Electronic structure of early transition metal oxides, $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$: What can we learn from photoelectron spectroscopy

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Abstract

Photoemission spectroscopy offers the unique possibility of mapping out the electronic structure of the occupied electron states. However, the extreme surface sensitivity of this technique ensures that only the surface and the near-surface regions of any sample are probed. An important question arises in this context—Is the electronic structure of the surface region the same as that of the bulk? We address this issue using two different series of vanadium oxides, $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$. Our results clearly establish that the electronic structure of the surface region is drastically different from that of the bulk in both these cases. We provide a method to separate the two contributions: one arising from the near-surface region and the other representative of the bulk. This separation allows us to deduce some very unusual behaviors of the electronic structures in these systems.

Keywords: Electron correlation; Surface and interface states; Photoelectron spectroscopy

1. Introduction

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. The Hubbard Hamiltonian $H = \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$ provides a simplistic quantitative description of the electron correlation, which displays explicitly the competition between the itinerant behavior of electrons via the hopping amplitude, t and the localization effects due to Coulomb repulsion, U . The bandwidth, W of the system is directly related to t ($W \sim 2zt$; z =coordination number). Thus, the effective correlation strength can be expressed as a function

of a single parameter, U/W . Experimentally, photoemission spectroscopy has been extensively employed due to its ability to probe the electronic structure directly. While this technique is highly surface sensitive, leading to a substantial contribution from the surface electronic structure, as observed in rare earth intermetallics [3], its extensive use to understand the bulk properties of transition metal (TM) oxides has been based on the implicit assumption of very similar electronic structures at the surface and in the bulk. This is in general a reasonable assumption in many systems, as has often been demonstrated by a good agreement between experimentally obtained photoemission spectra and calculated ones on the basis of the bulk electronic structures [4], most notably for the late (Mn–Ni) transition metal oxides. Interestingly, the early transition metal oxides exhibit a spectacular failure of the assumption of similar surface and bulk electronic structure. Notably, the late transition metal oxides exhibit large covalent mixing of the TM d levels with the ligand p levels. Early TM oxides, however, exhibit a different scenario. Large charge-transfer energy [5], Δ , defined by the energy required to transfer an

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electron from O p levels to TM d levels, compared to the hopping strength, t , leads to a substantially reduced overlap of the ligand levels with the transition metal d levels. This allows one to investigate the effect of electron correlation as well as of charge carrier doping in the TM d band with the ligand levels playing only a minor role. In order to extract meaningful information from photoemission studies of early transition metal oxides, it is, however, necessary to separate the surface and the bulk contribution to the experimentally obtained spectra.

In this article, we review the detail electronic structure of a typical early transition metal oxide family, $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$, as a function of electron interaction strength, followed by a discussion on another system, $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$, with changing carrier concentration. In $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$, Ca and Sr are homovalent (2+). The V–O–V bond angle is 160° in CaVO_3 and 180° in SrVO_3 [3]. Thus, the change in composition, x in $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ leads to a change in U/W without any change in charge carrier concentration. This is the simplest strongly correlated transition metal oxide system, since it remains paramagnetic down to the lowest temperature measured so far ($T=50$ mK), exhibit typical Fermi-liquid behavior and has nominally just one conduction electron per site of V^{4+} . On the other hand, the substitution of Ca^{2+} in place of La^{3+} in $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$ dopes holes in the valence band without any significant change in V–O–V bond angle [7–10]. Thus, these compounds are well suited for the experimental realization of a continuous tuning of U/W and doping, respectively and consequently, provide good testing ground for the predictions of the Hubbard model.

2. Experimental details

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. Polycrystalline samples of $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$ were prepared from congruently molten states which gives rise to large grains with strong inter grain bonding and <1% of the impurity phases at the grain boundaries. The characterizations exhibit the samples to be stoichiometric, homogeneous and single phasic [6,7]. Experiments were carried out using monochromatic sources at a base pressure of 2×10^{-10} mbar with a resolution of 0.45 eV for X-ray photoemission (XP), and 14 meV and 22 meV with He I and He II photons, respectively. Experiments at soft-X-ray energies were carried out using synchrotron radiation from the VUV beamline (Elettra, Trieste). The cleanliness of each sample surface was maintained by repeated in-situ scrapings with an alumina file or cleaving, thereby exposing fresh sample surfaces, and was monitored by O 1s and C 1s spectra in case of the XPS study, as well as by analyzing the spectra in the 9–12-eV binding-energy region in the UPS study. No chemical-impurity feature was observed for any of the

compositions studied. Reproducibility of the spectra with repeated cleaning processes was confirmed for each composition.

3. Results and discussion

In Fig. 1, the V $2p_{3/2}$ core level spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ exhibit three distinct features as marked in the figure for every composition in contrast to the single peak structure, expected from a homogeneous single-phase V^{4+} compound. Least-squared error analysis showed that the positions of the components, as well as the corresponding full widths at half maximum (FWHM) remain essentially 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. 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 suggest that a fraction of V^{4+} ions spontaneously phase separate, $2\text{V}^{4+} \rightarrow \text{V}^{3+} + \text{V}^{5+}$, maintaining the charge balance. Since the escape depth of the photoelectrons strongly depends on their kinetic energies, one can tune the surface sensitivity of the technique by changing the photon energies. We, thus, investigate V $2p_{3/2}$ feature as a function of the photon energy in Fig. 2. Interestingly, the relative intensity of V^{4+} signal reduces monotonically with the decrease in photon energy. This observation establishes that the charge dis-

Fig. 1. V $2p_{3/2}$ spectra at Al $K\alpha$ photon energy for different values of x in $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$.

Fig. 2. V $2p_{3/2}$ spectra of (a) CaVO_3 and (b) $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{VO}_3$ at different photon energies. All the other compositions exhibit similar trend. (c) Estimated λ values are plotted as a function of the square root of electron kinetic energy. Estimated λ values using TPP2M formula are also shown by solid lines. The dashed line shows the $E^{0.5}$ -behavior at high energies and thin solid line is the polynomial fit at low energies.

proportionation of V^{4+} to V^{3+} and V^{5+} occurs at the sample surface, while the bulk remains primarily in V^{4+} state.

The observed differences in the electronic structure of surface and bulk in these materials may be attributed to a change in the crystal-field symmetry at the surface and a difference in the electron correlation strength as described below. The VO_6 octahedra in $SrVO_3$ and $CaVO_3$ are nearly regular and this octahedral crystal field splits the d band into a triply degenerate t_{2g} band and a doubly degenerate e_g band. The up- and down-spin t_{2g} bands are split by a large exchange splitting, $J \cong 1$ eV. Therefore, one electron in the d band occupies the t_{2g} band. The surface, however, may exhibit a different symmetry. If the surface layer consists of a V–O layer, one apical oxygen of the VO_6 octahedra will be missing. Alternatively, if Sr/Ca–O layer is the terminating layer, ensuring an octahedral arrangement of oxygen around the V ions, a strong distortion is expected due to the absence of any further atomic layers. Both scenarios will lead to a significant deviation in the crystal-field symmetry from the octahedral (O_h) field towards a D_{4h} symmetry. Thus, the degeneracy of the t_{2g} band will be lifted to a doubly degenerate e_g band consisting of d_{xz} and d_{yz} orbitals, and the d_{xy} band (b_{2g} symmetry). In addition, the absence of periodicity along the surface normal will lead to a narrowing of the e_g band. Significant narrowing for the d_{xz} and d_{yz} bands has indeed been observed by Liebsch [11], while the d_{xy} band exhibits similar band dispersion as that in the bulk. Such a band narrowing leads to an enhancement of the effective electron interaction strength. A larger U/W is known to induce phase separation, as also observed in other systems [12]. A phase separation of the type $2d^1 \rightarrow d^0 + d^2$ is an interesting possibility, since both the configurations, d^0 and d^2 , are closed-shell configurations, representing particularly stable states.

The spectral intensity, $\rho(\epsilon)$ can be expressed as, $\rho(\epsilon) = (1 - e^{-d/\lambda})\rho^s(\epsilon) + e^{-d/\lambda}\rho^b(\epsilon)$ where $\rho^s(\epsilon)$ and $\rho^b(\epsilon)$ denote the surface and bulk responses, d is the thickness of the surface layer and λ is the escape depth of photoelectrons. Assuming that the cross-sections for V $2p_{3/2}$ photoionization from the atoms at the surface and in the bulk are identical, one can estimate d/λ experimentally from the extracted surface and bulk contributions shown in Figs. 1 and 2 using the relation surface/bulk = $e^{d/\lambda} - 1$. The estimated λ values are plotted in Fig. 2(c). While these λ values exhibit a trend similar to those observed in the universal curve, they are significantly different from the values obtained using Tanuma–Powell–Penn relations (TPP2M) [13].

It is now clear that the different charge states of V at the surface and in the bulk will lead to significantly different surface and bulk electronic structures. This is evident in Fig. 3, where the V $3d$ part of the UP (21.2 eV, 40.8 eV) and XP (1486.6 eV) valence band spectra of $CaVO_3$ and $SrVO_3$ are shown. We also show the XP spectral function obtained from LSDA band structure calculations for

$CaVO_3$ by solid line. The calculated spectrum exhibits *only one* feature at the Fermi energy, E_F representing the delocalized conduction electrons, usually termed as the 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 the incoherent feature being the spectral signature of the lower Hubbard band (LHB) and corresponds to electron states essentially localized due to electron correlations. The UP spectra of $CaVO_3$ and $SrVO_3$ are in agreement with previously published results [6,7], showing weaker coherent feature with the main feature centered at 1.5 eV. With the increase in bulk sensitivity in XP spectra, the coherent feature intensity increases significantly. The matrix element effects for the photo-excitations have negligible influence in the small energy window studied in the figure, since it is contributed solely by the V $3d$ states [9]. This study, thus, established for the first time that the surface and bulk electronic structures can be different in transition metal oxides.

We have already estimated the d/λ values at different electron kinetic energies from the core level spectra in Fig. 2. In Fig. 2(c), it is clear that $\lambda \propto \sqrt{E}$ at higher energies as is also suggested by the universal curve generally accepted in the photoemission community. Thus, (d/λ_{XP}) is found to be 0.52 ± 0.05 . The d/λ at He I energy has been estimated by performing a polynomial fit to the estimated d/λ at lower energies in Fig. 2(c) and found to be about 3.4. A narrow variation of less than 10% in the values of d/λ across the series indicates a reliable estimate. $\rho^s(\epsilon)$ and $\rho^b(\epsilon)$ can be calculated now analytically using the above values and are shown in the right panel 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 $\rho^b(\epsilon)$ and $\rho^s(\epsilon)$ according to the equation above, thus providing again a non-trivial check on the procedure adopted in these analysis.

$\rho^s(\epsilon)$ in Fig. 3 for $CaVO_3$ and $SrVO_3$ are invariably dominated by the incoherent feature, while $\rho^b(\epsilon)$ 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 $\rho^b(\epsilon)$ is still inconsistent with the LDA DOS due to the presence of the incoherent feature; therefore, we calculated [7] the spectral functions of the Hubbard Hamiltonian within the dynamical mean-field theory (DMFT) in the limit of large dimensions (or large lattice connectivity). The DMFT

Fig. 3. Valence band spectra of CaVO_3 and SrVO_3 .

equations are solved using Iterative Perturbation Theory (IPT) on a Bethe lattice. The theoretical results depend only on one parameter, U/W . These results are then multiplied by the Fermi-Dirac function at $T=120\text{ K}$ and convoluted with a Gaussian (FWHM=0.45 eV) to account for the experimental resolution. The calculated $\rho^b(\epsilon)$ (solid lines in Fig. 3) provide a remarkably good representation of the experimental results for $W=2.4\text{ eV}$ (CaVO_3) and 3.2 eV (SrVO_3), and $U=2\text{ eV}$. 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 $7.3\text{ mJ K}^{-2}\text{ mol}^{-1}$. We therefore obtain for the first time a unified understanding of the physics at two

vastly different energy-scales in this strongly correlated system based on the Hubbard model.

Since, V^{5+} ions have $3d^0$ electronic configuration, $\rho^s(\epsilon)$ derives entirely from V^{3+} . Interestingly, $\rho^s(\epsilon)$ of CaVO_3 in Fig. 2 has virtually 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 . We have simulated $\rho^s(\epsilon)$ in each case within the same DMFT formalism (dashed lines). The U/W required to simulate these $\rho^s(\epsilon)$ 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 $U/W=0.63$ and 0.83 for the bulk systems. This marked enhancement may be due to the reduced atomic coordina-

Fig. 4. (a) Valence band spectra of $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$ showing insulator to metal transition. (b) Surface sensitivity dependence by changing photon energies exhibit signature of different surface and bulk electronic structure.

tion 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 now focus on the systematic evolution of *doped* Mott–Hubbard systems and critically evaluate whether these experimental results can also be understood within the existing paradigms of electronic structure theories. We show the He I spectra for all the compounds near the V 3*d* emission region in Fig. 4(a). Each spectrum is dominated by the incoherent feature centered at 1.5 eV with no intensity at E_F for $x=0.0$ and 0.1. The intensity of the coherent peak increases gradually with increasing x ($x \geq 0.2$) suggesting a metal–insulator transition at $x=0.2$ in agreement with the transport properties. However, the complete dominance of the incoherent feature suggests again an overwhelming presence of correlation effects nearly localizing charge carriers even in the $x=0.5$ sample in contrast to the observed physical properties. The photon energy variation in Fig. 4(b) indicates again a qualitatively different electronic structure at the surface and in the bulk as observed in CaVO_3 .

We have extracted $\rho^b(\epsilon)$ and $\rho^s(\epsilon)$ in the same way as described before and plotted in Fig. 5. Open circles represent $\rho^s(\epsilon)$ with the spectra exhibiting a single feature around 1.5-eV binding energy. No intensity is observed at

E_F , suggesting an insulating character for the surface layer on both samples. It turns out that the surface spectral shape closely resembles the bulk electronic structure of LaVO_3 , which is an antiferromagnetic insulator. For comparison, we plot the resolution-broadened He I spectrum of LaVO_3 (solid curve) shifted by about 0.1 eV to higher binding energies to match the peak position. The similarity in the spectral functions of LaVO_3 and the extracted surface spectra of $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$ compounds is remarkable, which further establishes the insulating nature of the surface layers in the latter two materials.

Such an observation may not be unreasonable considering the previously mentioned possibility that two electrons in the surface electronic states of the parent compound, LaVO_3 , form a completely filled e_g up-spin band; this is a stable electronic ground state. Thus, Ca substitution would tend to lead to an admixture of d^0 and d^2 electronic configurations rather than to a homogeneously occupied fractional valence configuration. Both the configurations d^0 and d^2 are closed-shell configurations, corresponding to band-insulating phases and therefore represent particularly stable ground states as compared to that of the d^1 electronic state. Such charge disproportionations ($2d^1 \rightarrow d^0 + d^2$) at the surface have indeed been observed in other d^1 systems, like CaVO_3 and SrVO_3 [7]. Thus, the observation of the insulating surface

Fig. 5. Surface and bulk electronic structure of (a) $\text{La}_{0.7}\text{Ca}_{0.3}\text{VO}_3$, (b) $\text{La}_{0.6}\text{Ca}_{0.4}\text{VO}_3$, and (c) $\text{La}_{0.5}\text{Ca}_{0.5}\text{VO}_3$. Solid line represents the LaVO_3 spectra and stars show the simulated bulk spectra.

electronic structure can be attributed to a phase separation in the doped compositions, with the tendency towards such a phase separation being enhanced in the surface layer due to the different crystal-field symmetry and enhanced electron correlation as compared to the bulk.

Bulk spectra in Fig. 5 exhibit a systematic increase at E_F with increasing Ca, consistent with increasing conductivity in the series. However, the V 3d emission is still dominated by the incoherent feature in all the compositions suggesting a strong influence of electron correlation. The doping-dependent spectral function has been calculated within the single band Hubbard model both by DMFT and exact diagonalization techniques. These results indeed suggest the presence of the incoherent and coherent features in the spectra. However, any reasonable value of U/W with finite doping shows a much weaker contribution of the incoherent feature as compared to our experimental results. This weakened effect of correlation in the presence of large doping within a single band Hubbard model is understandable, since such doping reduces the average number of electrons per site considerably from 1.0. In the present case, there are 1.5 electrons per V site even for the highest doped case ($\text{La}_{0.5}\text{Ca}_{0.5}\text{VO}_3$). An extension of the calculations to include the multiband nature of the system within the Hubbard model does not improve the agreement between experiment and theory [8]. It is thus clear that present theoretical results based on the homogeneous Hubbard model to incorporate the strong electron correlations are not adequate for describing the spectral functions in these doped systems. It has been observed that calculations including the inhomogeneities intrinsic to such heterogeneous systems are more successful in describing the spectral functions of such systems [14,15]. In these cases, the local electronic structures of heterogeneous systems will retain their characteristic features due to the effects of disorder. A direct check would be to see if the spectral functions corresponding to the end members generate the spectral function observed for the intermediate compositions.

We add the bulk spectra of LaVO_3 and CaVO_3 according to the compositions of the two materials: $I(\epsilon) = 2(1-x)\rho_{\text{LaVO}_3}^b(\epsilon) + x\rho_{\text{CaVO}_3}^b(\epsilon)$, where x denotes the extent of doping. The results are shown by stars in Fig. 5. While there is a mismatch in relative intensities of the coherent and incoherent features, the presence of large intensities from the incoherent features is clearly visible in the simulated spectra in agreement with the extracted bulk spectra shown for these materials. This finding is quite significant considering the crudeness of this simulation. It suggests that the remnants of the electronic structures of LaVO_3 and CaVO_3 are somewhat retained in the compounds with intermediate compositions, as suggested by previous theoretical results [15]. Thus, the correct description of the electronic structure in this system needs a proper theoretical model, which would provide a rigorous basis for understanding the physical properties of these heterogeneous systems.

We now investigate the temperature dependence of the spectral function close to E_F in these highly correlated metallic systems using high energy resolution. The He II spectra of $\text{La}_{0.6}\text{Ca}_{0.4}\text{VO}_3$ collected at 78 K and 7 K are shown in Fig. 6. The spectra shown were normalized to the same integrated intensity. The incoherent feature representing the contributions from both the surface and bulk electronic structures exhibits significant modifications in lineshape, while the energy range (3 eV to 12 eV binding energies) containing essentially O 2p spectral contributions (not shown here) remains almost unchanged with temperature. This suggests that the changes observed in the V 3d spectral region in Fig. 6 are intrinsic and cannot be attributed to the effect of impurities. Temperature-dependent changes in the spectral lineshape have indeed been found in various calculations using a dynamical mean-field approach (DMFT) in the limit of infinite dimensions [1]. While the

Fig. 6. (a) He II spectra of $\text{La}_{0.6}\text{Ca}_{0.4}\text{VO}_3$ at 78 K and 7 K. (b) Spectra shown on an expanded scale close to E_F . Solid and open circles represent the 7 K and 78 K spectra, respectively. The spectral functions obtained by dividing the spectra by the resolution-broadened Fermi-Dirac distribution function and smoothing are shown by the solid (7 K) and the dashed curves (78 K), respectively. The inset shows the spectral DOS at 7 K obtained by dividing the Fermi distribution functions with E_F estimated from Ag-Fermi edge (solid line) and E_F shifted by ± 4 meV (dashed and dotted lines).

trend of the various observed changes is similar to that obtained in the calculations, the relative change in intensity of the incoherent feature seems to be much larger as compared to that in the coherent features.

In Fig. 6(b), we plot the near-Fermi-level region, which arises essentially due to the bulk contributions. It is clear that the intensity of the coherent feature is lower at 78 K as compared to 7 K. In order to check the thermal effect in terms of the Fermi–Dirac statistics controlling occupancies of states, we divided the spectral functions by the resolution-broadened Fermi–Dirac distribution function at the corresponding temperature. Since the experimental resolution broadening is rather small (10 meV), the divided spectra provide a good approximation for the spectral functions without the thermal influence. In order to investigate any possible influence of band structure effects, we have calculated the electronic band structure of CaVO_3 within the local density approximation using Linearized Muffin–Tin Orbital method within the atomic sphere approximations (LMTO–ASA). The convergence was achieved with 216 k -points within the Brillouin zone. The calculated total density of states, arising from the t_{2g} band, continuously increases with the decrease in binding energy [10]. In contrast to this calculated result, we observe a distinct dip at the Fermi level in the experimental spectra.

It is important to note here that the spectral density of states generated by the division of the Fermi distribution function is sensitive to the precise location of the Fermi level, E_F . Therefore, a careful determination of the Fermi level is necessary for this purpose. We have determined E_F by the Fermi cut off observed for silver at each temperature with a small step size (1 meV) and found it to be highly reproducible [16]. It is, however, necessary to verify whether a small change in the location of E_F can influence the spectral DOS and consequently render our conclusions uncertain. We, thus, divided the experimental spectra by the resolution-broadened Fermi–Dirac distribution function with the definition of E_F shifted from the experimentally determined position by ± 4 meV. The resultant spectral DOS are shown in the inset of Fig. 6(b) by dashed and dotted lines. In all the cases, the dip in the spectral intensity at E_F is clearly visible, establishing this observation beyond the uncertainties of experimental determination of E_F . While band structure results cannot explain this dip, according to Altshuler–Aronov theory [17], disorder in an interacting metallic system leads to a decrease in density of states at the Fermi level. Such an effect has been observed in other

transition metal oxides [16]. Thus, the observation of the dip at E_F may be attributed to the effect of disorder arising due to heterovalent substitution of Ca in place of La in these systems.

4. Conclusions

It is evident from our results that the surface electronic structure of early transition metal oxides can be *qualitatively* different from the bulk. This realization is essential in order to critically discuss and evaluate the experimental electronic structure in terms of the existing many-body theories and various bulk sensitive low-energy properties. We present an algorithm to extract the bulk related spectra from the total spectra using photon energy dependent measurements. It is shown that the DMFT calculations in the limit of infinite dimensions consistently describe the bulk electronic structure in homovalently substituted compounds such as $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$. However, the doped systems call for theoretical models beyond the homogeneous Hubbard model. In addition, our results show the first experimental realization of correlation-induced charge disproportionation in a real system.

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