calculations of V_2O_5.

Parameter	Value (eV)
Δ	0.70
U	5.5
$pd\sigma$	2.7
Dq	0.15
Ds	0.10
Dt	0.04
$pp\pi$-$pp\sigma$	0.70

The final states (Φ_f) were obtained by removing a V $3d$ electron (photoemission spectroscopy), adding a V $3d$ electron (BIS), adding an O $2p$ electron [O $1s$ x-ray absorption spectroscopy (XAS)], removing a V $2p$ electron (V $2p$ x-ray photoemission spectroscopy), and removing (adding) a V $2p$ $(3d)$ electron (V $2p$ XAS). The corresponding spectral weight $A(\omega)$ for each case was calculated using the sudden approximation,

$$I(\varepsilon) = \sum_f |\langle \Phi_f | \hat{O} | \Phi_i \rangle|^2 \delta(\varepsilon - E_f + E_i), \quad (1)$$

where Φ_i (E_i) is the ground state vector (energy), Φ_f (E_f) is the fth final state vector (energy), and $\hat{O}$ is the corresponding transition operator. The same approach was recently used to describe the electronic structure of VO_2 and V_2O_3.[26,27]

The values of the model parameters used in the calculation of V_2O_5 are listed in Table II (it is worth noting that the same set of parameters was used in all the calculations presented here). These values gave the best agreement with the experiment and are similar to previous estimates.[23] Further, these parameters follow the expected chemical trend in the V_2O_5-VO_2-V_2O_3 series.[23]

C. Band structure

The band structure was calculated using the standard local density approximation (LDA). The program used the full-potential linear-muffin-tin orbital method.[28] The exchange and correlation potential was calculated using the Vosko approximation.[29] The calculation was performed in the observed orthorhombic structure (space group *Pmmn*). The lattice parameters and atomic positions used in the calculation are given in Table III. The basis set for the valence electrons

TABLE III. Lattice parameters and atomic positions used in the band structure calculation of V_2O_5.

Parameter	Value (Å)
a	11.512
b	3.564
c	4.368
Atom	Position
V ($4f$)	0.101, 0.250, −0.108
O_v ($4f$)	0.104, 0.250, −0.469
O_c ($4f$)	−0.069, 0.250, 0.003
O_b ($2a$)	0.250, 0.250, 0.001

were $4s$, $4p$, and $3d$ for V and $2s$, $2p$, and $3d$ for O. The self-consistent potential and the density of states were calculated using 64 irreducible **k** points.

IV. RESULTS AND DISCUSSION

The calculated contribution of the main configurations to the ground state of V_2O_5 is given in Table IV. The ground state of V_2O_5 is dominated by the $3d^1\underline{L}$ and $3d^2\underline{L}^2$ configurations with a contribution of 75%. The relatively large weight of these configurations indicates that V_2O_5 is in the charge-transfer regime.[30] This conclusion is also supported by the relative value of the Δ and U cluster model parameters ($\Delta < U$).[30] The average occupation of the V $3d$ state, around 1.2, reflects the strong V $3d$–O $2p$ covalent bonding (this occupation is much larger than the nominal d^0 expected from a purely ionic model). The relatively large covalent contribution to the bonding in V_2O_5 is in accordance with previous works.[23]

Figure 2 compares the cluster model (bottom) and band structure (top) calculations of V_2O_5. The zero in the energy scale corresponds to a Fermi level pinned at the bottom of the conduction band. The results of the band structure calculation are in very good agreement with previous studies.[19,20] The calculated band gap, about 2.2 eV, is in close agreement with the experimental value of 2.2–2.3 eV.[7,8] The occupation of the V $3d$ orbitals obtained from the band structure calculation is about 1.6 (this value is slightly larger than that obtained from the cluster model calculation, around 1.2). The relatively large occupation of the V $3d$ states indicates again the strong V $3d$–O $2p$ hybridization.

TABLE IV. Contribution of the main configurations to the ground state of V_2O_5.

V_2O_5 ground state	
Configuration	Contribution
$3d^0$	20%
$3d^1\underline{L}$	47%
$3d^2\underline{L}^2$	28%

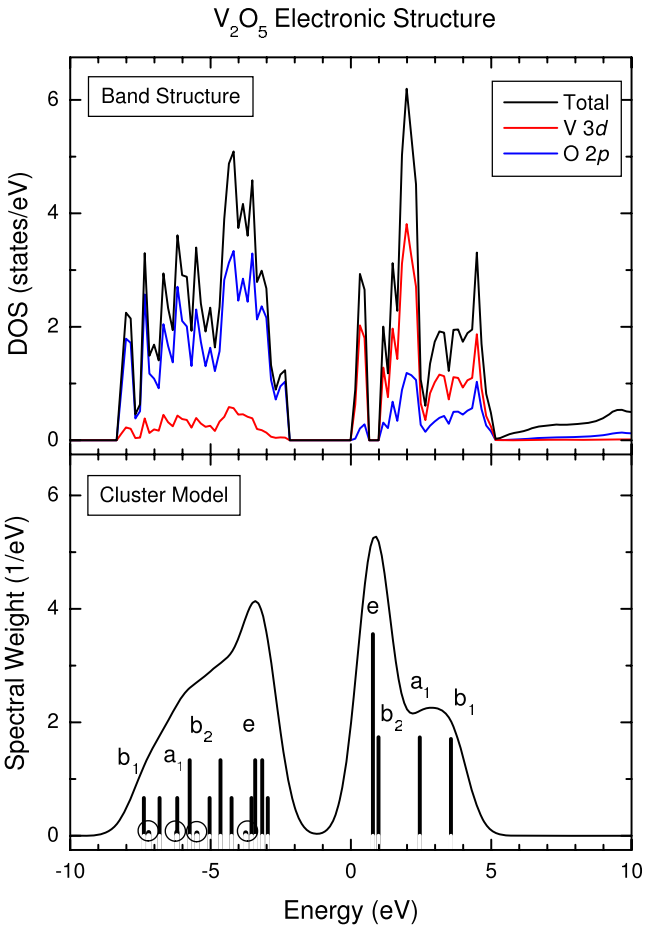

FIG. 2. (Color online) The spectral weight of V_2O_5 from the cluster model compared to the density of states from the band structure calculation.

The occupied states in the valence band go from −8.3 to −2.2 eV, with a total width of about 6.1 eV. The main contribution to the valence band comes from the O $2p$ states; the much smaller V $3d$ state contribution is due to V-O hybridization. The unoccupied electronic states in the conduction band start at 0.0 eV and extend to higher energies. The conduction band is mostly formed by the V $3d$ states from 0.0 to 5.1 eV, although there is some O $2p$ character mixed in due to the V-O hybridization. The V $3d$ band presents a split-off peak just above the Fermi level, which has an almost pure V $3d$ character, as well as two stronger structures about 1.0–2.5 and 2.5–5.1 eV, which have a larger V $3d$–O $2p$ admixture.

The cluster model calculation is a combination of the V $3d$ removal and addition spectral weight. The O $2p$ contribution was calculated in the square pyramid symmetry using a single particle approximation. The transitions were broadened with a 0.5 eV Gaussian to simulate band dispersion and energy resolution. The transitions from −7.4 to 3.0 eV are mostly related to the removal of an O $2p$ electron (where the main contribution to the final state Φ_f is given by the $3d^0\underline{L}$ configuration). These transitions are split due to the V $3d$–O $2p$ and O $2p$–O $2p$ interactions within the VO_5 pyramid. On the other hand, the transitions from 1.3 to 4.1 eV correspond mainly to the addition of a V $3d$

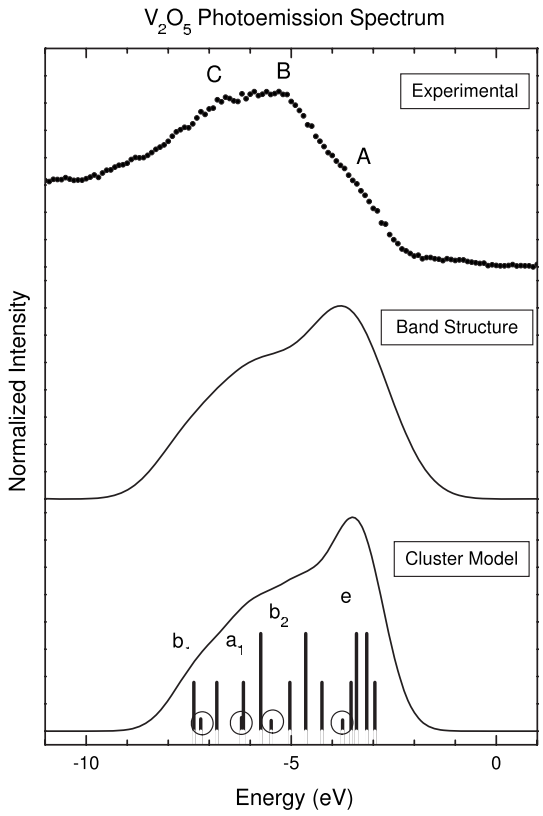

FIG. 3. Photoemission spectrum of V_2O_5 taken at 50 eV compared to the total DOS (band structure) and the spectral weight (cluster model).

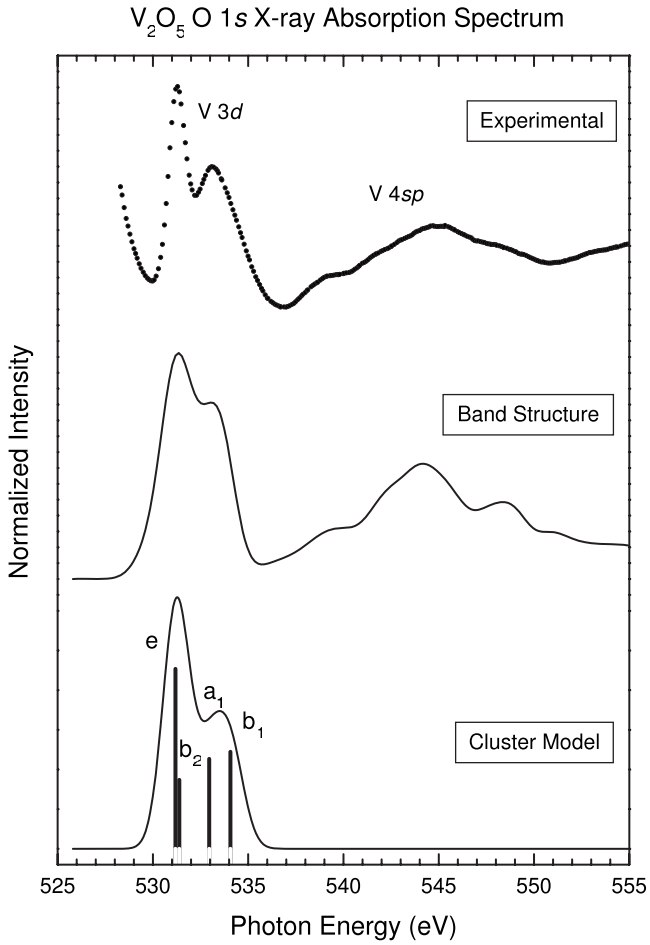

FIG. 4. O 1*s* x-ray absorption spectrum of V_2O_5 compared to the O 2*p* DOS (band structure) and the O 2*p* spectral weight (cluster model).

electron (where the main contribution to the final state Φ_f is given by the $3d^1$ configuration). These transitions are affected by the V 3*d*–O 2*p* interactions and crystal field effects (the peaks at 0.8, 1.0, 2.4, and 3.6 eV are related to the addition of an *e*, b_2, a_1, and b_1 electrons, respectively).

The first removal state, around 3.0 eV, corresponds to the removal of an O 2*p* electron with A_1 symmetry. The first addition state, about 0.8 eV, corresponds to the addition of a V 3*d* electron with *E* symmetry. The lowest energy optical excitation is thus of the *p*-*d* type, as expected in the charge-transfer regime.[30] This is in agreement with the assignment of the lower energy features in the reflectance spectrum.[9] The resulting band gap, about 2.5 eV, is slightly larger than the experimental value, 2.2–2.3 eV.[7,8] The calculated band gap increases with both the charge-transfer energy Δ and the $pd\sigma$ hybridization.

Figure 3 compares the experimental photoemission spectrum of V_2O_5 to the calculated spectral weight, as well as the total density of states (DOS) broadened with a 0.5 eV Gaussian to simulate the energy resolution (the V 3*d* and O 2*p* states were equally weighted because their corresponding cross sections are similar).[31] The experimental spectrum is in agreement with previous results,[9–11] and the total DOS is similar to previous LDA[19,20] and density functional theory (DFT) results.[22] The main contribution to the valence band spectrum of V_2O_5 is given by the removal of O 2*p* electrons. The experimental spectrum presents three main substructures: The first feature (A) is assigned to almost pure O 2*p* nonbonding states, whereas the next two structures (B and C) are attributed to V 3*d*–O 2*p* bonding states.

The above assignments are in agreement with the cluster model and band structure calculations. The band structure presents a relatively nonbonding O 2*p* band around the A feature, from −2.2 to −4.8 eV, whereas the V 3*d*–O 2*p* bonding mixture is relatively larger in the B-C region, from −4.8 to −8.3 eV. The cluster model spectrum also presents pure O 2*p* removal states around the A feature, from −3.0 to −5.0 eV, as well as mixed V 3*d*–O 2*p* removal states in the B-C region, from −5.8 to −7.4 eV. Finally, the small peaks around −3.7, −5.5, −6.2, and −7.2 eV correspond to the V 3*d* removal spectrum.

The cluster model and band structure results reproduce the positions of the structures in the spectra. The B and C structures in the photoemission spectrum are relatively enhanced with respect to the calculation. This spectrum was taken with a photon energy, which corresponds to the V 3*d*–V 3*d* resonance. The larger intensity of these features is thus attributed to the resonance of the V 3*d*–O 2*p* bonding states.[9] On the other hand, the present calculation is in good agreement with the off-resonance spectrum taken at 100 eV.[11]

Figure 4 compares the experimental O 1*s* x-ray absorption

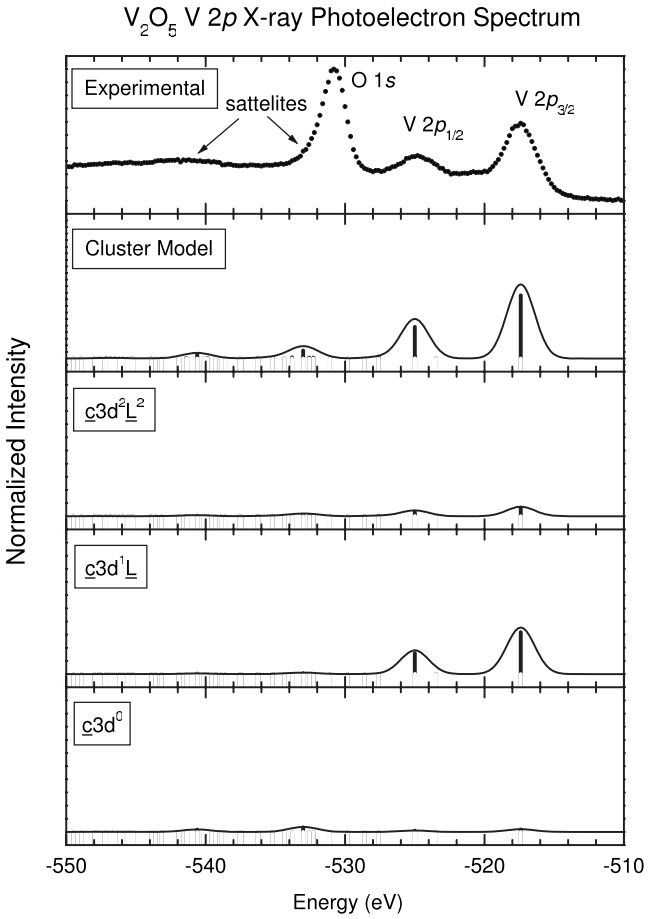

FIG. 5. V $2p$ x-ray photoelectron spectrum of V_2O_5 compared to the cluster model spectral weight projected into the main final state configurations.

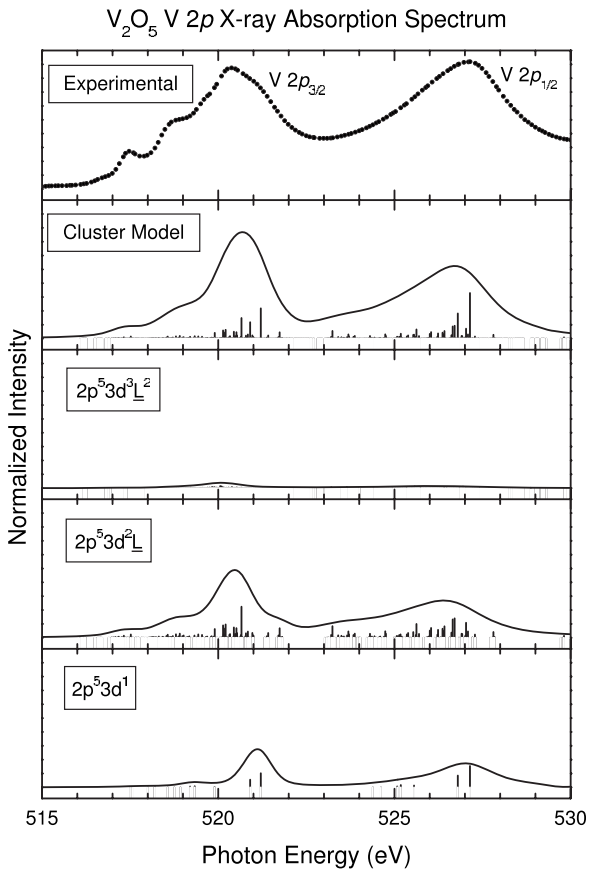

FIG. 6. V $2p$ x-ray absorption spectrum of V_2O_5 compared to the cluster model spectral weight projected into the main final state configurations.

spectrum of V_2O_5 to the calculated spectral weight, as well as the O $2p$ DOS broadened with a 0.6 eV Gaussian to simulate the energy resolution. The experimental spectrum is in agreement with previous results,[12,13] and the O $2p$ DOS is similar to previous LDA[19,20] and DFT results.[21] The band structure and cluster model calculations reproduce very well the main features in the experiment. The O $1s$ x-ray absorption spectrum corresponds to transitions from the O $1s$ level to unoccupied O $2p$ states. The first region, from 529 to 536 eV, is related to the O $2p$ character mixed with V $3d$ states, whereas the second region, from 536 to 551 eV, corresponds to the O $2p$ character mixed with V $4sp$ states. The V $3d$ region is split by the pyramidal crystal field effects into two subbands around 531 and 533 eV. The first subband corresponds to final states of e and b_2 symmetries, whereas the second subband is related to final states of a_1 and b_1 symmetries. The intensity of the a_1 and b_1 peaks is larger than in the addition state because of the larger V $3d$–O $2p$ mixing.

Figure 5 compares the V $2p$ x-ray photoelectron spectra of V_2O_5 to the cluster model calculation. The calculated spectrum was projected into the main final state configuration, and the discrete transitions were broadened with a 0.9 eV Gaussian. The V $2p$ level is split by the spin-orbit interactions into the V $2p_{3/2}$ (~517 eV) and V $2p_{1/2}$ (~525 eV) peaks. The V $2p_{3/2}$ and V $2p_{1/2}$ main peaks presents charge-transfer satellites around 533 and 540 eV, respectively (the charge-transfer satellite corresponding to the V $2p_{3/2}$ peak is hidden beneath the much stronger O $1s$ peak).

The calculation is in good agreement with the experiment and reproduces the energy and intensity of the different features in the spectrum. The main peaks are mostly due to the so called *well screened* $c3d^1\underline{L}$ configuration (where c denotes a hole in the core level), whereas the satellites are mainly related to the *poorly screened* $c3d^0$ configuration. The large O $2p$ contribution to the main peaks indicates again the strong V $3d$–O $2p$ covalent interactions. Finally, the charge-transfer satellite represents a many-body effect in a nominal $3d^0$ compound.

Figure 6 compares the V $2p$ x-ray absorption spectrum of V_2O_5 to the cluster model calculation. The calculated spectrum was also projected into the main final state configurations, and the transitions were broadened with a 0.4 eV (0.3 eV) Gaussian (Lorentzian). The V $2p$ level is again split by spin-orbit interactions into the V $2p_{3/2}$ (from 516 to 522 eV) and the V $2p_{1/2}$ (from 522 to 530 eV) absorption edges. The spectrum is related to V $2p \rightarrow$ V $3d$ transitions and is dominated by multiplet and crystal field effects.[32,33] The Slater integrals were reduced to 80% of their atomic values, and the C_{4v} crystal field parameters (Dq, Dt,

and Ds) are listed in Table II (the experimental spectrum cannot be reproduced by a calculation in a crystal field of O_h symmetry).

The calculation is in good agreement with the experiment and reproduces the main features in the spectrum. The spectral weight is dominated by the $2p^5 3d^2\underline{L}$ final state configuration, with a relative weight of 69%, whereas the relative contribution from the $2p^5 3d^1$ final state configuration is about 25%. This is related to the much larger contribution of the $3d^1\underline{L}$ configuration to the ground state because the $2p^5 3d^2\underline{L}$ final state configuration is reached via $2p^6 3d^1\underline{L} \rightarrow 2p^5 3d^2\underline{L}$ transitions. This result illustrates again the importance of the large V $3d-$O $2p$ covalent interactions, as well as the influence of many-body effects even in a nominal $3d^0$ compound.

The above results provide a complete description of the electronic structure of the V_2O_5 compound. The cluster model calculation explains both the core- and valence-level spectra with a single parameter set. The present results confirm that the V $3d-$O $2p$ covalent interaction plays a dominant role in the V_2O_5 material. The calculated V $2p$ x-ray photoelectron spectrum shows clear satellites due to many-body effects (this shows that electron correlation effects are also important in a nominal $3d^0$ compound such as V_2O_5). The calculated V $2p$ x-ray absorption spectrum is sensitive to the reduced symmetry of the crystal field. These two effects are thus crucial for a proper description of the electronic structure of the V_2O_5 oxide.

V. SUMMARY AND CONCLUSIONS

In summary, we studied the electronic structure of the V_2O_5 compound using cluster model calculations. The calculations included the strong V $3d-$O $2p$ interactions, the many-body effects, and the reduced symmetry of the V^{5+} ions. The ground state is highly covalent and is dominated by the $3d^1\underline{L}$ configuration with a relative weight of about 47%. This compound is in the charge-transfer regime, and the lowest energy optical excitations are of the p-d type. The value of the calculated band gap, 2.2–2.5 eV, is in good agreement with the experimental result, 2.2–2.3 eV. The cluster model results are in good agreement with band structure calculations. They also reproduce reasonably well both the core- and valence-level spectra of the V_2O_5 material. The present results confirm the importance of the strong V $3d-$O $2p$ covalent interactions. The results also indicate the influence of many-body effects and the reduced symmetry of the V^{5+} ions. These effects are crucial for a proper description of the electronic structure of the V_2O_5 compound.

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