

Minimal model needed for the Mott-Hubbard SrVO₃ compound

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We studied the electronic structure of the SrVO₃ compound using an extended cluster model. The calculation is compared to the photoemission and x-ray absorption/bremsstrahlung isochromat spectra. The calculated spectral weight correctly describes the experimental features in the SrVO₃ material. The results indicate that the O 2*p* states are essential to explain the data and must be included explicitly in any minimal model of this compound.

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I. INTRODUCTION

The transition-metal oxides are at the forefront of the current research in condensed-matter physics. The great attraction exerted by these materials is related to their interesting physical properties, for example, high- T_C superconductivity, colossal magnetoresistance, and metal-insulator transitions. This rich variety of physical properties is related to the highly correlated electronic structure of these materials. But despite extensive work, even the minimal model needed to address these materials remains controversial.

Some researchers propose either a periodic p - d or Anderson model which includes explicitly the O 2*p* states.¹ Others defend a somewhat simpler Hubbard or t - J model where the O 2*p* states are mapped out.² This reduction procedure appears to preserve the qualitative description of some low energy physical properties.³ But, it is not trivial to assume that the validity of this approach could be extended to all these properties. We show here that the O 2*p* states are crucial to explain the spectra of the Mott-Hubbard SrVO₃ oxide.

The valence band of SrVO₃ presents a coherent peak at the Fermi level and an incoherent structure around 1.6 eV.⁴ The spectral weight of the coherent peak is transferred to the incoherent structure in the Sr_{1-x}Ca_xVO₃ series.⁵ The dynamical mean-field theory (DMFT) attributed the coherent peak to quasiparticle excitations and the incoherent structure to the remnant of the lower Hubbard band.⁶ The decrease in the incoherent structure at higher photon energies was attributed to the larger correlation at the surface.⁷⁻¹⁰ The x-ray absorption (XAS) and bremsstrahlung isochromat (BIS) spectra show the coherent peak and the upper Hubbard band.^{11,12}

We study the electronic structure of SrVO₃ by exact diagonalization of an extended cluster model. The calculation is in agreement with photoemission and x-ray absorption/bremsstrahlung isochromat spectra. The incoherent feature in photoemission contains considerable O 2*p* character and it cannot thus be attributed to the remnant of the lower Hubbard band. Further, the spectral weight in the addition spectra is mostly dictated by crystal field rather than by correlation effects. The O 2*p* states are fundamental for a proper description and understanding of these spectroscopic results.

II. CALCULATION DETAILS

The model was used to study the core-level spectra in Mott-Hubbard systems,¹³ colossal magnetoresistance materials,¹⁴ and high- T_C superconductors.¹⁵ We applied the extended cluster model to study the valence and conduction bands of several Mott-Hubbard systems.¹⁶⁻¹⁸ The Hamiltonian of the model is given by

$$H = \sum_{m,\sigma} \varepsilon_{m\sigma}^d d_{m\sigma}^+ d_{m\sigma} + \sum_{m,\sigma} \varepsilon_{m\sigma}^p p_{m\sigma}^+ p_{m\sigma} + \sum_{m,m',\sigma,\sigma'} (U - J\delta_{\sigma\sigma'}) \times d_{m\sigma}^+ d_{m\sigma} d_{m'\sigma'}^+ d_{m'\sigma'} + \sum_{m,\sigma} T_m (d_{m\sigma}^+ p_{m\sigma} + \text{H.c.}) + H_{\text{eff}}, \quad (1)$$

where $d_{m'\sigma'}^+$ ($p_{m\sigma}$) creates (annihilates) a V 3*d* (O 2*p*) electron with energy $\varepsilon_{m'\sigma'}^d$ ($\varepsilon_{m\sigma}^p$). The index m denotes the orbital symmetry (t_{2g} or e_g) and σ denotes the corresponding spin projection. The first four terms in H represent the interaction within a single VO₆ cluster, whereas H_{eff} describes the inter-cluster contributions treated as an effective medium,

$$H_{\text{eff}} = \sum_{m,\sigma} \varepsilon_{m\sigma}^c c_{m\sigma}^+ c_{m\sigma} + \sum_{m,\sigma} T_m^* (d_{m\sigma}^+ c_{m\sigma} + \text{H.c.}), \quad (2)$$

where $c_{m\sigma}^+$ creates an electron in the effective medium with energy $\varepsilon_{m\sigma}^c$. The index m corresponds here to the t_{2g} symmetry, which is the character of the corresponding coherent fluctuations.

Figure 1 (top panel) depicts the main ingredients of the present model, showing the basal plane of a generic VO₆ cluster embedded in an effective medium. This represents the effective interactions with the other VO₆ octahedra in the lattice. The periodic p - d model is indeed equivalent to a single cluster embedded in an effective medium.¹⁹ The main energy scales are the d - d Coulomb repulsion energy U , the p - d charge-transfer energy $\Delta = \varepsilon^d - \varepsilon^p + U$, and the effective charge-transfer energy $\Delta^* = \varepsilon^d - \varepsilon^c + U$.¹³⁻¹⁵ The p - d hybridization is given by the T_σ (e_g symmetry) and $T_\pi \approx -T_\sigma/2$ (t_{2g} symmetry) parameters.

Figure 1 (lower panel) portrays the usual dynamical mean-field theory approach, showing a single V ion embedded in the effective medium. The main difference, in this

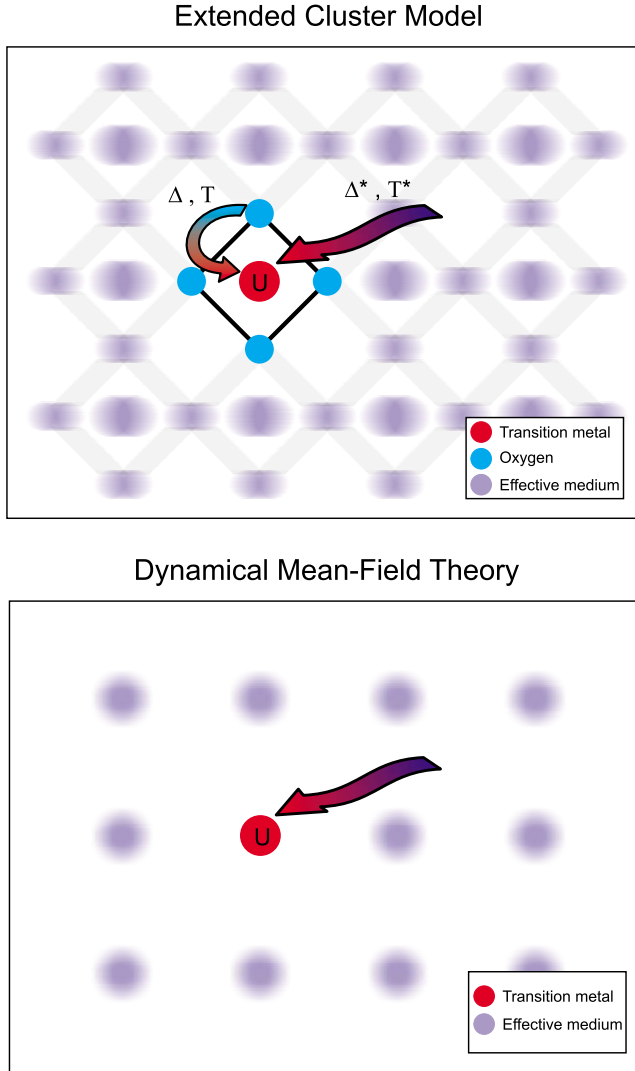


FIG. 1. (Color online) Schematic representation of the extended cluster model (top panel) and the conventional DMFT method (bottom panel). The charge-transfer energy (hybridization) from the ligand is Δ (T). The charge-transfer energy (hybridization) from the effective medium is Δ^* (T^*).

case, is that the charge fluctuations from the O $2p$ states are not considered explicitly.

The extended cluster model is solved by the standard configuration-interaction method. The ground state is expanded in the $3d^1$, $3d^2\bar{L}$, $3d^2\bar{C}$, $3d^0C$, and other configurations, where \bar{L} (\bar{C}) denotes a hole in the ligand (coherent) band.^{13–15} The multiplet splitting is given by the crystal field ($10Dq=1.8$ eV), the intra-atomic exchange ($J=0.4$ eV), and the p - p transfer integral ($pp\pi$ - $pp\sigma=0.8$ eV).^{16–18} The corresponding removal (addition) states are obtained from the ground state by removing (adding) an electron. Finally,

TABLE I. Main parameters used in the extended cluster model calculations (all values in eV).

Δ	U	T_σ	Δ^*	T^*
2.0	5.0	3.3	0.75	0.27

the removal and addition spectral weights $A(\omega)$ are calculated using the sudden approximation,

$$A(\omega) = \sum_i |\langle \psi_i^{N-1} | \hat{O} | \psi_0^N \rangle|^2 \delta(\omega - E_i^{N-1} + E_0^N) + \sum_i |\langle \psi_i^{N+1} | \hat{O}^\dagger | \psi_0^N \rangle|^2 \delta(\omega - E_i^{N+1} + E_0^N), \quad (3)$$

where \hat{O} is the corresponding transition operator, ψ_0^N (E_0^N) is the ground-state vector (energy), ψ_i^{N-1} (E_i^{N-1}) is the i th removal state vector (energy), and ψ_i^{N+1} (E_i^{N+1}) is the i th addition state vector (energy). The main parameters used in the calculation are listed in Table I and are in line with previous estimates.^{16–18}

III. EXPERIMENTAL DETAILS

The SrVO₃ sample was a single crystal grown by the floating zone method. A powder x-ray diffraction study confirmed that the sample was a single phase. The spectroscopic measurements were carried out at the LNLS in Campinas, Brazil. The O $1s$ XAS spectrum was measured at the SGM beamline using the total electron yield method. The energy resolution was set to 0.5 eV and the energy scale was calibrated using reference samples. The high energy (1840 eV) photoelectron spectroscopy (PES) spectrum was measured at the soft x-ray spectroscopy (SXS) beamline using an electrostatic analyzer. The energy resolution was about 0.4 eV and the energy scale was calibrated using a clean gold foil. The sample was scraped with a diamond file to remove surface contamination. The cleanness of the sample was confirmed by the absence of a shoulder in the O $1s$ peak. The core-level and valence-band spectra of SrVO₃ were already presented in Ref. 18.

IV. RESULTS AND DISCUSSION

The ground state of SrVO₃ is mostly given by the $3d^2\bar{L}$ (48%), the $3d^1$ (27%), and the $3d^2\bar{C}$ configurations (13%). The ground state of SrVO₃ is thus highly covalent and the mean $3d$ occupation is about 1.8 electrons. The dominant weight of the $3d^2\bar{L}$ configuration in the ground state is due to the relatively small value of Δ . In fact, the SrVO₃ compound is closer to the charge transfer ($\Delta < U$) than the Mott-Hubbard ($\Delta > U$) regime.²⁰ This means that the O $2p$ charge fluctuations appear at lower energies and cannot be excluded. The same argument applies to the cuprates where the Zhang-Rice singlet contains considerable O $2p$ character.

Figure 2 shows the total and partial spectral weight of SrVO₃ decomposed into the main final-state configurations. The removal spectrum is composed by the coherent peak about -0.4 eV and the incoherent feature around -1.6 eV. The coherent peak is mostly formed by the coherent screened $3d^1\bar{C}$ configuration and the incoherent structure is mainly due to a ligand screened $3d^1\bar{L}$ configuration. The incoherent feature is dominated by the O $2p$ states and cannot thus be attributed to the lower Hubbard band. In fact, the main $3d^0$ contribution to the removal spectrum of SrVO₃ is located at higher energies, around -7.0 eV.¹⁶

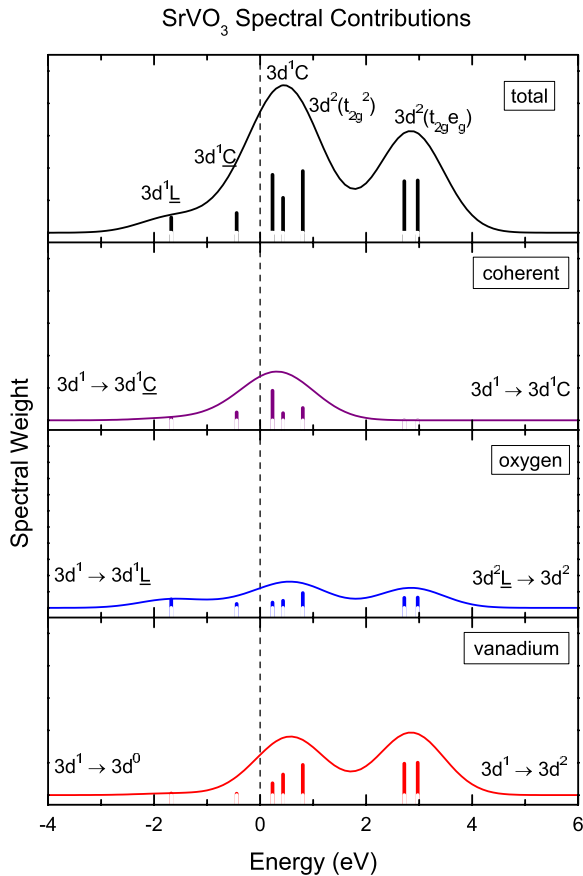


FIG. 2. (Color online) First removal and addition states of SrVO_3 projected into the main contribution to the spectrum: coherent, oxygen, and vanadium. The labels in the total spectra indicate the main final-state configuration of each transition.

On the other hand, the addition spectrum of the SrVO_3 compound is dominated by the $3d^2$ final-state configuration. These transitions are split by crystal field $10Dq$ into the t_{2g} states, around 0.4 eV, and the e_g states, about 2.8 eV. These states also show a considerable O $2p$ contribution due to the relatively large V $3d$ -O $2p$ hybridization. Finally, the coherent peak appears just above the Fermi level and is mainly related to the $3d^1C$ configuration. These results show that the first structure is not only due to the coherent peak and that the second structure cannot be directly attributed to the upper Hubbard band.

The lowest energy charge fluctuation across the Fermi level is between the first removal ($3d^1C$) and the first addition ($3d^1C$) states. These charge fluctuations are of the coherent type and give rise to the metallic character of this material. Please note that there is some O $2p$ character mixed in these states due to the large p - d hybridization. Further, the strong electron-electron interaction makes the SrVO_3 compound a highly correlated metal.

Figure 3 compares the photoemission spectra of SrVO_3 taken at high energy (1840 eV) and low energy (60 eV) from Ref. 11. The comparison shows that the relative intensity of the incoherent structure decreases at high energy. This is usually ascribed to an increase in the probing depth because the incoherent peak would come mostly from the surface.¹⁰ The present calculation shows that the incoherent peak presents a

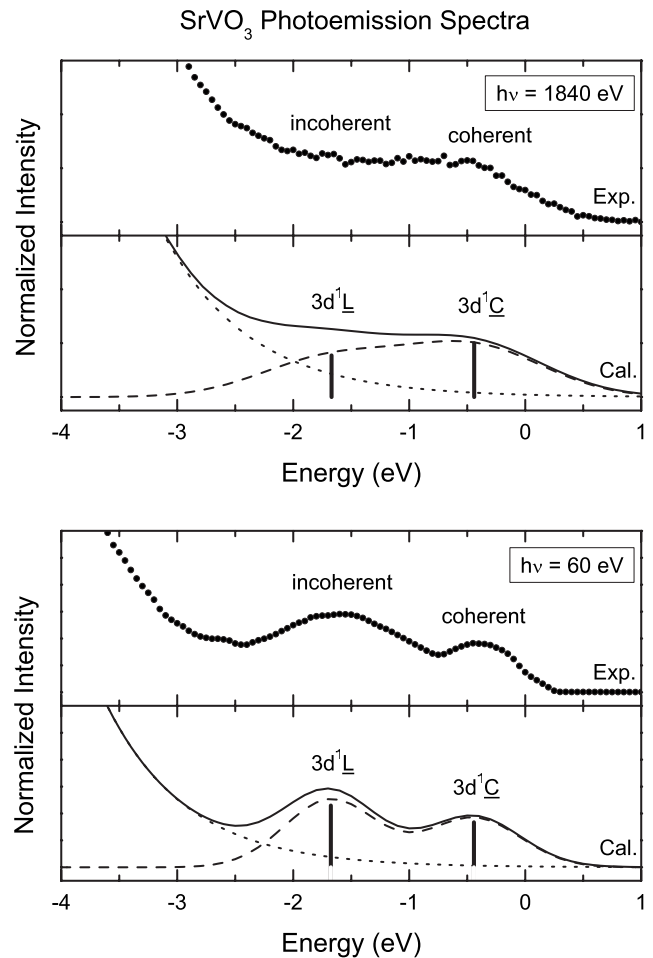


FIG. 3. Calculated removal spectra of SrVO_3 compared to the high energy (1840 eV) and low energy (60 eV), taken from Ref. 11 photoemission spectra. The coherent structure is mostly attributed to the coherent band ($3d^1C$), whereas the incoherent feature contains considerable O $2p$ character ($3d^1L$). The apparent decrease in the incoherent structure in the high energy spectrum is partially due to cross-section effects.

relatively large O $2p$ contribution ($3d^1L$). The decrease in the incoherent feature at high energy is here attributed to a reduction in the O $2p$ cross section. In fact, the calculated spectrum, weighted by the V $3d$ and O $2p$ cross sections,²¹ is in good agreement with the experiment.

Figure 4 (top panel) compares the calculated O $2p$ addition spectrum of SrVO_3 to the O $1s$ XAS spectrum. The XAS spectrum corresponds to transitions to O $2p$ character mixed with V $3d$ states. The spectral weight is split by crystal-field effects into the t_{2g} band, around 529 eV, and the e_g band, about 531 eV. The coherent contribution ($3d^1C$) appears greatly diminished because the O $1s$ XAS probes only O $2p$ states.

Figure 4 (bottom panel) compares the calculated addition spectrum of SrVO_3 with the BIS spectrum from Ref. 11. The BIS spectrum reflects the empty states and shows the V t_{2g} band, around 0.7 eV, and the V e_g band, about 2.9 eV. In this case, the coherent contribution ($3d^1C$) is larger than in XAS because BIS also probes V $3d$ states. However, the distribution of spectral weight in BIS is still dominated by crystal-field effects.

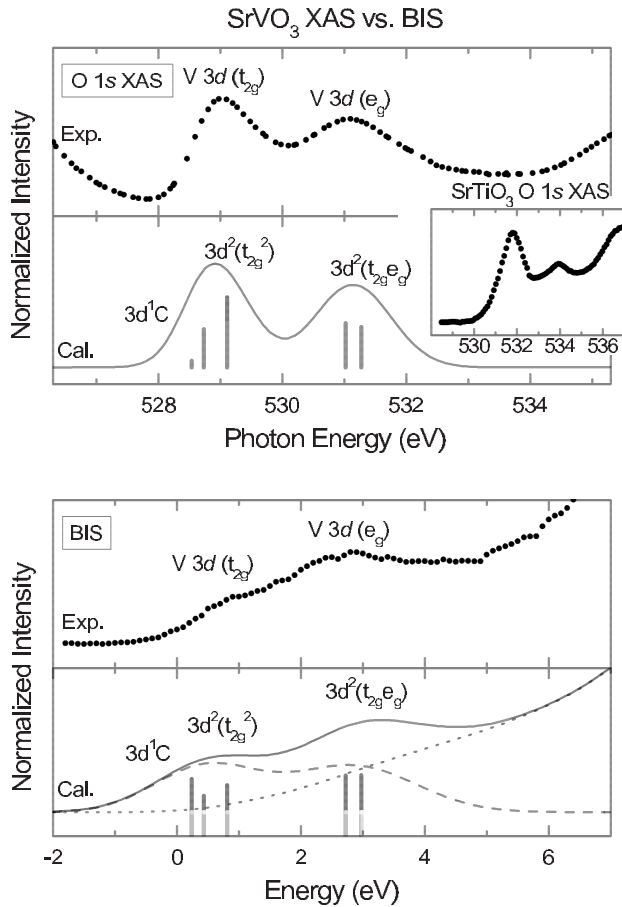


FIG. 4. Calculated addition spectra of SrVO₃ compared to the O 1s x-ray absorption (top panel) and bremsstrahlung isochromat (bottom panel) spectra. The spectral weight is split by crystal-field effects into the t_{2g} and e_g bands. The coherent contribution is greatly diminished in the O 1s x-ray absorption spectrum. The inset shows the O 1s x-ray absorption spectrum of the band insulator SrTiO₃.

The O 1s XAS spectra of SrVO₃ was recently compared to the DMFT unoccupied spectral weight.¹² The authors attributed the first structure to the coherent peak and the second feature to the upper Hubbard band. However, the present calculation shows that these structures are mostly due to the t_{2g} and e_g bands and that the coherent contribution is strongly

suppressed. The inset of Fig. 4 shows that a strong first structure appears even in the band insulator SrTiO₃.

Further, the first structure in the O 1s XAS spectrum of CaVO₃ is weaker than in SrVO₃.¹² The decreased intensity of this structure was attributed to a reduced coherent contribution, but our calculation shows that the coherent contribution is strongly suppressed in the XAS spectra. In fact, the smaller intensity of the first feature in CaVO₃ is related to a reduced O 2p-V 3d hybridization. All this evidence shows that it is misleading to attribute the first structure solely to the coherent peak.

Figure 4 shows that the first structure in the O 1s XAS spectrum is more prominent than in the BIS spectrum. This is due to differences in the transition probabilities, as well as the relatively larger integral background in BIS. This might help us to explain a general trend observed in the BIS spectra of most transition-metal compounds, where the first structure is usually weaker than in the corresponding O 1s XAS spectra. On the other hand, the conventional DMFT method predicts a strong coherent peak in BIS, which is not observed.

The above results show the need to include explicitly the O 2p states in the minimal model of the SrVO₃ compound. These states were neglected in the original DMFT studies of the metal-insulator transition in the Hubbard model.⁶ Later local-density approximation (LDA)+DMFT studies included the O 2p states in the low energy Hamiltonian using a down-folding technique.^{8,12} Finally, the need to include explicitly the correlation effect within a small cluster was recognized recently.²² The inclusion of O 2p many-body effects within the VO₆ cluster is the main strength of the present method.

V. SUMMARY AND CONCLUSIONS

In summary, we studied the electronic structure of the SrVO₃ compound using an extended cluster model. The present model provides a complete and satisfactory description of the electronic structure, key features to understand the first removal and addition states, and a consistent agreement with diverse spectroscopic results. The results show that the O 2p states should be included explicitly in any minimal model of SrVO₃. The same conclusion is expected to apply to other Mott-Hubbard systems, as well as to colossal magnetoresistance materials and high-temperature superconductors.

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