Correlation and surface effects in Vanadium oxides

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Recent photoemission experiments have shown strong surface modifications in the spectra from vanadium oxides as (V, Cr)$_2$O$_3$ or (Sr, Ca)VO$_3$. The effective mass is enhanced at the surface and the coherent part of the surface spectrum is narrowed as compared to the bulk. The quasiparticle weight is more sensitive at the surface than in the bulk against bandwidth variations. We investigate these effects theoretically considering the single-band Hubbard model for a film geometry. A simplified dynamical mean-field scheme is used to calculate the main features of the interacting layer-dependent spectral function. It turns out that the experimentally confirmed effects are inherent properties of a system of strongly correlated electrons. The reduction of the weight and the variance of the coherent part of the surface spectrum can be traced back to the reduced surface coordination number. Surface correlation effects can be strongly amplified by changes of the hopping integrals at the surface.

I. INTRODUCTION

A large class of transition-metal oxides display a metal-insulator transition (MIT) upon variation of pressure, temperature or chemical doping. According to effective one-particle theories these materials are normal metals. The observed transitions are caused by correlations. Typical materials that show such a behavior are vanadium oxides. There are numerous experimental and theoretical studies which describe and try to explain the physics of these materials. The electronic structure in the vicinity of the transition has been revealed by photoemission experiments. They show a certain internal structure of the 3d-derived bands on the metallic side of the transition. Essentially, there are two peaks in the angle-integrated spectral function $A(\omega)$: One is located at the Fermi energy and is usually called "coherent part" of the spectrum. The other structure, called "incoherent part", is located at higher binding energies. The metal-insulator transition is then driven by a redistribution of spectral weight from the coherent to the incoherent peak. At the critical point the weight of the coherent peak vanishes and the system undergoes the transition to the insulating phase.

While an effective one-particle theory as the local-density approximation within density-functional theory (DFT-LDA) can reproduce the coherent part of the spectrum apart from a renormalization factor, it fails to describe the incoherent part, which is caused by strong electron correlations. On the other hand, the correlation-induced MIT is a classical subject of many-body theory. If there is no long-range magnetic order in the metallic as well as in the insulating phase, the transition is known as the Mott-Hubbard transition. For band models there are early theories that describe the incoherent or the coherent part of the spectrum. Nowadays, with the dynamical mean-field theory (DMFT) there is a general approach at hand which includes and unifies both aspects. The DMFT reproduces the coherent (usually called quasiparticle resonance) as well as the incoherent (usually called lower Hubbard band, LHB) part of the spectrum. There is a third feature, the upper Hubbard band (UHB), which is not seen in photoemission experiments since it is located well above the Fermi energy. The DMFT yields a MIT as described above. For bulk systems LDA+DMFT calculations even can give quantitative results.

Recently, however, a number of studies have shown that the photoemission data have to be interpreted carefully. Especially, the surface sensitivity of photoemission has been reconsidered. It has been shown that a proper interpretation of the data cannot rely on the presumption that the electronic structure at the surface is almost the same as in the bulk. In fact, by comparing results from measurements with different surface sensitivities, it has been shown that the spectral function can be strongly modified at the surface compared with the bulk. It has been the intention of these studies to extract reliable bulk properties from the experimental data which can be compared with the results of LDA+DMFT theory, for example. However, also the layer dependence and surface modifications of the spectral function have been measured. These are interesting on its own. A number of qualitative trends can be deduced safely:

- The weight of the coherent part of the spectral function is reduced at the surface.
- The width or more accurately the variance of the coherent peak tends to be somewhat smaller at the surface.
- Changes of the bandwidth (and thus of the effective correlation $U$) affect the weight of the coherent part of the spectral function much more at the surface than in the bulk.

It is an interesting theoretical task to explain these trends and to reproduce the respective features in the spectral function $A(\omega)$.

In this paper we consider a system in a film geometry which exhibits a Mott-Hubbard MIT and investigate the layer dependence of the spectral function. The interesting question is whether the experimental findings are inherent properties of a film geometry of correlated electrons or whether additional modifications at the surface
are required, such as surface relaxation, surface phase separation or surface reconstruction. If the measured trends are generic they should be present in any model system that shows a Mott-Hubbard transition and has a layer geometry with surface(s). Thus, though the investigated materials usually require the study of multi-band models to account for the band degeneracy, the surface modifications and layer dependence of the spectral function can be investigated qualitatively using a single-band Hubbard model in a film geometry. The advantage is that a (semi-) analytical approach can be used which makes the physical mechanisms beyond the surface effects most explicit.

Of course, such a simple (semi-) analytical theory has to retain the fundamental physics of the Mott-Hubbard transition as described above. This rules out theories as static mean-field theory or Hubbard-III approximation since they do not give the correct three-peak structure of the spectral function. The three-peak structure of the spectral function or equivalently a two-peak structure of the imaginary part of the self energy is crucial for a qualitatively correct (mean-field) description of the Mott-Hubbard transition. A recent study has shown that experimental data can nicely be fitted once this condition is met. Here we will use the recently developed “two-site” DMFT. This is an approach which keeps the essence of the DMFT but simplifies the mean-field equations by a physically motivated approximation to allow for analytical calculations. The two-site DMFT is an extension of the linearized DMFT which meets the minimal condition mentioned above, i.e. leads to a three-peak structure of the spectral function with two Hubbard bands (incoherent peaks) and a quasiparticle resonance (coherent peak).

In the next section we specify the model assumptions and develop and discuss the two-site DMFT for a film geometry. In section III we discuss the reduction of the weight and the variance of the coherent spectral function. Section IV considers the topic of the enhanced sensitivity of the quasiparticle weight at the surface against bandwidth modifications.

II. MODEL AND THEORY

We investigate the single-band Hubbard model for a film geometry

$$H = -\sum_{ij\alpha\sigma} t_{ij}^{\alpha} c_{i\alpha\sigma}^\dagger c_{j\alpha\sigma} + \sum_{i\alpha\sigma} \frac{U_{\alpha}}{2} n_{i\alpha\sigma} n_{i\alpha-\sigma}$$  \hspace{1cm} (1)$$

Here $\alpha, \beta = 1, \ldots, d$ label the different layers parallel to the film surface(s). $d$ is the film thickness. The subscripts $i$ and $j$ refer to the sites within a layer and run from 1 to $N_{||}$, where $N_{||}$ is the number of sites per layer ($N_{||} \rightarrow \infty$). In the following the on-site energies and the interaction strengths are taken to be layer independent $t_{ij}^{\alpha} = t_0$ and $U_{\alpha} = U$. $t_0 = 0$ defines the energy zero. The hopping integrals $t_{ij}^{\alpha\beta}$ are assumed to be non-zero between nearest neighbors only and is taken to be layer independent, too. The nearest-neighbor hopping defines the energy unit $t_{ij}^{\alpha\beta} = t = 1$. Only at the surface the intra-layer hopping $t_{ij}^{11} = t_{11}$ or the hopping between the surface and the subsurface layer $t_{ij}^{12} = t_{12}$ may be modified ($t_{11}, t_{12} \neq t$) to simulate relaxation processes.

Exploiting the two-dimensional translational symmetry, the layer-dependent Green function reads

$$G_{\alpha\beta,\sigma}(k_{||}, \omega) = \left[ \omega + \mu - \tilde{t}(k_{||}) - \tilde{\Sigma}_{\sigma}(k_{||}, \omega) \right]^{-1} \hspace{1cm} (2)$$

$k_{||}$ is a wave vector of the two-dimensional Brillouin zone. The $d \times d$ matrix $\tilde{t}(k_{||})$ is the Fourier-transformed hopping matrix

$$t_{\alpha\beta}(k_{||}) = \frac{1}{N_{||}} \sum_{ij} t_{ij}^{\alpha\beta} e^{-i k_{||} (\mathbf{R}_i - \mathbf{R}_j)} \hspace{1cm} (3)$$

Within the DMFT the self-energy is local. The matrix $\tilde{\Sigma}(k_{||}, \omega)$ is diagonal and $k_{||}$ independent. In the following the spin index $\sigma = \uparrow, \downarrow$ is dropped since we are solely interested in the paramagnetic phase. The crucial point of the DMFT is the mapping of the lattice (Hubbard) model onto an appropriate single-impurity (Anderson) model (SIAM). The latter is defined in such a way that the impurity Green function and the self-energy of the impurity model are equal to the on-site Green function and the self-energy of the lattice model, respectively. The DMFT is exact in the limit of infinite spatial dimensions $D$ but can be applied as a proper mean-field theory to finite-dimensional systems, too.

The formulation of the DMFT for a film geometry is straightforward. The mapping has to be done for each layer. Consequently in our case $d$ different impurity models $H_{\text{imp}}^{(\alpha)}$, one for each layer $\alpha$, have to be defined. The impurity models can be solved independently for $\alpha = 1, \ldots, d$ but are coupled indirectly by a set of $d$ self-consistency relations. As the usual DMFT for a bulk system, the DMFT for a film geometry becomes exact for $D \rightarrow \infty$.

Within the two-site DMFT the mapping procedure is strongly simplified. The respective single-impurity Anderson models are replaced by models that consist of one correlated impurity site and one bath site only $H_{\text{imp}}^{(\alpha)} \rightarrow H_{2\text{-site}}^{(\alpha)}$. This allows for an exact solution of the impurity model. There are four parameters in the two-site model, two of them are already fixed: the energy level of the correlated site $\epsilon_{\alpha}^{(\alpha)} \equiv t_0 = 0$ and the interaction strength $U_{\alpha} = U$. The remaining two parameters, the hybridization between the two orbitals (sites) $V_{\alpha}$ and the one-particle energy of the bath site $\epsilon_{\alpha}$, are chosen such that the original self-consistency conditions are fulfilled in an integral way for the full spectral function and especially for its coherent part. A calculation completely analogous to the bulk case (see Ref. 17) yields
for hybridization $V_\alpha$:

$$V_\alpha^2 = \sum_{j\beta} \left( \rho_{ij}^{\alpha\beta} \right)^2 z_\beta, \quad (j\beta) \neq (i\alpha). \tag{4}$$

Here the definition

$$z_\alpha = \left( 1 - \left[ \frac{d\Sigma_\alpha(\omega)}{d\omega} \right]_{\omega=0} \right)^{-1} \tag{5}$$

is used. For metals $z_\alpha$ is the quasiparticle weight. Its inverse $z_\alpha^{-1}$ is the quasiparticle mass-enhancement factor. At the critical interaction for the metal-insulator transition there is a divergence of the effective mass: $z_\alpha(U_c) = 0$.

Finally, the one-particle energy of the bath site $\epsilon_\alpha^{\text{(a)}}$ is obtained from the second self-consistency condition:

$$n_\alpha^d = n_\alpha \tag{6}$$

$n_\alpha^d$ and $n_\alpha$ are the particle densities for the correlated site in the impurity model $H^{\text{(imp)}}_{\alpha\beta}$ and for a site in the $\alpha$-th layer of the lattice model, respectively.

Eqs. (3) and (5) define the parameters of the (two-site) impurity models. The latter can easily be solved numerically or (for half filling) analytically. The self-energy of the two-site model $\Sigma^{(\text{site})}_\alpha(\omega)$ is identified with the self-energy of the respective layer $\Sigma_\alpha(\omega)$. Now at once new quasiparticle weights $z_\alpha$ are given by Eq. (5).

Via Eq. (2) and the spectral theorem one obtains the new particle density for each layer $n_\alpha$. Therewith, a new set of impurity models can be defined. This circle has to be iterated until self-consistency is reached.

Almost analytic calculations are possible for the symmetric case of the paramagnetic phase at half-filling. Eq. (3) is now trivially fulfilled since $n_\alpha^d = n_\alpha = 1$ due to the manifest particle-hole symmetry, which requires $\epsilon_\alpha^{\text{(a)}} = \mu = \frac{U}{2}$. Furthermore, the two-site problem can be solved analytically. which gives the self-energy

$$\Sigma_\alpha(\omega) = \frac{1}{2} U + \frac{1}{8} \frac{U^2}{\omega - 3V_\alpha} + \frac{1}{8} \frac{U^2}{\omega + 3V_\alpha} \tag{7}$$

Thus Eq. (5) can be evaluated

$$z_\alpha = \frac{36V_\alpha^2}{36V_\alpha^2 + U^2} \tag{8}$$

Introducing the coordination number within a layer $q$ and between two layers $p$ (bulk coordination number: $q + 2p$), the mapping condition (3) can be written more explicitly

$$V_\alpha^2 = q t_\alpha^2 z_\alpha + p t_{\alpha+1}^2 z_{\alpha+1} + p t_{\alpha-1}^2 z_{\alpha-1} \tag{9}$$

For a bulk-system, where all quantities are layer independent, the last two equations give a single non-trivial solution and one recovers the Brinkmann-Rice result

$$z_\alpha(U) = 1 - \frac{U^2}{U_c^2}. \tag{10}$$

The critical interaction, however, is different and given by the linearized DMFT$^{\text{LS}}$ value

$$U_c = 6t\sqrt{2p + q}. \tag{11}$$

For a film geometry, Eqs. (3) and (9) constitute a set of nonlinear algebraic equations which can be solved by numerical means - even for large systems. Then the self-energy $\Sigma(\omega)$ (Eq. (7)) and the Green function $G(k,\omega)$ (Eq. (2)) can be calculated and finally also the spectral function

$$A_\alpha(\omega) = \frac{1}{2\pi \omega} \text{Im} \sum_k G_{\alpha\alpha}(k,\omega) \tag{12}$$

To make contact with the experimental findings discussed above, we have to determine the weight and the variance of the coherent part of the spectrum. These quantities can be obtained analytically: The coherent peak is described by the "coherent Green function" which is obtained by expanding the self-energy for small frequencies

$$\Sigma_\alpha(\omega) = a_\alpha + b_\alpha \omega + \mathcal{O}(\omega^2) \tag{13}$$

and inserting this expression into Eq. (2). For the self-energy (4) the parameters $a_\alpha$ and $b_\alpha$ are given by

$$a_\alpha = \frac{U}{2} = \mu$$

$$b_\alpha = -\frac{U^2}{36V_\alpha^2} = 1 - z_\alpha^{-1} \tag{14}$$

This yields for the coherent Green function

$$G^{(\text{coh})}_{\alpha\beta}(\omega) = \left[ \omega - \tilde{t} - i\omega \right]^{-1} \tag{15}$$

where $\tilde{t}$ is the real-space hopping matrix. The coherent spectral function is given by the imaginary part of the on-site element of the coherent Green function matrix:

$$A^{(\text{coh})}_\alpha(\omega) = -\frac{1}{\pi} \text{Im} G^{(\text{coh})}_{\alpha\alpha}(\omega + i0^+) \tag{16}$$

Its weight $w_\alpha$ and its variance $\Delta_\alpha^2$ are determined by the spectral moments $M^{(n)}_\alpha = \int_{-\infty}^{\infty} d\omega \omega^n A^{(\text{coh})}_\alpha(\omega)$:

$$w_\alpha = M^{(0)}_\alpha$$

$$\Delta_\alpha^2 = \left( M^{(2)}_\alpha - M^{(1)}_\alpha^2 \right) M^{(0)-1}_\alpha \tag{17}$$

To obtain the spectral moments, we perform a high-frequency expansion of the coherent Green function (see Ref. 20)

$$G^{(\text{coh})}_{\alpha\alpha}(\omega) = \frac{M^{(0)}_\alpha}{\omega} + \frac{M^{(1)}_\alpha}{\omega^2} + \frac{M^{(2)}_\alpha}{\omega^3}$$

$$= \frac{z_\alpha}{\omega} + \frac{z_\alpha^2 \sum_{\beta} (\delta_{\beta\beta} - (\alpha\alpha)) \epsilon_{\alpha\beta}^2}{\omega^3 \zeta^2} \tag{18}$$
This yields

\[ w_\alpha = z_\alpha \]
\[ \Delta_\alpha^2 = z_\alpha (q t_{\alpha\alpha}^2 z_\alpha + p t_{\alpha\alpha+1}^2 z_{\alpha+1} + p t_{\alpha\alpha-1}^2 z_{\alpha-1}) \] (19)

With these results at hand we can analyze the surface effects of the coherent part of the spectrum. Eqs. (8) and (9) turn out to be sufficient to discuss most surface effects. Additionally, we can calculate the full spectral function using Eq. (12).

III. SURFACE WEIGHT AND VARIANCE

Recall that the experiments show three characteristic surface modifications of the spectral density: a reduced weight and a tendency to a reduced variance of the coherent part of the spectrum and an enhanced sensitivity against bandwidth modifications at the surface. Let us start with the first two phenomena, which have been observed for (La, Ca)VO₃ (Ref. 13), for (Ca, Sr)VO₃ (Ref. 14 and Ref. 15), and for (V, Cr)₂O₃ (Ref. 11). We will discuss the spectra from CaVO₃ and SrVO₃ (Ref. 14, 15) as representative examples. In the spectra of both materials there are two peaks, the coherent peak near the Fermi energy and incoherent peaks at \( \omega \approx \pm 8 \). In the photoemission experiments only the occupied part of the spectrum is seen which leads to the observed two-peak structure. Compared with the experiments the different peaks are separated more clearly in Fig. 1. This is due to the fact that damping effects due to a finite imaginary part of the self energy are neglected completely in the two-site DMFT. Damping effects are expected to be less important for the coherent peak shown in Fig. 2. As can be seen in the figure and as is also noticed in Ref. 15, the shape of the coherent spectrum is well described by the uncorrelated \((U = 0)\) spectral function, apart from a correlation-induced scaling factor. This factor \( z \) can be identified with the quasiparticle weight \( z \) from Eq. (5). In Fig. 2 comparison is made with the free spectral function narrowed by a constant factor \( z = 0.46 \) for all layers (dotted lines). While this factor works well for the surface it is too small for the bulk. Hence the scaling factor and therefore the quasiparticle weight is reduced at the surface. This is the same trend as seen in the experiments.
However, the reduction is much weaker as in the experiments. A possible reason is that the sc(100) surface is rather closed, i.e. the ratio between the surface and the bulk coordination number \( \frac{b_z}{b_d} = \frac{5}{6} \) is near unity. In Fig. 3 we compare the quasiparticle weight \( z \) of the sc(100) surface with the ones of more open surfaces (sc(110) and sc(111)). Indeed the surface quasiparticle weight is more reduced if the surface is less closed.

In the inset the ratio between the surface and the bulk variance is shown. The surface variance is reduced for all interactions \( U \) which is in agreement with experiment. Again the reduction is more pronounced for the more open sc(111) surface (dot-dashed line). We can distinguish between a direct effect that is already present at \( U = 0 \) and is given by the ratio between the surface and the bulk coordination number (see Eq. (19)) and an additional indirect effect for finite interactions \( U \) which is due to correlations.

The results discussed so far are not at all specific to the considered low-index surfaces of a simple-cubic model structure. On the contrary, one can show analytically that (within the two-site DMFT) the reduction of the weight and the variance is inherent to any Mott-Hubbard system, irrespective of the special geometry. We consider a semi-infinite system \( (d \to \infty) \) with uniform parameters. We will show that the weight at the surface \( z_1 \) is smaller than the weight in the bulk \( z_b \) \( (0 < z_1 < z_b < 1 \text{ for } 0 < U < U_c) \). From Eqs. (8) and (9) one readily derives the recursion:

\[
    z_{\alpha+1} = \frac{z_{\alpha}}{1 - z_{\alpha}} \frac{U'^2}{p} - \frac{q}{p} z_{\alpha} - z_{\alpha-1}, \tag{20}
\]

where \( U' = \frac{U}{6} \) is defined for convenience. Now we find for the surface \( (\alpha = 1, z_0 \equiv 0) \)

\[
    z_1 = 1 - \frac{U'^2}{q + \frac{2}{z_1} p} \tag{21}
\]

On the other hand, from (10) and (11) we have for the bulk

\[
    z_b = 1 - \frac{U'^2}{q + 2p} \tag{22}
\]

Now suppose for the moment that for a given \( U \) \( (0 < U < U_c) \)

\[
    z_1 \geq z_b \tag{23}
\]

We will show that this leads to a contradiction. It follows from (21) and (22) that the assumption (23) requires

\[
    z_2 > z_1 \geq z_b \tag{24}
\]

Now assume that the relation

\[
    z_{\alpha} > z_{\alpha-1} \geq z_b \tag{25}
\]

is valid for arbitrary (fixed) \( \alpha \). Then \( \frac{1}{1 - \frac{z_b}{z_{\alpha}}} > 1 \) holds. We immediately get

\[
    \frac{1 - z_b}{1 - z_{\alpha}} + \left( \frac{1 - z_b}{1 - z_{\alpha}} - \frac{z_{\alpha-1}}{z_{\alpha}} \right) + \frac{q}{p} \left( \frac{1 - z_b}{1 - z_{\alpha}} - 1 \right) > 1 \tag{26}
\]

since the last two addends are positive. After some algebra one arrives at

\[
    \frac{(1 - z_b)(2p + q)}{(1 - z_{\alpha})p} - \frac{q}{p} \frac{z_{\alpha-1}}{z_{\alpha}} > 1 \tag{27}
\]
Using (22) and multiplying the inequality with $z_\alpha$ gives
\[
\frac{z_\alpha}{1-z_\alpha} \frac{U^2}{p} - \frac{q}{p} z_\alpha - z_{\alpha-1} > z_\alpha
\] (28)
The left hand side of this expression is just $z_{\alpha+1}$ as seen from Eq. (20). Hence
\[
z_{\alpha+1} > z_\alpha \geq z_b
\] (29)
It is shown that (29) directly follows from (25) and (25) holds for $\alpha = 2 \ldots \infty$. Consequently (29) holds for all $\alpha$.

On the other hand $z_\alpha$ has to converge against the bulk value $z_b$ for $\alpha \to \infty$
\[
z_\alpha \alpha \to \infty \rightarrow z_b
\] (30)
The last two statements (29) and (30) are contradictory. Hence our assumption (23), i.e. that $z_1$ equals or is greater than $z_b$, cannot be valid. Thus it is shown that the quasiparticle weight is reduced at the surface
\[
z_1 < z_b \quad \text{for} \quad 0 < U < U_c,
\] (31)
for uniform parameters, irrespective of the geometry.

A short and vivid explanation of this finding is based on the reduced coordination number at the surface. Let us compare Eq. (8) for the surface and for the bulk.
\[
V_1^2 = z_1 q + z_2 p,
V_2^2 = z_b q + z_b p + z_b p
\] (32)
There is a (positive) addend missing in the surface expression. This tends to reduce the surface parameter $V_1$ which causes a reduced quasiparticle weight $z_1(U)$ in turn (Eq. (8)).

All experiments discussed above show a reduced weight of the coherent peak at the surface. Some of them may even be interpreted as showing an insulating surface of a metallic bulk. However this is ruled out for uniform parameters. From Eq. (20) it follows immediately, that all layers are insulating if the quasiparticle weight of the first layer vanishes. (Recall that $z_0 = 0$.)

Similar considerations as for the weight apply for the variance. From Eq. (10) and (9) we have:
\[
\Delta_1^2 = z_1 V_1^2
\]
\[
\Delta_2^2 = z_b V_1^2
\] (33)
Using $V_1^2 = \frac{z_\alpha}{1-z_\alpha} U^2$ (from Eq. (8)) and Eq. (22) we end up with
\[
\frac{\Delta_1^2}{2p+q} = \frac{z_1^2}{z_b}
\]
\[
\frac{\Delta_2^2}{2p+q} = \frac{1-z_b}{1-z_1} \Delta_1^2
\] (34)
Since we already know $0 < z_1 < z_b < 1$ this immediately yields
\[
\Delta_1^2 < \Delta_2^2
\]
for any surface geometry and for uniform but arbitrary parameters.

Again, a closer look at (8) and (9) gives a vivid explanation of this finding: Starting from (10), we get for the surface and the bulk variance:
\[
\Delta_1^2 = z_1(qz_1 + pz_2)
\]
\[
\Delta_2^2 = z_2(qz_2 + pz_2 + pz_b)
\] (35)
Here one can see both effects that have been already discussed at Fig. 3. The direct effect is just the missing addend in the surface expression (similar to (32)). This reduces the surface variance even for $U = 0$. The indirect effect, which is due to correlations, is caused by the reduced surface weight $z_1(U) < z_b(U)$. Both effects add and result in a reduced variance at the surface as seen in Fig. 4.

Modified surface parameters. Even for the relatively open surface sc(111) the reduction of the quasiparticle weight at the surface is smaller as compared to the reduction found in the experiments. We therefore want to investigate whether a modified hopping at the surface (caused e.g. by a surface relaxation) can further reduce the spectral weight and the variance of the coherent peak. Indeed Fig. 4 shows a considerable influence of the surface hopping on the quasiparticle weight. If both, the hopping within the surface layer $t_{111}$ and the hopping between the surface and the subsurface layer $t_{12}$ are reduced (dot-dashed line) the weight of the coherent peak is almost negligible for a wide range of interactions strengths. This applies e.g. for $U = 10$ which is still far away from the bulk metal-insulator transition. Nevertheless, looking at the layer dependent spectral function (Fig. 5), there are strong correlation effects at the sur-
FIG. 6: The slope of the quasiparticle weight as a function of the hopping parameter $t$ for constant $U = 10$.

face. Now there is only a very narrow peak at the Fermi energy for $\alpha = 1$. This fits well to the experiments cited above. The inset of Fig. 4 shows analogous trends for the variance.

Summing up, one can state that both experimentally established trends, i.e. the reduced weight and the reduced variance of the coherent surface peak, are inherent features of a Mott-Hubbard system in a film geometry. Reduced hopping integrals at the surface may amplify both effects considerably.

IV. SENSITIVITY AGAINST BANDWIDTH VARIATIONS

Another surface effect is mentioned in Ref. 15 for (Sr, Ca)VO$_3$. Again, measurements with strong as well as with weak surface sensitivity have been performed. It is found that the surface weight $z_1$ is much smaller in CaVO$_3$ than in SrVO$_3$ while the quasiparticle weight in the bulk $z_b$ is almost the same. Both materials are expected to exhibit comparable interactions $U$. The difference is mainly the hopping integral $t$ which is smaller in CaVO$_3$. In other words, the experiments show that the slope of the function $z(t) - \frac{dz}{dt}$ is positive and much higher at the surface compared to the bulk. Fig. 6 shows this slope as a function of the hopping $t$ (and thus as a function of the bandwidth $W = 12t$) at a fixed interaction $U = 10$. Below the critical hopping $t_{\text{crit}} = 0.68$ the system is insulating. For the first case, a sc(100) surface, we can qualitatively reproduce the experimental result for a wide parameter range ($t > 0.85$). However the enhancement is very weak. As for the other surface effects, the enhancement becomes stronger for more open surfaces as well as for reduced hopping integrals at the surface. The experimental finding $\frac{dz_1}{dt} > \frac{dz_b}{dt}$ is thus expected for most parameters. However, the opposite scenario may be found as well for smaller hopping integrals $t$.

V. SUMMARY

We have reproduced and explained a number of surface effects recently detected by photoemission experiments from metallic Vanadium oxides. Within a simplified but reasonable DMFT scheme, it was shown analytically and numerically that the reduction of the quasiparticle weight and the variance of the coherent part of the spectrum at the surface are inherent properties of a system of correlated electrons. It was explicitly shown that these effects are caused by the reduced surface coordination number. Consequently, the surface modifications are stronger for an open surface. These effects can be amplified if the hopping integrals at the surface are reduced.

The situation is not so clear for the enhanced sensitivity of the surface quasiparticle weight $z_1$ against bandwidth variations. Though the experimental trend $\frac{dz_1}{dt} > \frac{dz_b}{dt}$ is found for a wide range of parameters, the opposite is true for parameters that are still realistic. Furthermore we did not find any region in the parameter space where $z_1$ changes considerably but $z_b$ is nearly insensitive against bandwidth variations. This subject needs also more clarification experimentally: In Ref. 14 for instance, where the same materials are investigated as in Ref. 15, the bulk quasiparticle weight still seems to change if one compares SrVO$_3$ and CaVO$_3$.

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