

Surface versus Bulk Coulomb Correlations in Photoemission Spectra of SrVO_3 and CaVO_3

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(Received 13 September 2002; published 3 March 2003)

Recent photoemission spectra of the perovskite series $\text{Ca}_x\text{Sr}_{1-x}\text{VO}_3$ revealed strong modifications associated with surface contributions. To study the effect of Coulomb correlations in the bulk and at the surface, the quasiparticle spectra are evaluated using the dynamical mean field theory. It is shown that as a result of the reduced coordination number of surface atoms correlation effects are stronger at the surface than in the bulk, in agreement with experiment.

DOI: 10.1103/PhysRevLett.90.096401

PACS numbers: 71.20.Be, 71.27.+a, 79.60.Bm

Photoemission is a key spectroscopy for the investigation of electronic properties of strongly correlated materials. Because of its surface sensitivity, there is growing concern to what extent the data are representative of bulk properties and whether they need to be corrected for surface effects influencing the one- and many-electron properties. For instance, earlier photoemission data on $\text{Ca}_x\text{Sr}_{1-x}\text{VO}_3$ [1,2] indicated that SrVO_3 is a strongly correlated metal and that CaVO_3 is close to a metal-insulator transition with very little spectral weight at the Fermi level. In contrast, low-frequency bulk probes found metallic behavior regardless of Ca concentration [3]. In view of the relative simplicity of these perovskites, this discrepancy is indeed astonishing. For this reason CaVO_3 has been intensively investigated [4].

To identify surface contributions in photoemission from $\text{Ca}_x\text{Sr}_{1-x}\text{VO}_3$, Maiti *et al.* [5] and Sekiyama *et al.* [6] performed measurements using a wide range of photon energies. As a result of the frequency dependent escape depth of the photoelectron, the spectra reveal striking variations evidently associated with surface modifications of the electronic structure: Emission from the coherent peak near the Fermi level is reduced and correlation-induced satellites have larger weight than in the bulk. On the other hand, the bulk emission from SrVO_3 and CaVO_3 was found to be remarkably similar, in agreement with low-frequency bulk measurements.

Strong spectral changes with photon energy were also observed on SrRuO_3 [7] and $\text{Ca}_x\text{La}_{1-x}\text{VO}_3$ [8]. Most likely, these are caused by surface contributions [9]. Another example is Sr_2RuO_4 for which earlier photoemission data appeared to be in conflict with de Haas–van Alphen measurements [10]. Recent experimental and theoretical work proved that this discrepancy can be resolved by accounting for the surface reconstruction of Sr_2RuO_4 which leads to significant changes in photoemission spectra [11].

The understanding of surface effects in photoemission from transition metal oxides is clearly important in order to distinguish them from bulk correlation phenomena. Although the electronic properties of strongly correlated materials are currently a field of intense experimental and

theoretical investigation [12–14] surface effects have thus far received little attention [15]. In the present work, we use the dynamical mean field theory (DMFT) [13,16,17] to evaluate the surface and bulk quasiparticle spectra of SrVO_3 . We show that because of the planar electronic structure of perovskite systems and the concomitant narrowing of the surface local density of states, correlation effects at the surface are more pronounced than in the bulk. In the perovskites, this enhancement is particularly strong since the local Coulomb energy is not far from the critical value for a metal-insulator transition. Such a trend had been predicted by Potthoff and Nolting [15] who studied the metal–insulator phase diagram for a semi-infinite simple cubic s band at half filling. Here we calculate the self-energy for a multiband system using a realistic local density of states appropriate for SrVO_3 and find qualitative agreement with photoemission [5,6]. We also comment on surface photoemission from CaVO_3 .

Electronic structure calculations for SrVO_3 within the local density approximation (LDA) [18] show that the conduction bands near E_F consist of degenerate t_{2g} bands derived from V^{4+} ($3d^1$) ions. The filled O $2p$ bands are separated from the t_{2g} levels by a gap of about 1 eV, and the cubic crystal field of the V-O octahedron shifts the e_g bands above the t_{2g} bands. The t_{2g} bands can be represented via a tight-binding Hamiltonian with diagonal elements of the form $h_{xy,xy}(k) = e_d + t_0(c_x + c_y) + t_1c_xc_y + [t_2 + t_3(c_x + c_y) + t_4c_xc_y]c_z$, where $c_i = 2\cos(k_i a)$, $i = x, y, z$, and a is the lattice constant. The t_i denote effective hopping integrals representing the V-O-V hybridization, where $t_{0,2}, t_{1,3}$, and t_4 specify the interaction between first, second, and third neighbors, respectively. Off-diagonal elements which vanish at high-symmetry points are very small and will be neglected.

Figure 1(a) shows the t_{2g} bulk bands of SrVO_3 . According to the planar electronic structure, the bulk density of states $\rho_b(\omega)$ exhibits the characteristic asymmetric peak related to the Van Hove singularity at the X point [see Fig. 1(b)]. The overall shape of the bulk density of states agrees with LDA calculations [18]. At the surface, the t_{2g} degeneracy is lifted since only the d_{xy} band exhibits strong dispersion within the surface plane (the z

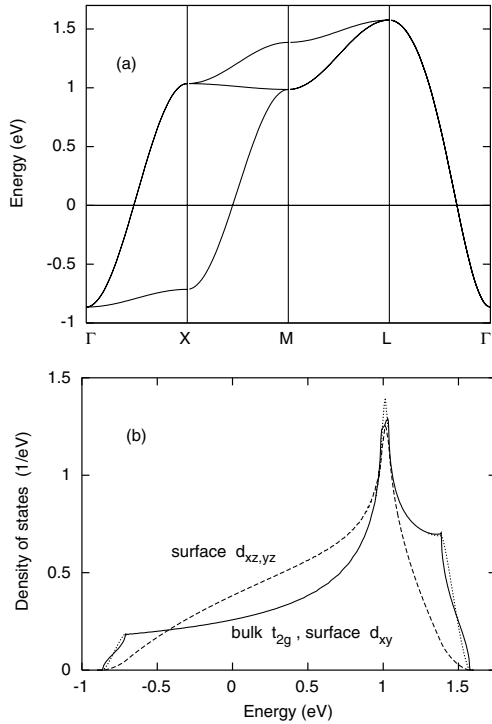


FIG. 1. (a) Tight-binding fit to LDA t_{2g} bulk bands of SrVO₃ ($E_F = 0$). (b) Solid curve: isotropic bulk density of states; dashed and dotted curves: local density of $d_{xz,yz}$ and d_{xy} states in the first layer of SrVO₃.

axis defines the surface normal). To evaluate the surface density of states, we use a Green's function formalism [19] for semi-infinite tight-binding systems. The tight-binding parameters are assumed to coincide with those in the bulk, except for a small surface potential to ensure charge neutrality.

Figure 1(b) shows the local density of states $\rho_s(\omega)$ of the $d_{xz,yz}$ bands for the surface layer of SrVO₃. Its weight is reduced at low and high energies but enhanced at intermediate energies. Thus, the effective width of $\rho_s(\omega)$ is smaller than that of $\rho_b(\omega)$ although their total widths are identical. The density of d_{xy} states nearly coincides with $\rho_b(\omega)$, reflecting the planar nature of t_{2g} states. It would be desirable to perform electronic structure calculations for SrVO₃ surfaces since they should provide a more accurate density of states. Nevertheless, the key effect discussed here, i.e., the narrowing of the local density of $d_{xz,yz}$ states, should hold quite generally.

To interpret the experimental photoemission data, we evaluate the quasiparticle spectra by accounting for local Coulomb correlations. According to the one-electron properties discussed above, we are dealing with a non-isotropic system where two narrow bands interact with a wider band. This situation is reminiscent of the layer perovskite Sr₂RuO₄, which essentially consists of Ru sheets containing two narrow $d_{xz,yz}$ bands interacting with a wide intraplanar d_{xy} band. The peculiar feature of this system is the fact the on-site Coulomb energy lies

between the single-particle widths of the nondegenerate t_{2g} bands: $W_{xz,yz} < U < W_{xy}$ [20]. In the present case, the difference between $d_{xz,yz}$ and d_{xy} bands at the surface is less pronounced so that $W_i < U$ for all three bands. Nevertheless, since in the first layer the effective width of $d_{xz,yz}$ states is reduced, the influence of Coulomb correlations on the surface bands should be stronger than on the wider bulk bands.

The key quantity characterizing the effect of Coulomb correlations is the complex self-energy. Since we neglect the weak hybridization between t_{2g} bands, $\Sigma(\omega)$ is diagonal in orbital space. Despite this simplification, a full description of correlations near the surface would be exceedingly complicated since, in principle, it would require a mixed momentum/real space approach in order to handle the loss of translational symmetry normal to the surface. This could be accomplished using a cluster formalism where the semi-infinite system is represented via a slab of finite thickness. Unfortunately, the planar character of t_{2g} orbitals leads to a slowly convergent local density of $d_{xz,yz}$ states, with many spurious $1/\sqrt{\omega}$ Van Hove singularities stemming from the quasi-one-dimensional hopping parallel to the surface. On the other hand, a cluster generalization of the DMFT is feasible today only for very small cluster size. We therefore ignore the momentum variation of the self-energy and assume that, for a given layer, it depends only on the local density of states within that layer. Additional coupling of the quantum impurity problems represented by the layers is probably small [15] and is neglected for computational reasons. The reduced dimensionality at the surface therefore enters the many-body calculation via the layer-dependent density of states. In view of the local Coulomb interaction, this assumption seems justified for qualitative purposes.

Before discussing the quasiparticle spectra derived within the DMFT, it is useful to compare the frequency dependence of the self-energy in the bulk and at the

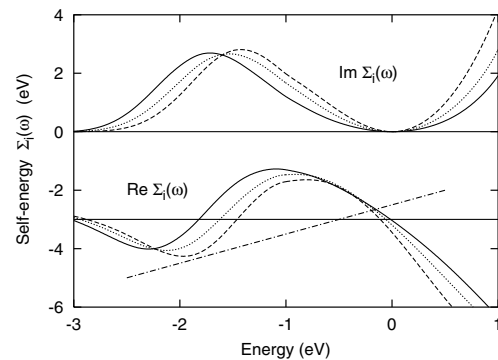


FIG. 2. Second-order self-energy of SrVO₃. Solid curves: bulk t_{2g} self-energy; dashed (dotted) curves: $d_{xz,yz}$ (d_{xy}) self-energy for surface layer. For clarity, the real part is shifted down by 3 eV. The straight line gives $\omega - \epsilon_k$ for $\epsilon_k = -0.5$ eV.

surface. For convenience, we give here the results obtained within non-self-consistent second-order perturbation theory since this provides a clear identification of the various orbital contributions to the diagonal elements $\Sigma_i(\omega)$ [20]. Figure 2 illustrates the second-order self-energy for $U = 4.3$ eV and $J = 0.7$ eV. The effective band narrowing at the surface yields a narrower distribution of $\text{Im} \Sigma_{xz,yz}(\omega)$ compared to $\text{Im} \Sigma_b(\omega)$ for the isotropic bulk. Because of the orbital mixing via the on-site Coulomb interaction $\text{Im} \Sigma_{xy}(\omega)$ lies between these two distributions. From the Kramers-Kronig relations, it then follows that $\text{Re} \Sigma_{xz,yz}(\omega)$ exhibits a more pronounced minimum below the band bottom than $\text{Re} \Sigma_b(\omega)$. Thus, as indicated by the line $\omega - \epsilon_k$ for a typical band energy ϵ_k , the surface satellite appears at a lower value of U than in the bulk. This qualitative picture is fully supported by the more accurate DMFT results discussed below.

In the DMFT, the self-energy elements $\Sigma_i(\omega)$ are functionals of the bath Green's functions $\mathcal{G}_i^{-1} = G_i^{-1} + \Sigma_i$. On-site Coulomb correlations are treated using the self-consistent multiband Quantum Monte Carlo (QMC) method (for a review, see Ref. [13]). The temperature of the simulation is 125 meV with 64 imaginary time slices and several runs using 10^5 Monte Carlo sweeps. The quasiparticle density of states is obtained via maximum entropy reconstruction [21].

Figure 3(a) shows the bulk quasiparticle spectrum of SrVO₃ for two Coulomb energies in the critical region for the formation of incoherent Hubbard bands which are seen as satellites in the photoemission spectra [5,6]. The exchange energy is $J = 0.7$ eV [22]. These results show that U must be larger than 4 eV to obtain the satellite. The peak near 2 eV above E_F corresponds to the upper Hubbard band and agrees with inverse photoemission data [2]. Although for $U = 4$ eV there is considerable correlation-induced band narrowing and an emerging satellite shoulder, a larger U yields an even narrower coherent feature near E_F , with the missing weight shifted to the lower and upper Hubbard bands. Note that $N_b(E_F) = \rho_b(E_F)$ which follows from the local approximation implicit in the DMFT for isotropic systems [23]. The most recent photoemission data [6] confirm this result.

The surface quasiparticle spectra for SrVO₃ are shown in Figs. 3(b) and 3(c). The lower Hubbard peak of the $d_{xz,yz}$ states is clearly visible already for $U = 4$ eV because of the narrower local density of states in the first layer. A larger U shifts the satellite to higher binding energies. The comparison with the spectra shown in Fig. 3(a) demonstrates that correlation effects for a fixed value of U are stronger at the surface than in the bulk: The coherent peak near E_F is narrower at the surface and the incoherent satellite feature is more pronounced than in the bulk, in agreement with experiment [5,6].

The surface quasiparticle density of d_{xy} states in Fig. 3(c) is intermediate between $N_b(\omega)$ and $N_s(\omega)$ for $d_{xz,yz}$. Although there is little single-electron hybridiza-

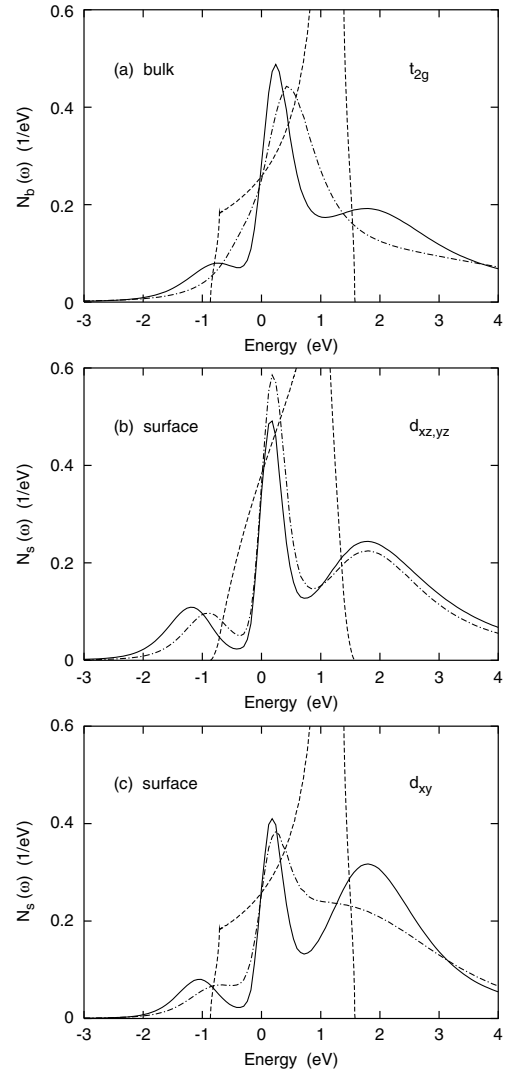


FIG. 3. Quasiparticle density of states of SrVO₃ derived from DMFT. (a) Bulk t_{2g} states, (b) surface $d_{xz,yz}$ states, and (c) surface d_{xy} states. Solid curves: $U = 4.3$ eV; dot-dashed curves: $U = 4.0$ eV; dashed curves: bare densities as in Fig. 1.

tion between t_{2g} bands, the local Coulomb interaction mixes them so that the d_{xy} surface spectrum involves contributions arising from the more strongly correlated $d_{xz,yz}$ states. Another consequence of the anisotropic surface self-energy is the correlation-induced charge transfer between subbands [20]. Here, we find that 0.06 electrons are shifted from the d_{xy} to the $d_{xz,yz}$ bands. The coupling between narrow and wide bands is a genuine multiband effect and underlines the fact that single-particle bands in the presence of local Coulomb interactions cannot be considered independently.

Note that the many-body reduction of the quasiparticle band width is much larger than the surface-induced one-electron band narrowing. On the other hand, since the on-site Coulomb energy is not far from the critical value for a metal-insulator transition, the band narrowing substantially enhances the influence of correlations at the surface.

It would be interesting to perform angle-resolved photoemission measurements to determine the correlation-induced band narrowing of the SrVO₃ t_{2g} bands. For instance, the energy at $\bar{\Gamma}$ should be only a few tenths of an eV below E_F instead of 1 eV as predicted by the LDA. Accordingly, the true t_{2g} bands should be considerably flatter than the single-particle bands. Also, measurements using polarized light could help to separate correlation effects in the d_{xy} and $d_{xz,yz}$ bands.

We finally comment on the difference between CaVO₃ and SrVO₃. According to bulk LDA calculations for CaRuO₃ [24], orthorhombic distortions cause a slight narrowing of the t_{2g} bands and a broadening of the Van Hove singularity above E_F . The same trend is found in CaVO₃ [25]. Assuming the same on-site Coulomb energy for the V⁴⁺ ions in CaVO₃ and SrVO₃, this effect implies a weak transfer of spectral weight from the coherent to the incoherent peak, in agreement with the recent photoemission data [5,6] and DMFT calculations [25]. At the surface, however, such a shift of spectral weight should be more pronounced because of the band narrowing discussed above, in particular, since U/W is rather large. This effect is indeed observed in the photoemission spectra [5,6]. For a more detailed analysis, it would be important to carry out electronic structure calculations for CaVO₃ surfaces to investigate orthorhombic distortions and possible reconstructions. The latter presumably would reduce hopping also within the d_{xy} band, thereby enhancing surface correlations. Also, studies of incomplete screening of U at surfaces would be useful.

In summary, we have performed DMFT quasiparticle calculations for SrVO₃ in the bulk and at the surface. As a result of the planar nature of the t_{2g} states and the surface narrowing of the local density of states on-site correlation effects are more pronounced at the surface than in the bulk, in agreement with photoemission data. The two-dimensional character of d states near E_F is one of the hallmarks of transition metal oxides. The surface-induced enhancement of correlation effects discussed in the present work should therefore be a phenomenon observable in many materials.

I thank A. Bringer for useful discussions and A. I. Lichtenstein for the QMC-DMFT code. I also thank S. Biermann for comments and for bringing Ref. [6] to my attention.

Note added.—After completion of this work, analogous QMC-DMFT calculations were reported for bulk SrVO₃ and CaVO₃ [25], demonstrating the similarity of these isoelectronic perovskite materials.

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