PHYSICAL REVIEW B **70**, 195112 (2004)

Surface and bulk electronic structure of $La_{1-x}Ca_xVO_3$

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(Received 26 June 2004; revised manuscript received 19 August 2004; published 16 November 2004)

We report on a photoemission study of the electronic structure of metallic $La_{1-x}Ca_xVO_3$, with $x=0.4$ and 0.5, using monochromatized He I, He II, and Al $K\alpha$ radiations. He II spectra obtained using monochromatic source exhibit large intensity for the coherent feature in contrast to the absence of this feature in the satellite subtracted spectra and establish that the minimum in the photoelectron escape depth appears at a kinetic energy $\leqslant 16$ eV in these metallic systems. As a function of photon energy, strong modifications of the spectral function in the valence-band region were observed, reflecting a difference in the electronic structure at the surface and in the bulk. Detailed analyses of the observed spectra reveal that the studied materials are good metals in the bulk, however, the surface layers are insulating as also reported earlier based on the spectra collected with lower resolutions [Maiti *et al.*, Phys. Rev. Lett. **80**, 2885 (1998)]. The insulating nature of the surface electronic structure can be attributed to the different local symmetry and enhanced electron correlation at the surface as compared to the bulk. The analyses of the bulk spectra and the temperature-dependent studies at high resolution exhibit a distinct dip in the density of states at the Fermi level that suggests a strong influence of disorder on the electronic structure.

DOI: 10.1103/PhysRevB.70.195112 PACS number(s): 71.30.+h, 71.27.+a, 79.60.Bm

I. INTRODUCTION

Insulator-to-metal transitions in correlated electron systems form an outstanding problem in condensed matter physics. It has often been found that certain systems, particularly transition-metal oxides, though expected to be metallic due to partially filled bands, exhibit insulating properties. The observation of an insulating behavior in such cases is attributed to the strong electron-electron Coulomb repulsion energy U between electrons in the partially filled orbitals. Such materials are known as Mott insulators. One can achieve an insulator-to-metal transition by reducing the magnitude of U with respect to the bandwidth W of the partially filled band, since the latter favors delocalization and hence the metallic state. Another convenient way to transform an insulating system to a metallic one is to dope it with charge carriers (electrons or holes). Photoelectron spectroscopy, which is highly surface sensitive, has been extensively used to study the bulk properties of transition metal oxides, always with the assumption that the electronic structure at the surface is essentially the same as in the bulk. For most of the late transition metal oxides, this assumption has been found to be reasonable.[1,2]

Recent investigations, however, exhibit a contrasting scenario for early transition metal oxide materials such as $Ca_{1-x}Sr_xVO_3$ and $La_{1-x}Ca_xVO_3$. The former one is a paramagnetic metal with one electron in the d band. Here, the substitution of Ca by Sr enhances the effective bandwidth W thereby reducing the effective electron correlation strength U/W.[3,4] For this system, it has been found experimentally that the surface electronic structure is qualitatively different from the one in the bulk:[5] while the latter corresponds to a highly metallic phase, the surface is close to a metal-insulator phase transition. $La_{1-x}Ca_xVO_3$, on the other hand, is quite different from $Ca_{1-x}Sr_xVO_3$. $LaVO_3$ is an antiferromagnetic Mott-insulator with two electrons in the d band. Replacing some of the trivalent La by divalent Ca leads to a doping of holes into the valence band. The V-O-V bond angle, one of the relevant parameters that determine the bandwidth, remains almost the same even in the doped compositions,[3,4,6] which means that one can dope holes in this system without a significant change of the effective electron correlation strength. As observed in transport as well as in photoemission (PE) measurements, 20% doping of hole states into the valence band leads to an insulator-to-metal transition in this system.[7,8]

For the metallic compositions of $La_{1-x}Ca_xVO_3$, i.e., for $x \geqslant 0.20$, a significant variation of the PE spectral function was observed as a function of photon energy. X-ray photoelectron spectra (XPS) and He I ($h\nu = 21.2$ eV) PE spectra of the valence band exhibited considerable density of states at the Fermi level implying a metallic character of these materials. The He II ($h\nu = 40.8$ eV) valence-band spectra reported earlier, on the other hand, exhibited finite intensity only below the Fermi level, indicating an insulating character with a finite band gap.[9] Since the escape depth, λ of photoelectrons has a minimum for photoelectron kinetic energies close to 50 eV,[10] the observation of an insulating behavior in the He II PE spectra and a metallic character in the He I and Al $K\alpha$ ($h\nu = 1486.6$ eV) PE spectra for compositions with $x \geqslant 0.20$ was explained on the basis of a different surface electronic structure as compared to the bulk. The interpretation of the He II valence-band spectra of the previous study, however, was complicated by the presence of satellite structures at and around E_F due to the admixture of the He II* satellite radiation ($h\nu = 48.4$ eV) from the unmonochromatized He photon source. Even though the PE intensity originating from the He II* satellite radiation was removed by a subtraction procedure, some ambiguities remain, since the relative intensity of He II* radiation as compared to He II depends on the specific conditions used in the measurement. This is particularly disturbing when the PE features close to E_F are low in intensity. It is therefore quite important to verify the observation of an insulating character in the He II PE spectra by using a monochromatized He II photon source; this was the main aim of the present study. A further incentive was the fact that the calculations based on linearized dynamical mean-field theory predicted a metallic surface phase for a bulk-insulating material, and also suggested that an insulating surface phase should not exist for a bulk metal.[11,12] While these calculations were performed for a half-filled *s* band, a situation that is significantly different from the highly degenerate *d* bands in the transition metal oxides, it is important to verify the validity of the previous conclusion of an insulating surface layer on a bulk-metallic material. Interestingly, a recent experimental observation[13] and subsequent theoretical interpretation[14] suggest a metallic ground state at the surface (interface) of a Mott insulator (Mott-insulator and band insulator), which has been attributed to electronic reconstruction at the surface/interface.

In the present work, we studied the spectral functions of samples with the highest level of doping and consequently the strongest metallic character using monochromatized photon sources. In the He II spectra, we indeed found some intensity at the Fermi level in contrast to previous observations. By combining the spectra recorded with monochromatized x-ray and UV sources, the surface and bulk spectral functions could be separately extracted. Despite finite PE intensity at E_F in the He II spectra, the surface spectral function was again found to exhibit a gap at E_F, confirming that the surface electronic structure is insulating even for highly metallic compositions. This result is discussed in terms of a different local symmetry at the surface as compared to the bulk. In addition, the spectral functions close to E_F derived from the spectra taken at temperatures of 78 and 7 K exhibit a distinct dip at the Fermi level, which suggests that disorder plays a significant role in determining the electronic structure of these systems.

II. EXPERIMENTAL

Polycrystalline samples of $La_{1-x}Ca_xVO_3$ (with $x=0.4$ and 0.5) were prepared from stoichiometric amounts of predried La_2O_3, $CaCO_3$, and V_2O_5. After calcining at 800 °C for 24 h, the mixtures were reduced in hydrogen atmosphere at 800 °C for 24 h, and the resulting samples were melted in a dc arc furnace in inert-gas atmosphere. For each sample, the composition was verified by energy-dispersive analysis of characteristic x-rays (EDAX) and found to be consistent with the nominal composition. The grain sizes of all these samples obtained from congruently molten states were found to be large with strong intergrain bonding. On the basis of powder x-ray diffraction (XRD) with a JEOL-8P x-ray diffractometer, all synthesized samples exhibit single phase. The oxygen stoichiometry, defined by δ in $La_{1-x}Ca_xVO_{3+\delta}$, was determined thermogravimetrically and found to be $\delta=-0.01$ and 0.00 for $x=0.4$ and 0.5, respectively. Transport measurements on these samples exhibit highly metallic conductivity down to the lowest temperature studied so far.[7] XPS measurements were carried out in a combined XPS-UPS-BIS VSW spectrometer at a base pressure of 1×10^{-10} mbar, using monochromatized Al $K\alpha$ radiation and an energy resolution of 0.8 eV [full width at half maximum (FWHM)]; the samples were cooled to liquid-nitrogen temperatures. In order to avoid any ambiguity arising from the presence of the satellites associated with the He I and He II radiations, we used a monochromatized UV source from Gammadata Scienta, and the experiments were carried out at 78 and 7 K employing a SCIENTA-SES200 electron analyzer. The experimental energy resolution was determined from the Fermi edge of Ag metal and was found to be 14 and 22 meV (FWHM) with He I and He II photons, respectively. The cleanliness of each sample surface was maintained by repeated *in situ* scrapings with an alumina file and was monitored by O 1*s* and C 1*s* spectra in the 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 *in situ* scrapings was confirmed for each composition.

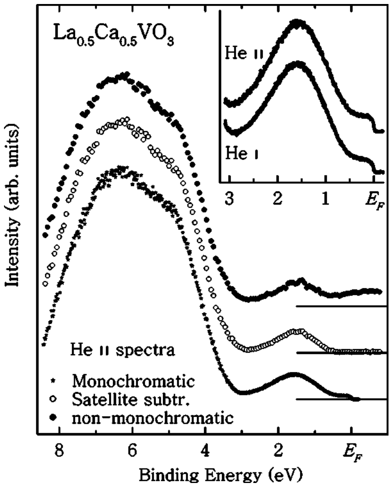

FIG. 1. Valence band spectra of $La_{0.5}Ca_{0.5}VO_3$ recorded with He II radiation from a monochromatic source (stars) and an unmonochromatized UV lamp (solid circles). The spectrum obtained after subtraction of contributions from the He II* satellite is shown by open circles. The inset gives the valence-band spectra close to E_F obtained with He I and He II radiation from monochromatic source.

III. RESULTS AND DISCUSSIONS

The difficulties that can arise in the analysis of spectra recorded with nonmonochromatized He radiations, depending on the spectral weight at the Fermi level, are illustrated in Fig. 1. Here, we show He II spectra obtained from $La_{0.5}Ca_{0.5}VO_3$ using a nonmonochromatized (solid circles) and monochromatized UV source (stars). The intense broad peak between 4 and 9 eV binding energies observed in both spectra is due to PE from O 2p states, with very similar spectral shapes in this energy region. The spectral intensity between E_F and 3.5 eV binding energy arises primarily from V 3d-like states,[8] with the peak close to 1.5 eV binding energy being known as a signature of the lower Hubbard band (LHB); it therefore represents electronic states that are localized due to strong electron correlation, and is termed “incoherent feature.” The spectrum obtained by nonmonochromatized He II radiation is significantly distorted in the neighborhood of E_F, with a high intensity at E_F and even a distinct feature above E_F. The feature above E_F can be readily identified as the O 2p-related emission excited by He II* radiation, i.e., with a photon energy that is 7.6 eV higher than that of He II radiations; such energetically shifted replicas are often referred to as satellite features. This satellite contribution can be removed by standard procedures.[15] The satellite corrected He II spectrum is shown by open circles in Fig. 1; it appears to be essentially similar to the raw spectrum except near and above the E_F region. Most importantly, the satellite corrected spectrum does not exhibit any noticeable intensity close to the Fermi level corresponding to the “coherent feature” representing the delocalized states. This suggests a band gap and an insulating character, in sharp contrast to the spectrum obtained with a monochromatized He II source (stars in Fig. 1), reflecting the inadequacies of the satellite subtraction procedure adapted earlier for the metallic compositions.[9] This problem arises primarily because of the fact that the intense O 2p signal obtained due to He II* photon energy overlaps with the weak coherent feature corresponding to the He II spectrum. Thus, a small error in the spectral normalization leads to a significant error for the coherent feature.

In the inset of Fig. 1, we compare the valence band spectra close to E_F obtained from monochromatized He I and He II radiations. In addition to the incoherent feature peaking at about 1.5 eV, a finite PE intensity with a distinct structure is clearly observed at E_F in the He II spectrum. An analogous coherent feature is also seen in the He I spectrum, consistent with previous work.[9] Interestingly, the intensity of the coherent feature in the He II spectrum is higher than that observed in the He I spectrum. Resistivity measurements clearly suggest that the bulk of this heavily doped sample is highly conducting.[7] Thus, this comparison suggests that the He II spectrum is more bulk sensitive than the corresponding He I spectrum. In other words, the mean escape depth for valence band photoelectrons is smaller with He I radiation compared to that with He II radiation in contrast to the usual expectation.

The escape depth of photoelectrons without suffering any inelastic scattering strongly depends on the material properties. A system with a finite energy band gap forbids low-energy electronic excitations below a certain energy. This fact tends to push the minimum in the escape depth towards higher energy in insulators. In metallic systems, however, the presence of substantial density of states at and near the Fermi level allows low-energy excitations. This is possibly the origin of the shift in the minimum of λ towards a lower energy in the present case.

In order to investigate the contribution of a distinct surface electronic structure to the recorded spectra, we begin with the parent insulating phase $LaVO_3$, and show its XPS spectrum (open circles) and resolution-broadened He I spectrum (solid line) in Fig. 2. In spite of a substantial change in the photon energy, there is hardly any change in the line shape of the spectra for this compound. Additionally, this result also establishes that the energy dependence of the photoemission cross section across the width of this feature arising from V 3d states is negligible. This insensitivity clearly shows that the surface and bulk electronic structures are essentially identical in this insulating phase.

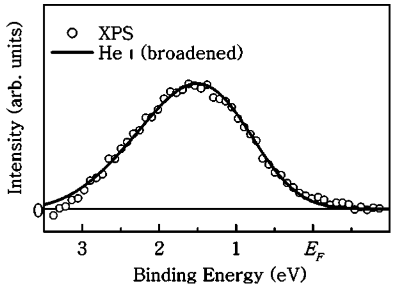

FIG. 2. XPS valence-band spectra (open circles) of $LaVO_3$. The resolution-broadened He I spectrum (solid curve) reproduces the XPS spectrum almost exactly.

The V 3d valence-band spectra of $La_{0.6}Ca_{0.4}VO_3$ and $La_{0.5}Ca_{0.5}VO_3$ recorded with the three monochromatic photon beams are displayed in Figs. 3(a) and 3(b), respectively. All the spectra were normalized to the same integrated intensity. Both the incoherent and coherent features appear in all the spectra, with a clear dominance of the incoherent feature in every case. An increase in photon energy causes the relative intensity of the coherent feature to grow. This trend is clearly observed when comparing the UPS spectra with the XPS spectra, suggesting that the photon energy corresponding to the most surface-sensitive case is close to 21.2 eV or even lower. The spectral modifications with photon energy

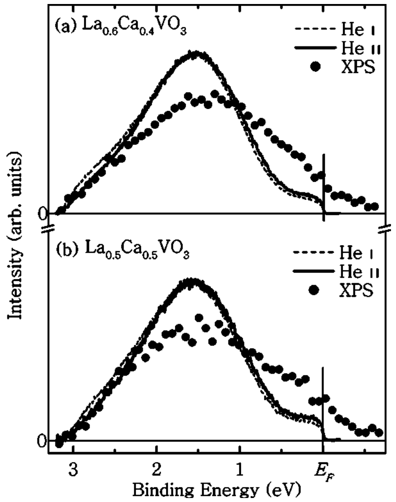

FIG. 3. Valence-band spectra of (a) $La_{0.6}Ca_{0.4}VO_3$ and (b) $La_{0.5}Ca_{0.5}VO_3$ recorded with He I (dashed curve), He II (solid curve), and Al $K\alpha$ radiations (solid circles). It is clear that the increase in photon energy leads to a transfer of spectral weight from the incoherent feature to the coherent feature.

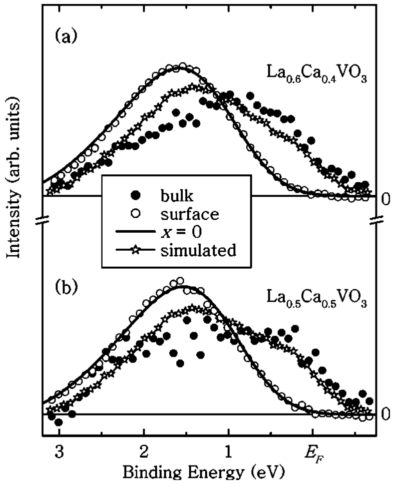

FIG. 4. Spectral functions corresponding to the bulk (solid circles) and surface (open circles) electronic structure of $La_{1-x}Ca_xVO_3$ for (a) $x=0.4$ and (b) $x=0.5$. The resolution-broadened He I spectrum of $LaVO_3$ (solid curve) is plotted on the surface spectra after shifting it by 0.1 eV to higher binding energies; it is remarkable, how well this spectrum reproduces the surface spectra. The stars represent the spectral function simulated by the sum of composition-weighted bulk spectra of the end members ($LaVO_3$ and $CaVO_3$).

show that the electronic structure of $La_{1-x}Ca_xVO_3$ is significantly different at the surface and in the bulk, in overall agreement with earlier observations.[9]

We now turn to the question of how to extract the surface and bulk electronic structures from the present PE spectra. From the energy dependence of the spectral line shape shown in Fig. 3, it is *a priori* not possible to consider any of the spectra as representative for the surface or bulk spectral function. We note here that d/λ, with d being the thickness of the surface layer with an altered electronic structure, could be estimated reliably well for $Ca_{1-x}Sr_xVO_3$ at various electron kinetic energies.[5] Since the crystal structures of $Ca_{1-x}Sr_xVO_3$ and $Ca_{1-x}La_xVO_3$ are very similar, we assume here that d/λ estimated for $Ca_{1-x}Sr_xVO_3$ for Al $K\alpha, (d/\lambda)_{XPS}=0.52$, and for the He I radiation $(d/\lambda)_{HeI}=1.77$, apply also to $La_{1-x}Ca_xVO_3$. In order to confirm the stability of this approach against the substantial uncertainties in estimating the (d/λ) values, we note that a variation of about 15% in $(d/\lambda)_{HeI}$ does not give rise to noticeable changes in the extracted surface and bulk electronic structures. These estimates of (d/λ) suggest that while the XPS spectra are characterized by about 60% of bulk electronic structure, only about 17% of the He I spectra should be due to bulk contributions. If we assume that the escape depth of the photoelectrons from the valence band is about 20 Å for Al $K\alpha$ radiations, we obtain an effective surface layer thickness of about 10 Å, corresponding to about 3 atomic layers. The escape depth for valence electrons in UPS then turns out to be about 6 Å.

The extracted surface and bulk spectral functions of $La_{1-x}Ca_xVO_3$ are plotted in Figs. 4(a) and 4(b) for $x=0.4$ and 0.5, respectively. The extracted bulk spectral functions are shown by solid circles, revealing a relatively high spectral intensity at E_F. This reflects the metallic character of the two samples consistent with the bulk transport properties. The large linewidth of this extracted feature is due to the experimental resolution broadening in XP spectra that are used to arrive at the true bulk spectral features. Open circles represent the surface electronic structure with the spectra exhibiting a single feature around 1.5 eV binding energy. No intensity is observed at E_F, suggesting a highly 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 the two $La_{1-x}Ca_xVO_3$ compounds is remarkable, which further establishes the insulating nature of the surface layers in the latter two materials.

While the bulk is found to be metallic, an interesting observation in the bulk spectral functions is the strong incoherent feature spreading down to about 3 eV binding energies. This suggests that strong electron correlation effects influence the bulk electronic structure significantly. The presence of incoherent features has been observed in the doping-dependent spectral functions calculated within a single-band Hubbard model using dynamical mean-field theory (DMFT).[16] However, any reasonable value of U/W does not produce such a large intensity of the incoherent feature in presence of such large doping levels. 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.[9] 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.[17,18] 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. This exercise has already been performed in Ref. 9. However, the experimental bulk spectral function of $CaVO_3$ was not available in that study, which forced us to calculate the bulk spectra by incorporating electron correlation perturbatively on the *ab initio* results.

In the present work, we add the bulk spectra of $LaVO_3$ and $CaVO_3$ (from Ref. 5) according to the compositions of the two materials $I(\epsilon)=[2(1-x)I_{LaVO_3}(\epsilon)+xI_{CaVO_3}(\epsilon)]$, where x denotes the extent of doping. The results are shown by stars in Fig. 4. 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 the two 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.[18] 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.

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 crystal structures of the end members $LaVO_3$ and $CaVO_3$ are both orthorhombic, where six oxygens form an octahedral cluster around V. These VO_6 octahedra in the two materials are nearly regular, with very small distortions. The regular 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 $J \sim 1$ eV. Therefore, the two electrons in the d band occupy the up-spin t_{2g} band and assume a high-spin configuration. The insulating phase in this partially filled system is known to arise from strong electron correlation. This is consistent with the fact that the bulk system transforms readily to a metallic state when doped by a fractional hole per V site. 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 a La-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. Defining the surface normal as the z axis, d_{xz} and d_{yz} electrons are expected to experience a similar crystal field, thereby forming a doubly degenerate e_g band; this band will be lower in energy than the d_{xy} band. Thus, the two d electrons will completely fill the up-spin e_g band, with all other bands being empty. It is interesting to note here that while the insulating phase appears in the bulk electronic structure due to the presence of strong electron correlation, the different crystal symmetry is expected to result in a band-insulating phase in the surface electronic structure. 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,[19] 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 correlation strength.

Doping of hole states via substitution of trivalent La ions by divalent Ca ions reduces the electron count from 2 in the d bands. It has been found both from transport studies and photoelectron spectroscopy that 20% hole doping leads to an insulator-to-metal transition in the bulk of this material. However, as shown by the present results, the doped compositions exhibit an insulating surface electronic structure even for the highest doped samples studied so far. 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. In addition, a larger U/W at the surface is known to lead to a phase separation, as also observed in other systems.[20] Such charge disproportionations $(2d^1 \rightarrow d^0 + d^2)$ at the surface have indeed been observed in other d^1 systems, such as $CaVO_3$ and $SrVO_3$.[5] Thus, the observation of the insulating surface 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.

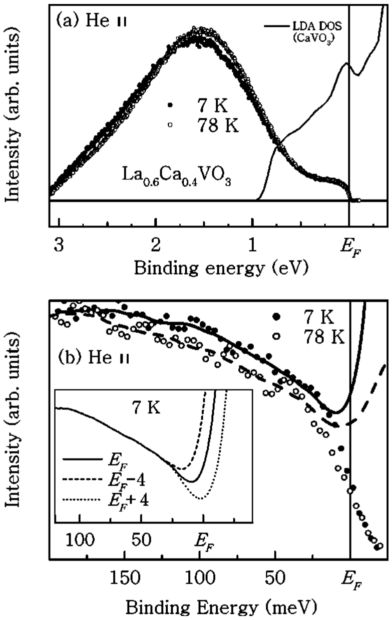

FIG. 5. (a) He II spectra of $La_{0.6}Ca_{0.4}VO_3$ at 78 and 7 K. The solid line shows the calculated TDOS of $CaVO_3$ corresponding to the t_{2g} band. (b) Spectra shown on an expanded scale close to E_F. Solid and open circles represent the 7 and 78 K spectra, respectively. The spectral functions 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).

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 $La_{0.6}Ca_{0.4}VO_3$ collected at 7 and 78 K are shown in Fig. 5. 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 line shape, while the energy range (3 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. 5(a) are intrinsic, representing some changes in the underlying electronic structure. Temperature-dependent changes in the spectral line shape have indeed been found in various calculations using dynamical mean-field approach (DMFT) in the limit of infinite dimensions.[16,21] While the 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. 5(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 ($\sim$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 approximation (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, is shown in Fig. 5(a). It is evident from the figure that the density of states continuously increases with the decrease in binding energy. 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.[22] 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. 5(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,[23] 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.[24] 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.

IV. CONCLUSIONS

In summary, we have investigated the electronic structure of $La_{1-x}Ca_xVO_3$, for $x=0.4$ and 0.5, using monochromatic photon sources. We observed finite spectral intensity at the Fermi level in the He II spectra using a monochromatized source in contrast to previous He II spectra, corrected for satellite contributions. This demonstrates that the use of a monochromatic photon source is essential when there are overlapping features. The spectral functions corresponding to the insulating phase were found to be independent of the photon energy suggesting identical electronic structures at the surface and in the bulk. In the metallic compositions, however, a significant modification of the spectral function was observed with the probing photon energy. The gradual decrease in coherent-feature intensity with a decrease in photon energy down to 21.2 eV in the metallic samples indicates that the minima in the escape depth of the valence photoelectrons in the metallic compositions appears at kinetic energies $\leqslant$16 eV. We extract the surface and bulk spectral functions based on the spectra obtained using monochromatized sources. The absence of the coherent feature in the surface spectra establishes that the surface of this system is insulating. Such an insulating nature can be attributed to the different symmetry and enhanced electron correlation strength at the surface as compared to the bulk. While the bulk spectra indicate highly metallic character consistent with their bulk properties, the bulk electronic structure is still dominated by the incoherent feature. The spectra at low temperatures recorded with high-energy resolution exhibit a dip at the Fermi level indicating strong influence of disorder on the electronic structure.

ACKNOWLEDGMENTS

The authors thank A. Liebsch for useful discussions and the Department of Science and Technology, Government of India, for financial assistance. The work in Berlin was supported by the Deutsches Zentrum für Luft- und Raumfahrt e.V., Project No. INI-012-99, and the Deutsche Forschungsgemeinschaft, Grant No. Sfb-290, TP A06.

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