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

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We investigate the electronic structure of Ca$_{1-x}$Sr$_x$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 and experimentally 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, its extensive use to understand the bulk properties of transition metal (TM) oxides 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 Ca$_{1-x}$Sr$_x$VO$_3$.

Ca$_{1-x}$Sr$_x$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$_3$. Thus, Ca$_{1-x}$Sr$_x$VO$_3$ is ideally suited for the systematic study of the competition between local interactions and itinerancy, 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. 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 $k_B T$ ($\sim 1$ 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 Ca$_{1-x}$Sr$_x$VO$_3$ with the escape depth $\lambda$ 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 $\gamma$, 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 Ca$_{1-x}$Sr$_x$VO$_3$ were prepared by floating zone method and characterized by x-ray diffraction, Laue photography and thermogravimetric analysis as described elsewhere. The characterization 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 Ka 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 $2 \times 10^{-10}$ 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 Ca$_{1-x}$Sr$_x$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 homogene-
ous 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 $V \, 2p_{1/2}$ signals from $V_2O_5$, $VO_2$ 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 sug-
gest 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 in-
tensity 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, repro-
duce also the $Mg \, K\alpha$ spectrum remarkably well with a
smaller intensity of $V^{4+}$ component. This shows that the
electronic phase separation of $V^{4+}$ to $V^{3+}$ and $V^{5+}$
occur 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 dif-
ferent 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 $He \, \iota$
($21.2 \, eV$), $He \, \II$ ($40.8 \, eV$) and $Al \, K\alpha$ photo-excitation.
All the spectra are shown after subtracting the tail of the
$O \, 2p$ band appearing at higher binding energies [12]. We
also show the X-ray 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 corre-
sponds to electron states essentially localized due to
electron correlations. The relatively surface-sensitive $He$
$\iota$ and $\II$ spectra in both cases are in agreement with pre-
viously published results [13], showing a weaker coherent
feature with a main feature centered at $\sim 1.5 \, eV$. How-
ever, the more bulk-sensitive $Al \, K\alpha$ excited spectra ex-
bhit 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-excitation
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 modi-
fications 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 contribu-
tions 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 $\lambda$ is the mean free path of photoelec-
trons. Once the value of $d/\lambda$ is known for two spectra
(for example XPS and $He \, \iota$), 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 $V \, 2p_{1/2}$ spectra, which are determined at each $x$ from the spectral decom-
position, 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 ($E \approx 735 \, eV$) 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 [5],
$\lambda_{Mg}/\lambda_{Al}$ 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. $d/\lambda$ for the valence elec-
trons ($E \cong 1480 \, eV$) is estimated to be $0.52 \pm 0.05$ for the
total 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, $d/\lambda_{He \, \iota}$ for the
valence band spectrum excited with $He \, \iota$ radiation.
Unfortunately, there is no universally accepted dependence
of $\lambda$ on $E$ in the low energy limit. Thus, we assume that
$\lambda_{Sr/VO}/\lambda_{He \, \iota}$ 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 fi-
nal results for $\rho^b(\omega)$ and $\rho^s(\omega)$ are not very sensitive to
this particular choice of $\lambda_{Sr/VO}/\lambda_{He \, \iota} = 3.4$ [17]. Thus ob-
tained $\rho^s(\omega)$ 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 combina-
tions of $\rho^s(\omega)$ and $\rho^b(\omega)$ according to the equation above,
thus providing a nearly-trivial check on our proce-
dures [18].

$\rho^s(\omega)$ in Fig.3 for $CaVO_3$ and $SrVO_3$ are invariably
dominated by the incoherent feature, while \( \rho^i(\omega) \) 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 \( \rho^i(\omega) \) 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) \( [4] \). 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 \( F_\beta(\gamma) \) (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 \( \text{CaVO}_3 \) and \( \text{SrVO}_3 \), respectively with \( U=2 \) eV, similar to the results in related strongly correlated compounds such as \( \text{V}_2\text{O}_3 \) \( [13] \). 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 mJK\(^{-2}\)mol\(^{-1}\) for \( \text{SrVO}_3 \) and \( \text{CaVO}_3 \). These are in good agreement with the corresponding experimental values of 6.4 and 7.3 mJK\(^{-2}\)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 \textit{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 \textit{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 3\( d^0 \) 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 \( \text{CaVO}_3 \) has virtually no intensity at \( E_F \) suggesting an insulating state, while that of \( \text{SrVO}_3 \) has a finite intensity at \( E_F \) signifying a metal. Such a change can possibly be attributed to a more distorted crystal structure of \( \text{CaVO}_3 \) compared to that in \( \text{SrVO}_3 \) \( [23] \). 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 \( \text{SrVO}_3 \) and \( \text{CaVO}_3 \), 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 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: \textit{i.e.}, to find out whether the standing conflict between the theoretical and experimental results on the systematic evolution of \textit{doped} Mott-Hubbard systems can also be resolved within the existing paradigms of electronic structure theories.

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**Figure Captions:**

Fig. 1 V 2p3/2 core level spectra (open circles) of Ca1−xSrVO3 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 2p3/2 spectra of CaVO3 at Mg Kα (solid circles) and Al Kα (open circles) photon energies. The solid line is the simulated Mg Kα spectrum in terms of three components.

Fig. 2 Experimental valence band photoemission spectra in the V d band region of CaVO3 and SrVO3 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 ρs(ω) (open circles) and ρσ(ω) (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 CaVO3 and SrVO3, respectively for different photon energies along with the synthesized spectra (solid lines) obtained from ρs(ω) and ρσ(ω).
Ca$_{1-x}$Sr$_x$VO$_3$

$x = 1.0$

Intensity (arb. units)

Binding energy (eV)

Fig. 1: Maiti et al.
Fig. 2: Maiti et al.
Fig. 3: Maiti et al.