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Understanding the bulk electronic structure of $Ca_{1-x}Sr_xVO_3$

Kalobaran Maiti,[1,2] U. Manju,[1] Sugata Ray,[1] Priya Mahadevan,[3] I. H. Inoue,[4] C. Carbone,[5] and D. D. Sarma[1,*]
[1]*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*
[2]*Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005, India*
[3]*Department of Physics, Indian Institute of Technology, Chennai 600036, India*
[4]*Correlated Electron Research Center (CERC), AIST Tsukuba Central 4, Tsukuba 305-8562, Japan*
[5]*Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Area Science Park, I-34012 Trieste, Italy*

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We investigate the electronic structure of $Ca_{1-x}Sr_xVO_3$ using careful state-of-the-art experiments and calculations. Photoemission spectra using synchrotron radiation reveal a hitherto unnoticed polarization dependence of the photoemission matrix elements for the surface component leading to a substantial suppression of its intensity. Bulk spectra extracted with the help of experimentally determined electron escape depth and estimated suppression of surface contributions resolve outstanding puzzles concerning the electronic structure in $Ca_{1-x}Sr_xVO_3$.

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For several decades, the Hubbard model has been the archetype to understand a wide variety of electronic and magnetic properties in strongly correlated electronic systems, such as transition metal compounds. It is now well understood that an increasing effect of electron correlation, measured by the ratio of the intrasite Coulomb interaction strength U and the bare bandwidth W tends to make the system more localized in terms of an increasing effective mass, tendencies toward eventual opening of a band gap, and the formation of a local moment. Dynamical mean-field theory (DMFT) represents one of the most successful approaches[1] to capture most of these features. However, the parameter values of such a model Hamiltonian need to be fixed by comparison of theoretical predictions with various experimental results. Photoelectron spectroscopy (PES) has been extensively used over the last two decades for this purpose. An extreme surface sensitivity of this technique[2] coupled with the possibility of a drastically altered surface electronic structure compared to that in the bulk may make the direct application of PES to understand bulk properties impossible.[3–10] This has, indeed, been conclusively demonstrated for certain early transition-metal oxides.[4–10] Thus, it becomes necessary to devise a reliable method to separate the bulk and the surface electronic structures[6,7] before a detailed understanding can be obtained.

In this context, $Ca_{1-x}Sr_xVO_3$ $(0 \leq x \leq 1)$ has firmly established itself as one of the most interesting systems, providing a critical testing ground for the state-of-the-art theories in the recent past.[7,9,11–14] This is primarily due to the continuous tunability of the structural parameters arising from the fact that the V-O-V bond angle across the series changes progressively from 180° in $SrVO_3$ to 160° in $CaVO_3$.[15] Thus, the V d-bandwidth, W, and consequently, the correlation strength, U/W, are expected to vary systematically with x in $Ca_{1-x}Sr_xVO_3$. A recent calculation based on linearized muffin-tin orbital (LMTO) method within the local-density approximation (LDA), indeed, established that the bandwidth changes from about 2.8 eV for $SrVO_3$ to 2.4 eV for $CaVO_3$, representing an impressive 14% change in W.[12] On the experimental side, the γ values from specific-heat measurements[15] are 6.4 and 8.6 mJ K^{-2} $mole^{-1}$ for $SrVO_3$ and $CaVO_3$ respectively, consistent with the expected larger U/W value for $CaVO_3$. In sharp contrast, most recent photoemission results[9] have been interpreted as suggesting almost identical electronic structures across the series independent of the composition, x, in $Ca_{1-x}Sr_xVO_3$. This unexpected result, apparently inconsistent with more than 25% increase in γ and a 14% decrease in W, has naturally created a lot of interest, prompting us to make a critical evaluation of the electronic structure of this series of compounds. Present results establish that there is an unexpected and unusually strong polarization dependence of the spectral intensity of the surface component in the experimental spectra. When this is taken into account along with experimentally determined photoelectron escape depth λ, the electronic structure can be described consistently along with the mass enhancement and the reduction in the bandwidth, resolving the puzzling aspects of the electronic structure of this important class of compounds.

Single-crystal samples were prepared by floating zone method and characterized by x-ray diffraction, Laue photography, and thermogravimetric analysis as described elsewhere.[15] The photoemission (XP) measurements were carried out on cleaved single-crystal surfaces at VUV-beamline, Elettra, Trieste, Italy, and the experimental resolution was 20–200 meV, depending on the incident photon energy of 20–800 eV. We observe that the spectra from cleaved and scraped samples are essentially identical as shown later in Fig. 2(e). This is not surprising since there is no well-defined cleavage plane in the perovskite structure. Thus, cleaving leads to an irregular fractured surface instead of a flat cleaved surface.

It is well established that the surface and bulk electronic structures are significantly different in vanadates. The delineation of the surface and bulk contributions in the photoemission spectra requires reliable estimates of λ, which sensitively depends on the electron kinetic energy (KE).

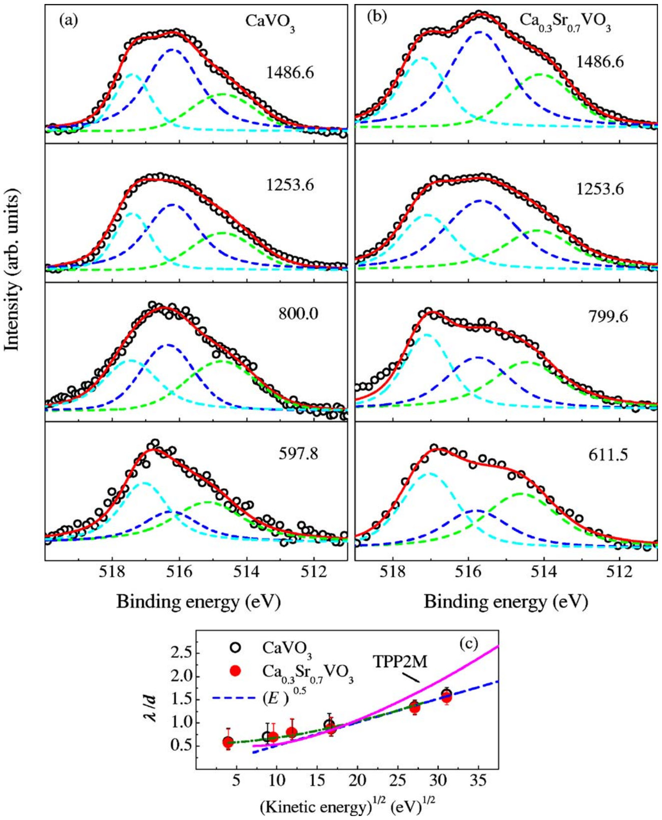

FIG. 1. (Color online) V $2p_{3/2}$ spectra of (a) CaVO$_3$ and (b) Ca$_{0.3}$Sr$_{0.7}$VO$_3$ at different photon energies. The 1486.6 and 1253.6 eV spectra of CaVO$_3$ and 1486.6 eV spectrum of Ca$_{0.3}$Sr$_{0.7}$VO$_3$ are adapted from Ref. 7. Solid lines show the fit using three Voigt functions (dashed lines) representing the contributions from V^{3+}, V^{4+}, and V^{5+} entities. (c) Estimated λ/d vs $\sqrt{\mathrm{KE}}$. λ/d at KE=16 eV is obtained from the valence band analysis (Refs. 7 and 8). Dotted-dashed line shows the trend at low energies. The solid line represents the calculated escape depth using TPP2M relations (Ref. 16).

Fortunately, a nearly unique aspect of the electronic structure of this series allows us to make such estimates of λ. V^{4+} in these compounds charge disproportionates to V^{3+} and V^{5+} species at the surface.[7] This is convincingly demonstrated in Fig. 1, showing the V $2p_{3/2}$ core-level spectra at different photon energies for CaVO$_3$ and Ca$_{0.3}$Sr$_{0.7}$VO$_3$. Spectra corresponding to other compositions are similar to these spectra. Three distinct features at about 514.5, 516, and 517 eV represent the signatures of V^{3+}, V^{4+}, and V^{5+} species, respectively. With a decrease in photon energy, the intensity of the bulk V^{4+} peak continuously decreases compared to the intensities of the surface related V^{3+} and V^{5+} features. The ratio of surface and bulk contributions in $2p$ spectra $[(\text{surface}/\text{bulk})=e^{d/\lambda}-1$, d is the effective surface depth$]$ provides an estimate of λ in units of d. Thus, estimated λ/d values [see Fig. 1(c)] exhibit linear dependence with $\sqrt{\mathrm{KE}}$ for KE$\geqslant$200 eV as expected from the universal curve.[2] λ/d is found to decrease continuously with KE down to ~16 eV, presumably due to the presence of various low-energy excitations in these metallic systems. Notably, these experimentally determined values of λ/d are significantly different from those estimated using Tanuma, Powel, and Penn (TPP2M) formula.[16]

The valence-band spectra exhibit a series of intriguing results, not realized thus far. For example, the normal emission spectra of CaVO$_3$ [Fig. 2(b)] with $h\nu$=40.8 eV photons from linearly polarized synchrotron and unpolarized laboratory (He II) sources are drastically different. The relative intensity of the incoherent feature at ~1.5 eV is substantially less in the synchrotron spectrum compared to the He II spectrum. This, without any change in the photon energy and, consequently, in the electron escape depth or in energy resolution (specifically kept the same) is curious. Second, the ratio of the coherent and incoherent feature intensities in the 275 eV synchrotron spectra in Fig. 2(c) is larger than that observed even in Al $K\alpha$ (1486.6 eV) spectrum on the same sample.[7] Since, the electron escape depth cannot be larger at $h\nu$=275 eV compared to that at $h\nu$=1486.6 eV, it is evident that the incoherent feature is underestimated in the synchrotron data compared to the spectra with a laboratory source. The surface electronic structure contributes primarily to the incoherent feature. Thus, a suppression of the relative intensity of the incoherent feature suggests that the photoemission matrix elements for the surface-related states is strongly reduced in the case of polarized synchrotron radiation compared to unpolarized laboratory source.

To substantiate these observations, we performed several experiments on various samples under different experimental conditions. These experiments reveal a strong dependence of the coherent-to-incoherent intensity ratio on the angle of incidence, ϕ [see Fig. 2(a)] at any fixed photon energy from the synchrotron source, as illustrated by normalizing all the spectra at the incoherent features of CaVO$_3$ in Fig. 2(c) and SrVO$_3$ in Fig. 2(d). This strong angular dependence of the relative intensities is roughly independent of the excitation photon energy. For example, a change in ϕ from 45° to 25° at $h\nu$=275 eV [Fig. 2(d)] leads to a reduction in the relative intensity of the coherent feature of SrVO$_3$ by about 14.6%. This is remarkably similar to the reduction of ~13.8% at $h\nu$=800 eV observed for a similar change in ϕ [Fig. 2(e)]. We note that such an angular dependence of spectral intensities is not observed with any unpolarized laboratory sources.

Since the angle between the detector and the incident beam in the experimental setup shown in Fig. 2(a) is fixed at 45°, a change in ϕ also changes the angle of electron emission, θ thereby being capable of changing the surface sensitivity. This may provide an alternate explanation for the change in relative spectral features. Hence, we investigate the valence-band spectra at the same surface sensitivity, but with different incidence angles by making the emission angle to be $+\theta$ and $-\theta$ with respect to the surface normal. A representative case in terms of spectra collected at ϕ=55° and 35° incidence angles is shown in Fig. 2(c). Despite same surface sensitivity ($\theta=\pm 10°$), the coherent feature is significantly smaller at ϕ=35° than that at 55°.

In order to ensure that the above results are not artifacts arising from uncertainties in defining precise θ or ϕ due to the unavoidable absence of a well-defined cleavage plane in such cubic systems, we have simultaneously probed V $2p_{3/2}$ core-level spectra that provide an internal measure of surface

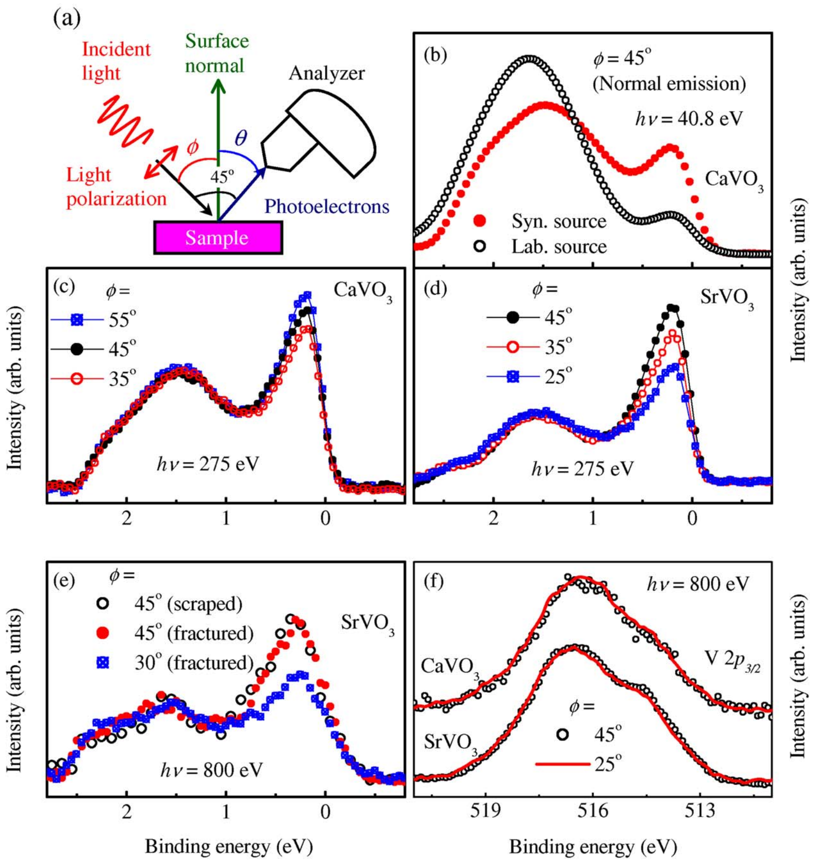

FIG. 2. (Color online) (a) Schematic of the photoemission plane. (b) Valence-band spectra of $CaVO_3$ at 40.8 eV using laboratory and synchrotron sources. (c) $CaVO_3$ at 275 eV, (d) $SrVO_3$ at 275 eV, and (e) $SrVO_3$ at 800 eV. The 800 eV spectral line shape from scraped (open circles) and fractured (solid circles) $SrVO_3$ surfaces are very similar. (f) V $2p_{3/2}$ spectra using 800 eV photons.

sensitivity based on distinctly different surface and bulk spectral features. We chose $h\nu = 800$ eV for this purpose, since the core photoelectrons then have the same kinetic energy as those of valence electrons excited with $h\nu = 275$ eV. The core-level spectra in Fig. 2(f) at $\phi = 45°$ and 25° (65° also shows similar behavior) for *both* $CaVO_3$ and $SrVO_3$ do not exhibit any observable change, establishing similar surface sensitivity over this range of angles. This is understandable, as the surface contribution at normal emission is found to be about 66.4% ($d/\lambda \sim 1.09$). A change in ϕ by 20° leads to a surface contribution of 68.7%, representing a change of only about 2%. These observations, thus, establish that the spectral changes with ϕ in Fig. 2(b)–2(e) are not due to a change in the surface sensitivity, but is, indeed, related to an intrinsic reduction in the surface contribution. Although the exact origin of this effect is unclear, the existence of this effect is unambiguously established by the present experimental results. In the following, we briefly discuss the uniqueness of the surface electronic structure vis-a-vis that of the bulk, which provide some clue to understand the observed effects, at least qualitatively.

The bulk electronic structure of $Ca_{1-x}Sr_xVO_3$ can be described essentially in terms of a single d-electron distributed over the triply degenerate t_{2g} bands. The crystal symmetry at the surface, however, is expected to be lowered compared to the octahedral field in the bulk, leading to a local D_{4h} symmetry. We have confirmed this expectation by carrying out first-principle's plane-wave pseudopotential band-structure calculation with full geometry optimization involving a large supercell of $SrVO_3$ in a slab configuration. Resulting partial densities of states (PDOS) at the surface layer are shown in Fig. 3(a). It is evident in the figure that the single d-electron occupies essentially quasi-one-dimensional d_{zx} and d_{yz} bands, while the d_{xy} band, which continues to be two-dimensional at the surface, remains almost unoccupied. The dipole matrix element, $M_{fi} = \langle \psi_f | A.p | \psi_i \rangle$ (ψ_i and ψ_f are the initial and final state wave functions) in the expression of photoemission cross section $[I(\epsilon) \propto |M_{fi}|^2 f(\epsilon)\delta(\epsilon)$; $f(\epsilon) =$ Fermi-Dirac distribution function$]$ is a function of both momentum p and the vector potential A and therefore, the polarization of the incident photons. Thus, the surface-related band states will have stronger matrix element effects with polarized synchrotron light compared to the bulk states due to the lifting of degeneracies at the surface; such difference will not be significant for the unpolarized light source.

We now extract the bulk contributions $I^b(\epsilon)$ from the synchrotron spectra collected at 275 and 40.8 eV using the d/λ from Fig. 1(c) in the relation, $I(\epsilon) = \alpha(1 - e^{-d/\lambda})I^s(\epsilon) + e^{-d/\lambda}I^b(\epsilon)$. α, the polarization-induced reduction of the surface intensity, is found to be 0.2 ± 0.05 by comparing the spectra recorded with $h\nu = 40.8$ eV in Fig. 2(b).[17] We needed to use a slightly different α at 275 eV ($\sim 0.1 \pm 0.05$) to avoid unphysical negative intensities. Such a small variation in α is expected for a fractured surface due to the uncertainties in defining the surface normal. The extracted $I^b(\epsilon)$ are shown in Fig. 3(b). Interestingly, $I^b(\epsilon)$ of $CaVO_3$ and $SrVO_3$ are significantly different exhibiting the relative intensity of the coherent feature compared to the incoherent one is distinctly larger for $SrVO_3$; this is, indeed, what should be expected from the fact that the bandwidth in $SrVO_3$ is significantly

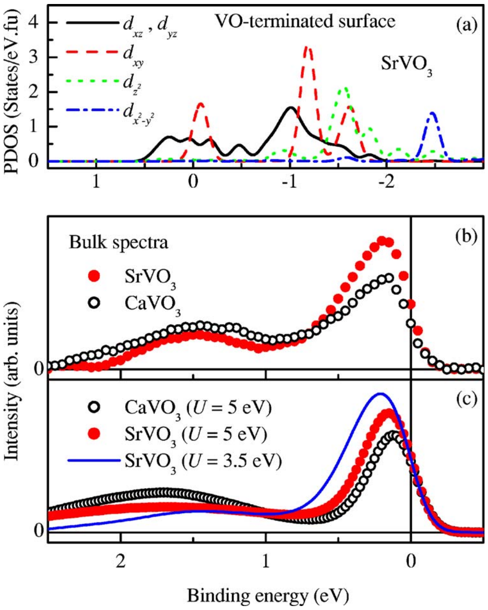

FIG. 3. (Color online) (a) Calculated V 3d PDOS at VO-terminated surface. (b) Extracted bulk spectral functions of SrVO$_3$ (solid circles) and CaVO$_3$ (open circles). (c) LDA+DMFT results adapted from Ref. 12.

larger. This expectation appears to be fully justified by the results of a most sophisticated *ab initio* LDA+DMFT calculations reported recently,[12] which is adopted in Fig. 3(c) for U=5 eV. These calculated spectra, with a distinctly larger relative intensity of the coherent feature in SrVO$_3$ compared to CaVO$_3$, exhibit similar differences in the electronic structures of these two compounds, leading to a unified understanding of this interesting class of compounds and removing the latest puzzling aspects of its reported electronic structure. We also stress the point that the present results are consistent with the significant enhancement in γ of CaVO$_3$ compared to SrVO$_3$;[7] this is another experimental fact that would be difficult to reconcile with the earlier reported identical electronic structure for the two compounds. It is, however, to be noted that though there is a good qualitative agreement between the present experimental results and the independent theoretical ones, Figs. 3(b) and 3(c) also underlines the same interestingly and possibly significant quantitative discrepancies between theory and experiment. Specifically, the incoherent features appear at higher energies in the calculations compared to experimental results, though the relative intensities are reasonably well described. When the energy position of the incoherent feature is brought to better agreement by a reduction in U, the calculated relative intensity becomes unreasonably low, as illustrated in Fig. 3(c) for SrVO$_3$ with U=3.5 eV. This is strongly reminiscent of the Ni satellite problem, where a simultaneous quantitatively accurate description of both the satellite (incoherent feature) intensity and the energy position has remained elusive. The present results suggest that this may be a more general problem related to the description of strongly correlated transition-metal-based systems in terms of the simple Hubbard model and require further theoretical inputs.

Keeping in mind the above-mentioned caveat, the present results still clearly establish that the linear polarization of synchrotron radiation plays a key role in determining the spectral line shape in these systems. The experimentally determined bulk spectra provide an understanding of the electronic structure in Ca$_{1-x}$Sr$_x$VO$_3$, consistent with experimental γ values, calculated change in the d-bandwidth and the geometrical and/or structural trends across the series, thereby resolving the puzzle concerning the structure-property relationship in this interesting class of compounds.

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*Also at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 012, India.

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