Non-local coherent screening in the bandwidth controlled \( \text{Ca}_{1-x}\text{Sr}_x\text{VO}_3 \) series

R.J.O. Mossanek\(^a\), M. Abbate\(^a\)*, A. Fujimori\(^b\)

\( ^a\)Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19091, 81531-990 Curitiba PR, Brazil

\( ^b\)Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

We studied the electronic structure of the \( \text{Ca}_{1-x}\text{Sr}_x\text{VO}_3 \) series using a cluster model. Both the coherent and incoherent structures in photoemission correspond to well screened states. The coherent structure \((3d^1\text{C})\) is mostly due to a non-local coherent screening, whereas the incoherent feature \((3d^1\text{L})\) is mainly related to the ligand screening. The poorly screened state \((3d^0)\) forms the lower Hubbard band and appears deeper in energy. The increased distortion in the series decrease the V-O-V angle and thus the non-local transfer integral \( T^* \). This produces the observed transfer of spectral weight from the coherent to the incoherent structure. A further decrease of \( T^* \) would eventually induce a bandwidth controlled metal-insulator transition.

PACS: 79.60.Bm; 71.28.+d; 71.30.+h

Keywords: \( \text{Ca}_{1-x}\text{Sr}_x\text{VO}_3 \), bandwidth control, photoemission, cluster model, non-local screening, metal-insulator transition.

Highly correlated systems present strong Coulomb correlations \( U \) and relatively small bandwidth \( W \). In these systems, the variations in the \( U/W \) ratio affect their electronic structure and physical properties. A large \( U/W \) ratio inhibits charge fluctuations, eventually producing a metal-insulator transition. The metal-insulator transition can be controlled by changing either the bandwidth or the band filling [1].

The \( \text{Ca}_{1-x}\text{Sr}_x\text{VO}_3 \) series allows controlling the one electron bandwidth at a fixed \((3d^1)\) band filling [1]. The bandwidth is changed due to a distortion caused by the different ionic radius of the \( \text{Sr}^{2+} \) and \( \text{Ca}^{2+} \) ions. In particular, \( \text{SrVO}_3 \) has a cubic perovskite structure with a V–O–V angle of around 180°, whereas the \( \text{CaVO}_3 \) compound is orthorhombic with a V–O–V angle of about 160°. The orthorhombic distortion decreases the inter-cluster hopping thus reducing the one electron bandwidth.

Early photoemission spectra of \( \text{Ca}_{1-x}\text{Sr}_x\text{VO}_3 \) show a coherent peak and an incoherent structure [2,3]. The spectra present a systematic transfer of spectral weight from the coherent to the incoherent peak in the series. The transitions from the coherent and incoherent features are also reflected in optical measurements [4,5]. The changes in the effective mass \( m^* \) obtained from the optical measurements were large [5], although the effective mass \( m^* \) deduced from the electronic specific heat did not change much [6].

The coherent structure in the spectra can be related to the calculated \( V \) 3d density of states [2,3]. But the incoherent feature reflects a distinct many body effect within the photoemission process. DMFT calculations attribute the coherent structure to the quasi-particle peak, and the incoherent feature to the remnant of the lower Hubbard band [7,8]. Recent studies focused on the higher correlation at the surface [9], as well as on the energy dependence of the photoemission spectra [10-12].

In this work, we studied the electronic structure of the \( \text{Ca}_{1-x}\text{Sr}_x\text{VO}_3 \) series using a cluster model. The calculation includes a non-local coherent screening to account for the metallic charge fluctuations. Both the coherent and incoherent structures are well-screened states, while the poorly-screened state appears only at deeper energies. The main parameter is the non-local transfer integral \( T^* \) which decreases with the lattice distortion. This produces the observed transfer of spectral weight from the coherent to the incoherent structure.

The cluster considered in this work was a \( \text{V}^{4+} \) ion surrounded by an \( \text{O}^{2-} \) octahedra. The cluster model was solved using the standard configuration interaction method. The ground state was expanded in the \( 3d^{1}, 3d^1\text{L}, 3d^1\text{L}^2, 3d^1\text{C}, 3d^1\text{L}^2, 3d^1\text{CL}, 3d^1\text{C}^2 \), etc. configurations, where \( \text{L} \) denotes a hole in the \( \text{O}2\text{p} \) orbitals. The main parameters of the model were the charge-transfer energy \( \Delta \), the Mott-Hubbard energy \( U \) and the p-d transfer integral \( T_\sigma \). The removal state was obtained by removing an electron from the ground state. Finally, the photoemission spectra was calculated using the sudden approximation. The main parameters of the cluster model were \( \Delta = 2.8 \text{ eV}, U = 5 \text{ eV}, \) and \( T_\sigma = 3.3 \text{ eV for } \text{SrVO}_3 \). The values of \( \Delta \) and \( U \) remain constant, but the value of \( T_\sigma \) decreases to 2.8 eV in \( \text{CaVO}_3 \). The crystal field splitting was \( 10Dq = 2.1 \text{ eV} \) and the p-p transfer integral was \( \text{pp} - \text{pp} = 1.3 \text{ eV} \). These values of the parameters gave the best results and are in good agreement with previous reports [13].

Besides the usual local ligand screening, the calculation included a non-local coherent screening. This comes from a extended state at the Fermi level and is related to the metallic charge fluctuations. The ground state was therefore expanded in the \( 3d^{1}, 3d^1\text{L}, 3d^1\text{L}^2, 3d^1\text{C}, 3d^1\text{L}^2, 3d^1\text{CL}, 3d^1\text{C}^2 \), etc. configurations.
denotes a hole in the coherent band. This process was recently included in spectroscopic studies of V$_2$O$_3$ [14] and VO$_3$ [15], following the original ideas proposed by Kotani and Toyozawa [16] and Bocquet et al. [17]. The extra parameters, in this case, are the charge transfer $\Delta^*$ and the transfer integral $T^*$ [14].

The value of $\Delta^*$ is roughly related to the width of the occupied part of the one-electron V 3d band. On the other hand, the transfer integral $T^*$ is related to second order V-O-V hopping processes. The values of both $\Delta^*$ and $T^*$ are reduced as the V-O-V angle decreases in the series (the value of $T_\sigma$ is also reduced due to the distortion, although the reduction is smaller than for $T^*$).

The ground state of SrVO$_3$ is formed mainly by the 3d$^1$ (27%), 3d$^1$L (48%), and 3d$^1$C (12%) configurations. The ground state of CaVO$_3$ is formed mostly by the 3d$^1$ (29%), 3d$^1$L (47%), and 3d$^1$C (12%) configurations. The covalent mixture between the V 3d and O 2p states (3d$^1$C configurations) is rather large because $\Delta$ is small and $T_\sigma$ is large. The coherent contribution to the ground state (3d$^1$C) is larger because, although $\Delta^*$ is small, $T^*$ is much smaller.

Figure 1 shows the removal spectra of SrVO$_3$ and CaVO$_3$ projected on the main final state configurations. For SrVO$_3$, the coherent structure about $-0.4$ eV is formed mainly by the 3d$^1$C configuration (24%), whereas the incoherent feature around $-1.6$ eV is formed mostly by the 3d$^1$L configuration (35%). The lower Hubbard band appears only at $-7.2$ eV and is formed mainly by the 3d$^0$ configuration (55%).

The value of $U$ dictates the position of the 3d$^0$ configuration before the hybridization is switched on. In turn, the values of $\Delta$ and $\Delta^*$ are related to the initial positions of the 3d$^1$L and 3d$^1$C configurations. The $T_\sigma$ ($T^*$) hybridization pushes the 3d$^1$L (3d$^1$C) configuration towards the Fermi level, while the 3d$^0$ configuration is pushed to larger binding energies. Finally, the $T_\sigma$ ($T^*$) hybridization is also related to the relative intensity of the 3d$^1$L (3d$^1$C) configuration.

The distribution of the spectral weight in CaVO$_3$ is similar to that in SrVO$_3$, as in Fig. 1. The coherent structure about $-0.4$ eV is formed mainly by the 3d$^1$C configuration (31%), whereas the incoherent feature around $-1.6$ eV is formed mostly by the 3d$^1$L configuration (44%). This is in agreement with resonant photoemission spectra of CaVO$_3$ [18], which show a resonant enhancement of the feature about $-1.6$ eV. Finally, the lower Hubbard band around $-6.4$ eV is formed mainly by the 3d$^0$ configuration (56%).

The results above show that both the coherent and incoherent features correspond to well screened states. The screening charge of the incoherent structure comes from the local ligand channel (3d$^1$L), whereas the coherent feature comes from the non-local coherent channel (3d$^1$C). On the other hand, the poorly screened state (3d$^0$) corresponds to the lower Hubbard band. The system is in the charge transfer regime, $\Delta (\Delta^*) < U$, with the 3d$^1$L (3d$^1$C) states close to the Fermi level [19]. Finally, the lowest energy (metallic) charge fluctuations involve transitions from 3d$^1$L to 3d$^2$ states.

The coherent structure, mostly 3d$^1$C, has an almost pure V 3d character, whereas the incoherent feature, mainly 3d$^1$L, is of mixed O 2p–V 3d character. Indeed, the 3d$^1$L final state can only be obtained from the 3d$^1$L ground state by removing a V 3d electron. But the 3d$^1$L final state can be reached by removing a V 3d electron (from 3d$^1$L) or an O 2p electron (from 3d$^1$L). Figure 2 shows the relative weight of the V 3d and O 2p contributions to the removal spectra. The relative cross sections of the V 3d and O 2p levels were adjusted to a photon energy of $21.2$ eV [20]. These results show that at low photon energy the incoherent structure contains considerable O 2p weight. But, the relative cross section increases the V 3d contribution for higher photon energies, see below.

Figure 3 shows the coherent and incoherent removal spectra along the Ca$_{1-x}$Sr$_x$VO$_3$ series. The $T^*$ parameter changes from 0.27 to 0.22 eV, $\Delta^*$ from 0.75 to 0.55 eV, and $T_\sigma$ from 3.3 to 2.8 eV. The calculations are in qualitative agreement with the experimental spectra taken from Ref. 2. In particular, the results reproduce the transfer of spectral weight from the coherent to the incoherent region. This transfer of spectral weight takes place through a non-trivial second order process. The spectral weight goes from the 3d$^1$L to the 3d$^0$ configuration via the $T^*$ hybridization, and then back to the 3d$^1$L configuration through the $T_\sigma$ transfer integral (there is not any single particle matrix element between the 3d$^1$L and the 3d$^1$C configurations). The crucial parameter here is the transfer integral $T^*$ of the non-local screening channel. The decrease of the V-O-V angle in the series reduces the effective inter-cluster transfer integral $T^*$. This causes the decrease of the coherent peak and the transfer of spectral weight to the incoherent peak. A further reduction of $T^*$, below a critical value, would suppress the metallic charge fluctuations. This effect is responsible for the metal-insulator transition in the YTiO$_2$–LaTiO$_3$–SrVO$_3$–VO$_3$ series [21]. The lattice distortion in Ca$_{1-x}$Sr$_x$VO$_3$ is not large enough to reach the critical value, and therefore the otherwise expected bandwidth controlled metal-insulator transition is not realized.

There is a controversy in the interpretation of the low energy photoemission spectra of Ca$_{1-x}$Sr$_x$VO$_3$. This concerns the relative bulk or surface character of
the coherent and incoherent structures. The relative correlation effects at the surface are indeed enhanced due to the reduced dispersion [9]. But the variation in the spectra cannot be explained by changes in the surface sensitivity, because the spectra were obtained using the same photon energy and thus the same sampling depth. A more drastic variation is observed in the spectra of the YTiO$_3$–LaTiO$_3$–SrVO$_3$–VO$_2$ series, where the weight of the coherent structure is completely suppressed in the insulating phase [21]. The same effect is observed in the insulating phase of VO$_2$ where the coherent feature also disappears [15]. The suppression of the coherent structure, in these cases, cannot be explained in terms of surface effects.

Recent energy dependent photoemission studies showed an increase of the coherent peak [10–11]. This enhancement was attributed to a relatively larger bulk character of the coherent structure, because a higher energy photoelectron has a relatively larger escape depth. Figure 4 shows the calculated photoemission spectra at 21.2 eV (UPS) and 1486.6 eV (XPS). The calculated results are in good agreement with the experimental UPS and XPS spectra taken from Ref. 10. Thus, the changes in the spectra can be mostly attributed to the energy dependence of the cross section. The small discrepancy between the calculation and the experiment is attributed to residual surface effects.

There is an apparent discrepancy in the physical properties of the Ca$_{1-x}$Sr$_x$VO$_3$ material. The changes in the excitation spectra are larger than in the thermodynamics properties. This difference can be reconciled taking into account the relative weight of the coherent contribution. The coherent contribution to the ground states (3d$^4$C) in SrVO$_3$ (12%) and CaVO$_3$ (12%) are similar. But the coherent structure in the removal spectra (3d$^1$C) is 25% larger for SrVO$_3$ than for CaVO$_3$. This suggests that thermodynamics properties should change little in the Ca$_{1-x}$Sr$_x$VO$_3$ series; whereas the excitation spectra, like photoemission and optical spectra, should present larger changes. This helps to explain why the effective mass m* obtained from the electronic specific heat do not change [6]; whereas the effective mass m* deduced from the optical response decreases 25% from SrVO$_3$ to CaVO$_3$ [5] (the changes in the optical m* are in agreement with the observed decrease in the coherent structure above). The above results show that the different physical properties should be compared with caution.

In conclusion, we studied the electronic structure of the Ca$_{1-x}$Sr$_x$VO$_3$ series using a cluster model. Both the coherent and incoherent structures in photoemission correspond to well screened states. The coherent structure (3d$^4$C) is mostly due to a non-local coherent screening, whereas the incoherent feature (3d$^1$L) is mainly related to the local ligand screening.

The poorly screened state (3d$^0$) forms the lower Hubbard band and appears deeper in energy. The increased distortion in the series decrease the V-O-V angle and thus the non-local transfer integral T*. This produces the observed transfer of spectral weight from the coherent to the incoherent structure. A further decrease of T* would eventually induce a bandwidth controlled metal-insulator transition.

References

*Corresponding author: miguel@fisica.ufpr.br

1. M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
2. I.H. Inoue et al., Phys. Rev. Lett. 74, 2539 (1995).
3. K. Morikawa et al., Phys. Rev. B 52, 13711 (1995).
4. M.J. Rozenberg et al., Phys. Rev. Lett. 76, 4781 (1996).
5. H. Makino et al., Phys. Rev. B 58, 4384 (1998).
6. I.H. Inoue et al., Phys. Rev. B 58, 4372 (1998).
7. E. Pavarini et al., Phys. Rev. Lett. 92, 176403 (2004).
8. I.A. Nekrasov et al., Phys. Rev. B 72, 155106 (2005).
9. A. Liebsch, Phys. Rev. Lett. 90, 096401 (2003).
10. K. Maiti et al., Europhys. Lett. 55, 246 (2001).
11. A. Sekiyama et al., Phys. Rev. Lett. 93, 156402 (2004).
12. R. Eguchi et al., Phys. Rev. Lett. 96, 076402 (2006).
13. A.E. Bocquet et al., Phys. Rev. B 53, 1161 (1996).
14. M. Taguchi et al., Phys. Rev. B 71, 155102 (2005).
15. R.J.O. Mossanek and M. Abbate, cond-mat/0601611.
16. A. Kotani, Y. Toyozawa, J. Phys. Soc. Jpn. 37, 912 (1974).
17. A.E. Bocquet et al., Phys. Rev. B 52, 13838 (1995).
18. H.F. Pen et al., Phys. Rev. B 59, 7422 (1999).
19. J. Zaanen, G.A. Sawatzky, and J.W. Allen, Phys. Rev. Lett. 55, 418 (1985).
20. J.J. Yeh and I. Lindau, Atom. Data Nucl. Data 32, 1 (1985).
21. A. Fujimori et al., Phys. Rev. Lett. 69, 1796 (1992).
Figure 1: Removal spectra of SrVO$_3$ and CaVO$_3$ projected on the main final state configurations.

Figure 2: Removal spectra of SrVO$_3$ and CaVO$_3$ projected on the V 3d and O 2p contributions.

Figure 3: Experimental and calculated photoemission spectra of the Ca$_{1-x}$Sr$_x$VO$_3$ series taken from Ref. 2.

Figure 4: Experimental and calculated UPS and XPS spectra of the Ca$_{1-x}$Sr$_x$VO$_3$ series taken from Ref. 13.