

Electronic structure of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$: a tale of two energy-scales

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We investigate the electronic structure of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ using photoemission spectroscopy. Core level spectra establish an electronic phase separation at the surface, leading to distinctly different surface electronic structure compared to the bulk. Analysis of the photoemission spectra of this system allowed us to separate the surface and bulk contributions. These results help us to understand properties related to two vastly differing energy-scales, namely the low energy-scale of thermal excitations ($\sim k_B T$) and the high-energy scale related to Coulomb and other electronic interactions.

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The electronic structure of strongly correlated transition metal oxides has attracted a great deal of attention both theoretically [1] and experimentally [2] due to many exotic properties exhibited by these systems such as high temperature superconductivity and colossal magnetoresistance. In order to investigate such issues, photoemission spectroscopy has been extensively employed due to its ability to probe the electronic structure directly. While this technique is highly surface sensitive as observed in rare earth intermetallics [3], its extensive use to understand the bulk properties of transition metal (TM) oxides [4] is based on the implicit assumption of very similar electronic structures at the surface and in the bulk. We observe a spectacular failure of this assumption in $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$.

$\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ is a solid solution of CaVO_3 and SrVO_3 where the bandwidth W can be systematically controlled due to a buckling of the V-O-V bond angle from $\sim 180^\circ$ in SrVO_3 to $\sim 160^\circ$ in CaVO_3 [5]. Thus, $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ is ideally suited for the systematic study of the competition between local interactions and itineracy, which leads to several strong correlation effects. This system is arguably the simplest strongly correlated transition metal oxide, since it remains paramagnetic down to the lowest temperature measured so far ($T = 50$ mK), has typical Fermi liquid behavior and has nominally just one conduction electron per site of V^{4+} . Despite these facts, important aspects of its fundamental physics remain unclear, particularly in terms of its contrasting high-energy spectroscopic and low-energy thermodynamic properties [1,6]. The spectroscopic properties and the thermodynamic properties belong to vastly different energy scales: the former corresponds to a high energy (typically $10 \sim 10^3$ eV) perturbation to the system, while the latter probes electrons typically within $k_B T$ (~ 1 meV) of E_F . There is indeed *a-priori* no reason to believe that the same model physics will be valid in both the regimes.

In this study, we observe a strong dependence of the photoemission spectra from $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ with the escape depth λ of the photoelectrons, signifying very different surface and bulk electronic structures. The core level spectra exhibit an electronic phase separation at the surface, possibly due to an enhanced correlation effect and leading to a distinctly different surface electronic structure compared to that of the bulk. We present a method to separate the surface and bulk contributions from the total spectrum for any given composition. From the analysis of the bulk spectra, we deduce the values of the electronic specific heat coefficient γ , which agree well with the experimentally observed values. Thus, this study provides the first coherent understanding encompassing the experimental spectra and the measured thermodynamical properties, employing current theoretical approaches for strongly correlated systems.

Single crystalline samples of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ were prepared by floating zone method and characterized by x -ray diffraction, Laue photography and thermogravimetric analysis as described elsewhere [5]. The characterizations exhibit the samples to be stoichiometric (error bar $< 1\%$), homogeneous and single phasic. The x -ray photoemission (XP) measurements were carried out with a monochromatized Al $K\alpha$ source with a total resolution of 0.45 eV and the resolution for the ultraviolet photoemission (UP) measurements were 80 meV. Sample surfaces were cleaned by periodical scrapings and the cleanliness was confirmed by the absence of C 1s feature and the oxygen 1s impurity feature. Experiments were carried out at 120 K at a pressure of 2×10^{-10} mbar. A large acceptance angle ($\pm 10^\circ$) along with the scraped surface allow us to probe the angle integrated spectral functions which was further confirmed by the reproducibility of the spectra after each trial of scraping.

In Fig. 1, we show the V $2p_{3/2}$ core level spectra from $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ for various values of x . It is evident from the figure that even for CaVO_3 and SrVO_3 , it does not

have the single peak structure, expected from a homogeneous single phase V^{4+} compound; instead, three clear features can be seen (as marked) for every composition. Least-squared error analysis showed that the positions of the components, as well as the corresponding full widths at half maximum (FWHM) remain the same across the series. Most significantly, the intensity ratio between the first and the last components are always approximately in the ratio of 1 : 1. We find that the energy separations and the spectral widths of these three components agree with the V $2p_{3/2}$ signals from V_2O_3 , VO_2 and V_2O_5 , suggesting that the peaks 1, 2 and 3 arise from V^{3+} , V^{4+} and V^{5+} entities. The equal intensities of the V^{3+} and V^{5+} signals in these stoichiometric compounds suggest that a fraction of the V^{4+} ions spontaneously phase separate, $2V^{4+} \rightarrow V^{3+} + V^{5+}$, maintaining the charge balance. By changing the photon energy between Al $K\alpha$ (1486.6 eV) and Mg $K\alpha$ (1253.6 eV), thereby modestly changing the surface sensitivity of the technique, we find that with increasing surface sensitivity, the relative intensity of V^{4+} signal reduces in all the cases, as shown in the inset of Fig.1 in the case of $CaVO_3$. Interestingly, the three components simulating the Al $K\alpha$ spectrum, reproduce also the Mg $K\alpha$ spectrum remarkably well with a smaller intensity of V^{4+} component [7]. This shows that the electronic phase separation of V^{4+} to V^{3+} and V^{5+} occurs at the sample surface. Such a thing can occur *via* two distinctly different mechanisms, namely due to the presence of a negative U [8–10], or due to the presence of strong correlation effects [11]. We believe the latter to be the driving force in the present case, as discussed later.

It is thus clear that the different charge states of V at the surface and in the bulk will lead to significantly different electronic structures corresponding to the surface and the bulk. This is evident in Fig. 2 where we show the valence band spectra of $CaVO_3$ and $SrVO_3$ at He I (21.2 eV), He II (40.8 eV) and Al $K\alpha$ photo-excitations. All the spectra are shown after subtracting the tail of the O $2p$ band appearing at higher binding energies [12]. We also show the XP spectral function obtained from LSDA band structure calculations for $CaVO_3$ by solid line in the figure. The calculated spectrum exhibit *only one* feature for the V $3d$ emissions at the Fermi energy, E_F representing the delocalized conduction electrons and usually termed as coherent feature. All the experimental spectra exhibit a second feature centered at about 1.5 eV in addition to the coherent feature. This feature is normally termed as incoherent feature being the spectral signature of the lower Hubbard band (LHB) and corresponds to electron states essentially localized due to electron correlations. The relatively surface-sensitive He I and II spectra in both cases are in agreement with previously published results [13], showing a weaker coherent feature with a main feature centered at ~ 1.5 eV. However, the more bulk-sensitive Al $K\alpha$ excited spectra exhibit much larger coherent features compared to the UP

spectra. While there is a large difference in the change in photoemission cross sections for the photo-excitations from O $2p$ and V $3d$ states at these photon energies, this matrix element effects have negligible influence in the small energy window studied here contributed solely by the V $3d$ states. This has been explicitly verified in a similar system, $LaVO_3$ [14]. Thus, these spectral modifications establish that the electronic structures near the surface and in the bulk are significantly different in these compounds.

One can go beyond this qualitative discussion and present a method to separate the intrinsic surface and bulk contributions out of the total photoemission spectrum. We note that the total spectrum $\rho(\omega)$ at any given photon energy can be expressed as; $\rho(\omega) = (1 - e^{-d/\lambda})\rho^s(\omega) + e^{-d/\lambda}\rho^b(\omega)$, where $\rho^s(\omega)$ and $\rho^b(\omega)$ denote the surface and bulk responses, d is the thickness of the surface layer and λ is the mean free path of photoelectrons. Once the value of d/λ is known for two spectra (for example XPS and He I), one can obtain $\rho^s(\omega)$ and $\rho^b(\omega)$ analytically.

The intensity ratios from the surface (components 1 and 3) and the bulk (component 2) in the V $2p_{3/2}$ spectra, which are determined at each x from the spectral decomposition, yield a value of $d/\lambda = 0.65$ for V $2p$ electrons with a kinetic energy E of about 965 eV ($\sim h\nu - BE$). The simulation of the Mg $K\alpha$ spectrum ($E \sim 735$ eV) of $CaVO_3$ represented by the solid line in the inset of Fig.1 in terms of the three components results in $d/\lambda = 0.76$. Considering $\lambda \propto \sqrt{E}$ in the high energy limit [15], $\lambda_{Mg}/\lambda_{Al}$ is expected to be $\sqrt{735/965} = 1.15$, whereas the spectral analysis suggest $\lambda_{Mg}/\lambda_{Al} = 0.76/0.65 = 1.17$, in very good agreement with the expected value, providing confidence in our analysis. d/λ for the valence electrons ($E \cong 1480$ eV) is estimated to be 0.52 ± 0.05 for the entire series, a narrow variation of less than 10% across the series indicating a reliable estimate of this parameter. We also need to estimate the quantity, $d/\lambda_{He I}$ for the valence band spectrum excited with He I radiation. Unfortunately, there is no universally accepted dependence of λ on E in the low energy limit. Thus, we assume that $\lambda_{XPS}/\lambda_{He I}$ in $Ca_{1-x}Sr_xVO_3$ is the same as in the closely related series $Ca_{1-x}La_xVO_3$ [16]; and note that the final results for $\rho^b(\omega)$ and $\rho^s(\omega)$ are not very sensitive to this particular choice of $\lambda_{XPS}/\lambda_{He I} = 3.4$ [17]. Thus obtained $\rho^s(\omega)$ and $\rho^b(\omega)$ are shown in the main frame of Fig. 3. In order to ascertain the reliability of the above procedure, we have recorded the valence band spectra of this series for a number of different photon energies using synchrotron radiation from the VUV beamline (Elettra, Trieste). These spectra were successfully synthesized, as shown in the insets by solid lines, using linear combinations of $\rho^s(\omega)$ and $\rho^b(\omega)$ according to the equation above, thus providing again a non-trivial check on our procedures [18].

$\rho^s(\omega)$ in Fig.3 for $CaVO_3$ and $SrVO_3$ are invariably

dominated by the incoherent feature, while $\rho^b(\omega)$ contains a large coherent feature with smaller, but substantial contributions from the incoherent feature. This suggests a highly metallic character of the bulk electronic states, while the surface states are essentially localized. Notably, this observation is significantly different from rare earths where only a quantitative change was observed in terms of a modest narrowing of the bandwidth or changing the extent of mixed valency [3]. We note that the $\rho^b(\omega)$ is inconsistent with the LDA DOS due to the presence of the correlation driven incoherent feature; therefore, we have calculated the spectral functions of the Hubbard Hamiltonian within the dynamical mean-field theory (DMFT) that becomes exact in the limit of large dimensions (or large lattice connectivity) [1]. The DMFT equations are solved using Iterated Perturbation Theory (IPT) on a Bethe lattice which captures some realistic features [1]. Thus, the theoretical results depend only on two parameters U and W . These parameters were varied to obtain calculated spectra in agreement with the experimentally obtained ones for both the surface and the bulk spectral functions in each case. The resulting theoretical results are multiplied by the Fermi-Dirac function ($T=120\text{K}$) and then convoluted with the total experimental resolution (a Gaussian with FWHM=0.45 eV).

The calculated $\rho^b(\omega)$ (solid lines) are superimposed on the experimental data in Fig. 3, providing a remarkable agreement in both cases. The values of W simulating the spectra are 2.4 eV and 3.2 eV in CaVO_3 and SrVO_3 , respectively with $U = 2$ eV, similar to the results in related strongly correlated compounds such as V_2O_3 [19]. Most significantly, the *same* parameter values yield for the specific heat coefficient, which is a much lower energy probe than PES, the values $\gamma = 3.7$ and $5.5\text{mJ K}^{-2}\text{mol}^{-1}$ for SrVO_3 and CaVO_3 . These are in good agreement with the corresponding experimental values of 6.4 and $7.3\text{mJ K}^{-2}\text{mol}^{-1}$ [20]. We therefore obtain for the first time a unified understanding of the physics at two vastly different energy-scales in this strongly correlated system, solely based on the assumption of the Hubbard model as an effective model [21]. It is to be noted here that $N(E_F)$ from DMFT [22] is about half of that obtained from the *ab initio* LDA calculations. Since the self-energy within DMFT is momentum independent due to the local nature of the correlations, $N(E_F)$ remains unrenormalized by U [23]. This suggests that one should rule out a naive combination of LDA and DMFT methods as a candidate for an *ab initio* technique in correlated systems, which is a subject of strong current interest.

We now briefly comment on $\rho^s(\omega)$, representing the average surface electronic structure, arising from the V^{3+} and V^{5+} dominated regions. V^{5+} ions have $3d^0$ electronic configuration and therefore do not contribute any photoemission signal over the probed energy range; thus, the $\rho^s(\omega)$ in Fig. 3 arises entirely from surface regions with V^{3+} species. Interestingly, $\rho^s(\omega)$ of CaVO_3 has vir-

tually no intensity at E_F suggesting an insulating state, while that of SrVO_3 has a finite intensity at E_F signifying a metal. Such a change can possibly be attributed to a more distorted crystal structure of CaVO_3 compared to that in SrVO_3 [5,13]. We have simulated $\rho^s(\omega)$ in each case within the same DMFT formalism, and shown by the dashed lines overlapping the experimental data in Fig. 3. The U/W required to simulate these $\rho^s(\omega)$ are 1.5 and 2 for SrVO_3 and CaVO_3 , respectively. Thus, there is evidently a strong enhancement of U/W at the surface compared to $U/W=0.63-0.83$ for the bulk in the series. This marked enhancement may be due to the reduced atomic coordination at the surface and/or surface reconstruction, which would give rise to a decrease in W and an increase in U compared to the bulk. We believe that this enhanced correlation effect at the surface is also the driving force for the observed electronic phase separation [11], in a way reminiscent of the manganites; however, one important distinction between the two is that the latter is a doped metallic system, while $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ is a nominally undoped metallic system.

In conclusion, our present work has established that the surface electronic structure of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ is fundamentally different from that in the bulk. The bulk electronic structure obtained in the present study allows for the first time a unified understanding of the low- and the high-energy scale physics of this system within DMFT calculations based on the Hubbard model. This technique may also give a clue to understand one basic and important open question which still lies ahead, but possibly within our reach: *i.e.*, to find out whether the standing conflict between the theoretical and experimental results on the systematic evolution of *doped* Mott-Hubbard systems can also be resolved within the existing paradigms of electronic structure theories.

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- [18] We find that the required d/λ values interpolate between those for the Al $K\alpha$ and He I radiations, as expected.
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- [21] The new data for $\rho^b(\omega)$ *riden of surface contributions* is the crucial difference with respect to similar analysis in the previous work [6].
- [22] In DMFT we assume a semi-elliptical DOS of bandwidth W .
- [23] In an earlier study [13], a nonlocal selfenergy was suggested phenomenologically to reduce the value of $N(E_F)$. However, due to the large surface contribution to the PES spectra an unphysically large effect of the nonlocal self-energy was obtained.

Figure Captions:

Fig.1 V $2p_{3/2}$ core level spectra (open circles) of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ for various values of x , exhibiting the existence of three distinct spectral features marked 1, 2 and 3. Dashed lines and solid lines represent the three components and the total calculated spectra, respectively.

Inset shows the comparison of V $2p_{3/2}$ spectra of CaVO_3 at Mg $K\alpha$ (solid circles) and Al $K\alpha$ (open circles) photon energies. The solid line is the simulated Mg $K\alpha$ spectrum in terms of three components.

Fig. 2 Experimental valence band photoemission spectra in the V d band region of CaVO_3 and SrVO_3 using three different photon energies, 21.2 eV (solid circles), 40.8 eV (open circles), and 1486.6 eV (+ centered circles). All the spectra are broadened upto the resolution of XP (1486.6 eV) spectra. The solid line represents the XP spectral function obtained from LSDA band structure calculations.

Fig. 3 Extracted $\rho^b(\omega)$ (open circles) and $\rho^s(\omega)$ (solid circles) obtained from the spectra shown in Fig. 2. The solid and dashed lines superimposed on the spectra are the results of DMFT calculations. Insets I and II show the comparison of experimental valence band photoemission results (open circles) of CaVO_3 and SrVO_3 , respectively for different photon energies along with the synthesized spectra (solid lines) obtained from $\rho^b(\omega)$ and $\rho^s(\omega)$.

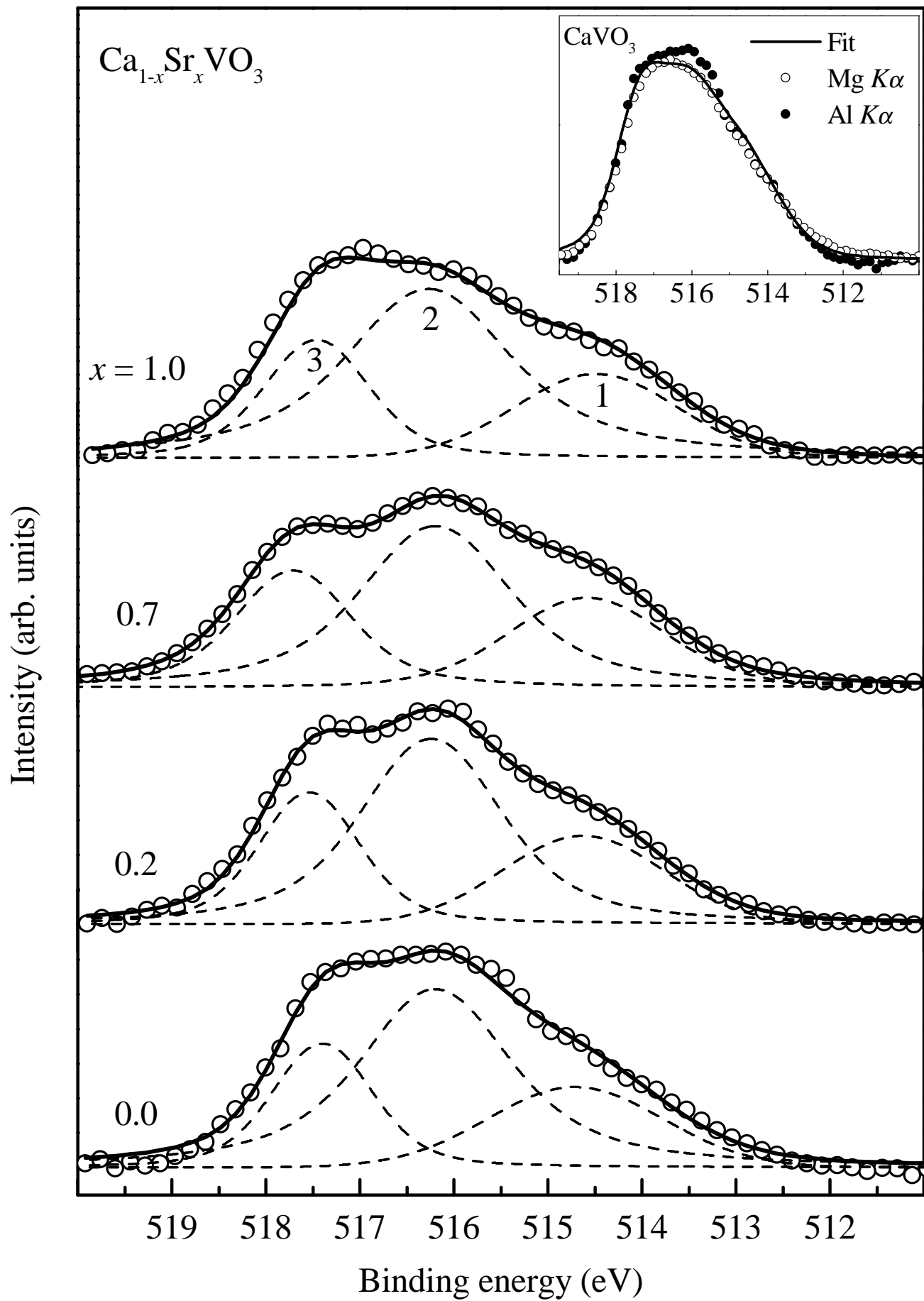


Fig. 1 : Maiti *et al.*

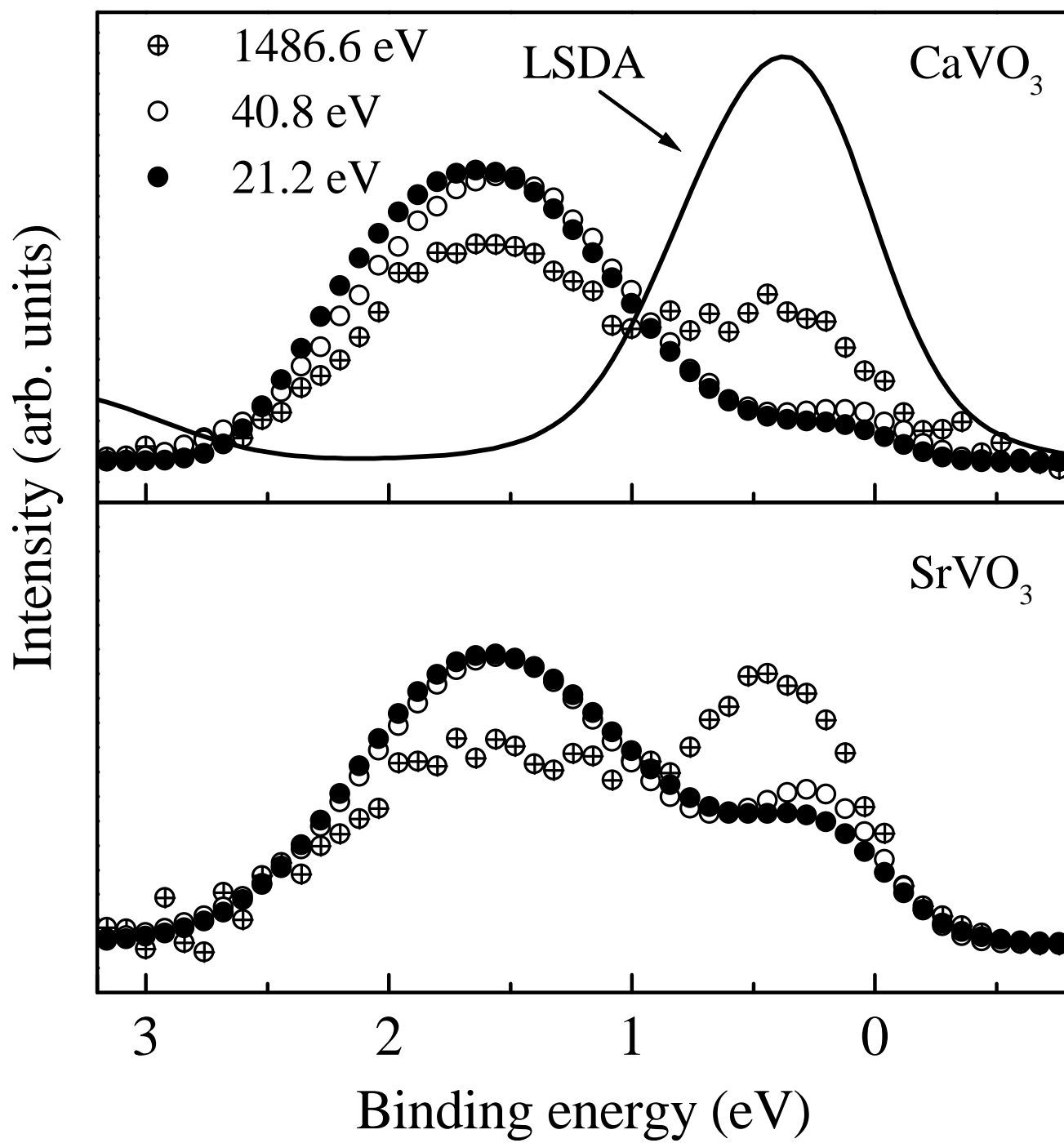


Fig.2 : Maiti *et al.*

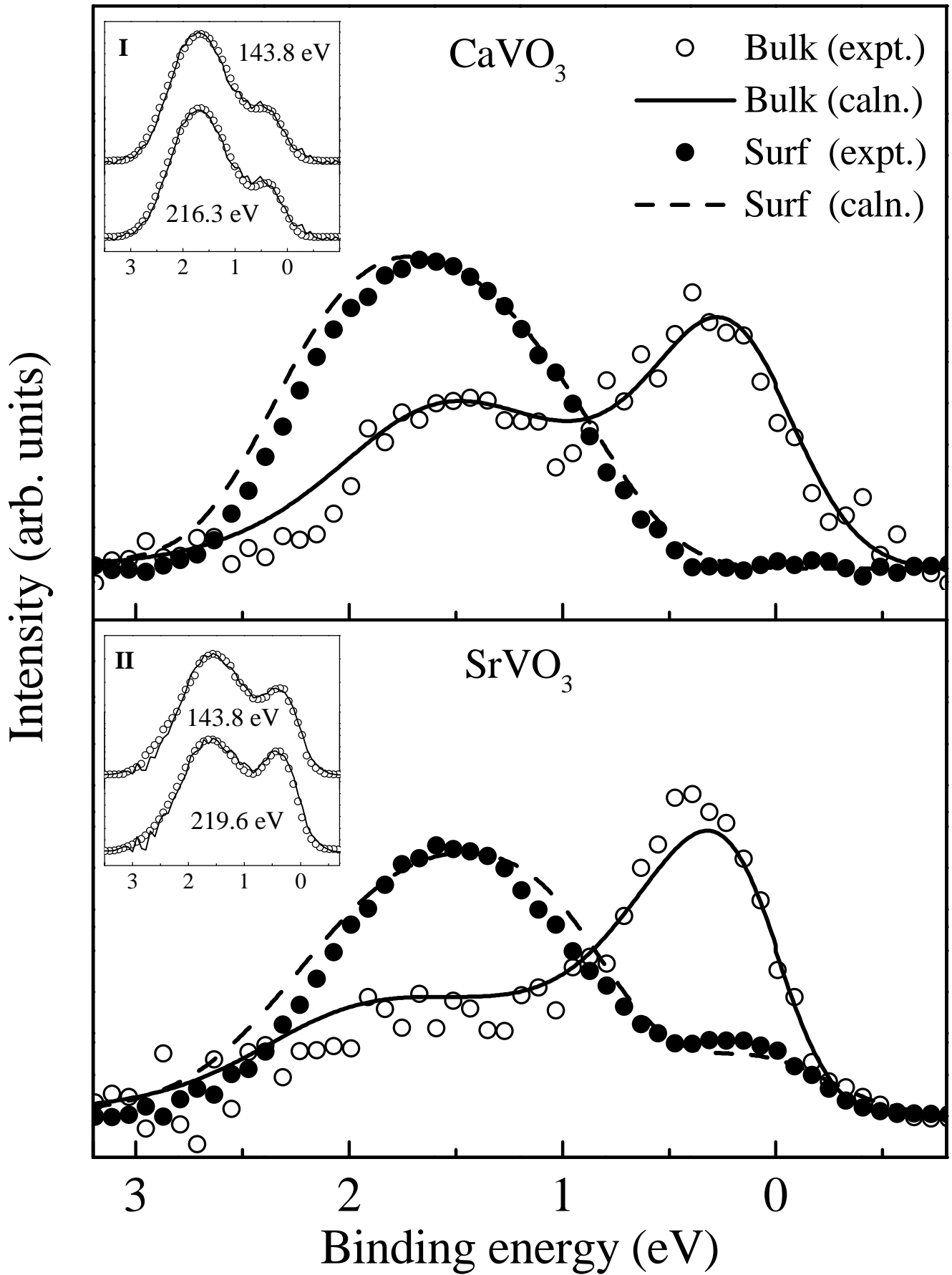


Fig. 3 : Maiti *et al.*