Realistic modeling of the electronic structure and the effect of correlations for Sn/Si(111) and Sn/Ge(111) surfaces

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The correlated electronic structure of the submonolayer surface systems Sn/Si(111) and Sn/Ge(111) is investigated by density-functional theory (DFT) and its combination with explicit many-body methods. Namely, the dynamical mean-field theory and the slave-boson mean-field theory are utilized for the study of the intriguing interplay between structure, bonding and electronic correlation. In this respect, explicit low-energy one- and four(sp²-like)-band models are derived using maximally-localized Wannier(-like) functions. In view of the possible low-dimensional magnetism in the Sn submonolayers we compare different types of magnetic orders and indeed find a 120° antiferromagnetic ordering to be stable in the ground state. With single-site methods and cellular-cluster extensions the influence of a finite Hubbard $U$ on the surface states in a planar and a reconstructed structural geometry is furthermore elaborated.

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I. INTRODUCTION

Strong electronic correlations lead to many of the most interesting phenomena in modern condensed matter physics, such as superconductivity, the metal-insulator transition or local moment magnetism. It is well known that the effect of these many-body effects depend heavily on the interplay between structure, bonding, and the degree of order within the effective dimensionality of the given problem. While the study of realistic bulk systems in this context has been rather extensive in recent years, those investigations may only provide insight into the effect of dimensionality via reasonably justified quasi-dimensions due to large crystalline anisotropies. In this respect the study of surface systems has the advantage that by an intelligible tuning of the coupling between the adsorbate and the substrate, quasi-lowdimensionality can be created more efficiently. Besides, there are many surface-sensitive experimental probe techniques in order to reveal the electronic structure more directly than in the bulk. Hence the research on specific surface materials problems may add substantially to the understanding of the general problem of strong quantum correlations.

There has been an increased interest in adsorbate systems involving semiconducting substrates since more than a decade. These often exhibit dangling-bond-derived surface states with rather small bandwidths. While Mott criticality is hardly seen on the free surfaces because of structural reconstructions, certain adsorbate atoms forming (sub)monolayers stabilize hybridized narrow-band surface states down to low temperatures. The most prominent of this kind are the so-called α-phase surfaces, where the canonical structure is described by a $\sqrt{3}\times\sqrt{3}R30^\circ$ triangular array of adsorbate atoms within an 1/3 monolayer coverage on a (111) semiconductor substrate, resulting in a half-filled surface band. Due to the rather large interatomic distances between the adsorbate atoms ($\sim$7Å) the latter becomes indeed rather narrow. Mott-insulating phases in such systems are believed to be realized in e.g., K/Si(111), whereas a transition to a correlation-driven charge-density-wave phase takes place in Pb/Ge(111).

In this respect, the α-phase systems Sn/Si(111) and Sn/Ge(111) are of central interest due to the unusual properties they exhibit at low temperatures. It has been recently verified by Modesti et al. that the planar α-Sn/Si(111) surface exhibits a metal-insulator transition below 60 K. No structural reconstruction appears to accompany this transition, since it was observed that the $\sqrt{3}\times\sqrt{3}R30^\circ$ periodicity is stable at least down to around 6 K. The question of magnetic ordering within the insulating regime, i.e., the formation of an antiferromagnetic (AFM) Mott-insulating state, has been raised because of band foldings revealed by low $T$ photoemission experiments leading to a $3\times3$ periodicity. In contrast, the structurally and electronically very similar α-Sn/Ge(111) surface shows vastly different behaviour. There a transition from the $\sqrt{3}\times\sqrt{3}R30^\circ$ phase at room temperature to an $3\times3$ symmetry below 200K takes place. Two competing ground-state configurations of the Sn atoms seem to exist in the latter temperature range, with the so called 2D-1U (i.e., two Sn atoms down, one Sn atom up with respect to the planar triangular structure) state in favor of 6 meV/adatom against the competing 1D-2U configuration. The $\sqrt{3}\times\sqrt{3}R30^\circ$ periodicity observed at room temperature is understood as a result of the rapid fluctuations of the system between these two states. It is still a matter of debate whether or not the system displays a surface Mott transition similar to the Sn/Si(111) system. The finding of a Mott insulating phase in α-Sn/Ge(111) below 20K by Cortes et al. has apparently not been confirmed by other groups.

The electronic structure of the α surface phases poses an interesting problem in the context of strong electron correlation. Early phase-diagram studies of such adlayer structures within the Hartree-Fock approximation showed the possibility for various orderings. Since the narrow-band surface state is mainly...
derived from a hybridization of the Sn(5p_z) state with the underlying Si states, one deals with Coulomb correlations in an effective 5p system (assuming a Hubbard-like interaction). Calculations based on standard density-functional theory (DFT) show\textsuperscript{14,15} in the case of $\sqrt{3}\times\sqrt{3}R30'\text{ Sn/Si(111)}$ indeed an isolated half-filled surface band of width $W\sim0.3\text{ eV}$. Additionally, the named $3\times3$ reconstruction in Sn/Ge(111) is verified within DFT\textsuperscript{26–28}. Correlation effects beyond the local density approximation (LDA) and the generalized gradient approximation (GGA) have been investigated by Profeta and Tosatti\textsuperscript{29} within the LDA+U method\textsuperscript{30}, establishing a Hubbard $U$ for the single Sn(5p_z) orbital. In this scheme, Mott-insulating Sn/Si(111) (with assuming ferro-/ferrimagnetic order) is reached for $U\sim2\text{ eV}$, but the authors find a $U\approx4\text{ eV}$ from constrained calculations more appropriate, also to cope with a gap size of order $\sim0.3\text{ eV}$. This rather large value for the local Coulomb interaction differs from $U_{\text{eff}}\sim1.15\text{ eV}$ obtained in elder constrained LDA calculations designed for a minimal model describing the surface band\textsuperscript{15}. Concerning $\alpha$-Sn/Si(111) there are speculations\textsuperscript{4,13,20} about a realization of the quasi-twodimensional (2D) correlated triangular lattice problem, including the possibility of antiferromagnetism or spin-liquid physics and $d$-wave superconductivity.

In this work we want to investigate the importance of electronic correlations and their interplay with the structural data in the $\alpha$-Sn/(Si,Ge)(111) phases. By means of a combination of realistic DFT band-structure schemes with advanced many-body techniques, the aim is to clarify the differences stemming from the (Si,Ge)(111) substrates and to reveal to which extent Coulomb correlations can give rise to the observed and perhaps still-to-be observed phenomena. Albeit some relevant work has already been performed in this direction, namely Ref.\textsuperscript{13,15,20}, there remain still many open questions. For instance, the minimal Hubbard model derived by Flores et al\textsuperscript{15} has not truly been numerically treated and the arguments given concerning the influence of structural reconstructions on a possible Mott criticality lack a local picture of the involved orbitals. The LDA+U method utilized in Ref.\textsuperscript{20} is designed for long-range-ordered insulating states and neglects as a static technique quantum fluctuations (even in the Mott state). Hence correlations in the metallic regime are usually described incorrectly and magnetic tendencies are often overestimated. Moreover, the experimental data is far from being conclusive, e.g., concerning the appearance of local moment physics and eventual magnetic ordering.

### II. THEORETICAL APPROACH

Realistic theoretical schemes for correlated condensed matter, combining traditional band-structure approaches with explicit many-body techniques have been quite successful in the last decade in dealing with various problems in strongly correlated physics. The most prominent of such schemes is the combination of DFT with the dynamical mean-field theory (DMFT), the so-called LDA+DMFT\textsuperscript{22,23} framework. While in standard DFT correlation effects are only taken into account in an averaged way by making reference to a homogeneous-(like) electron gas, the named combined approach allows for explicit many-body effects on an operator level by still keeping important band-structure details from LDA. The DMFT technique\textsuperscript{24,25} is able to incorporate all onsite quantum fluctuations and thereby may describe quasiparticle (QP) as well as atomic excitations (i.e., Hubbard bands) on an equal footing. A alternative combined approach is given by interfacing the Gutzwiller- or the slave-boson mean-field technique with DFT\textsuperscript{26–28}. In this more simplified treatment the QP lifetime remains infinite, thus omitting the full frequency dependence of the self-energy. Hence only low-energy features may be addressed in the spectral function and hence high-energy Hubbard bands are not accessible. However importantly, the local atomic multiplets are still present with an effective static character in the generalized theory\textsuperscript{29–31}.

Due to the subtle dependencies of the $\alpha$-Sn/(Si,Ge)(111) surface electronic structure on the structural data, care must be taken in its proper determination. We used an implementation\textsuperscript{32} of the highly-accurate mixed-basis pseudopotential (MBPP) technique\textsuperscript{33} for this task. This DFT band-structure code employs normconserving pseudopotentials\textsuperscript{34} and an efficient combined basis consisting of plane waves and a few localized orbitals. Since the magnetism of these surface systems is very subtle, we additionally performed computations within the projector-augmented-wave (PAW) method\textsuperscript{35} for the specific study of magnetic ordering. Thereby one is able to lift the possible limitations due to the use of pseudo-crystal wave functions. Two implementations of the PAW formalism, namely the CP-PAW\textsuperscript{36} code and the Vienna Ab-initio Simulation Package (VASP)\textsuperscript{37} code, were applied, which also allow for the investigation of noncollinear spin orderings. The actual calculations were performed by employing a slab geometry where care was taken in using a well converged lateral k-point mesh (up to a $25\times25$ grid for the magnetic structures).

We combined the DFT approach with two many-body techniques, namely the DMFT with a Hirsch-Fye quantum Monte-Carlo impurity solver\textsuperscript{38} and the rotationally invariant slave boson (RISB) method\textsuperscript{39,40} in saddle-point approximation. Note that in the single-site problem the RISB technique may also be understood as a quasiparticle impurity solution to DMFT. The employed mean-field version of the RISB method is in its character and nature of approximation very similar to the state-of-the-art Gutzwiller technique\textsuperscript{39,40}.

For the actual interfacing of DFT with the many-body approaches a suitable downfolding procedure of the relevant problem to a local basis (the correlated subspace) is needed (see e.g., Ref.\textsuperscript{41,42}). The choice is in most cases a matter of convenience, since many physically sound
frameworks that provide a representation of the band-structure within a minimal local Wannier(-like) basis are applicable. The coherent connection of the crystal problem to such a tailored basis is the key point, rather than the peculiarities of the (restricted) projected local viewpoint itself. It is important to realize that the extended (crystal, surface or chain) problem, although composed of atoms, is not an atomic problem. Of course, in a subsequent many-body treatment the minimal interacting hamiltonian has to be adjusted to the characteristics of the chosen local basis. Up to now, the results of such many-body approaches are not exceedingly sensitive to the very details of the selected correlated subspace, once the number and character of orbitals is agreed on. In that sense, the here utilized maximally-localized Wannier (MLWF) scheme thus provides a reliable local basis for the materials under consideration.

III. DFT INVESTIGATION AND MLWF DESCRIPTION

A. Single-site Sn unit cell

In order to investigate the electronic structure of the 1/3 monolayer of tin atoms on the semiconductor $\sqrt{3} \times \sqrt{3} R30^\circ$ surfaces we first utilized slab geometries incorporating a single Sn atom within the full unit cell. Thus the surfaces are modeled by a supercell with three bilayers of (Si,Ge) separated by sufficiently large vacuum regions. Note that in this section we model the Sn submonolayer in each case as flat, although a distortion in $z$ direction is observed for true Sn/Ge(111) (see section III B). The Sn atoms are placed in the $T_4$ sites of the surface while the bottom of the slab is saturated with hydrogen atoms (see Fig. 1). Structural relaxations by minimizing the atomic forces have been performed with fixed position of the lowest substrate layer. The bulk chosen lattice constants and relaxed Sn-Sn nearest-neighbor distances are (5.43, 6.65)Å and (5.65, 6.93)Å for Sn/Si(111) and Sn/Ge(111), respectively. An energy cutoff of 16 Ryd for the plane-wave part of the mixed-basis set was used for all calculations. Localized functions were introduced for Si(3$s$,3$p$), Ge(3$d$,4$s$,4$p$) as well as Sn(4$d$,5$s$,5$p$).

![FIG. 1: (Color online) Left: Top view onto the employed $\sqrt{3} \times \sqrt{3} R30^\circ$ (red) and $3 \times 3$ (green) surface unit cells. Right: Side view of the slab geometry for Sn/Si(111) surface (bottom) and the distorted 1U-2D Sn/Ge(111) surface (top).](image)

![FIG. 2: (Color online) GGA-PBE DOS for Sn/(Si,Ge)(111) in the $\sqrt{3} \times \sqrt{3} R30^\circ$ structure. (a) Total DOS together with local Sn DOS and (b) shown via contributions from different atoms within the supercell (for the labeling of the substrate atoms see Fig. 1). (c) Angular-momentum resolved plot of the Sn DOS. Note that in the latter plot the 5$p_x$ and 5$p_y$ curves lay on top of each other.](image)
FIG. 3: (Color online) Top: Surface band structure for the Sn/Si(111)-\(\sqrt{3}\times \sqrt{3}R30^\circ\) system, with fatbands for the Sn(5p) orbitals (blue/grey: \(p_x, p_y\); red/lightgrey: \(p_z\)). The bulk Si band structure is shown in the background. Middle: Derived Wannier band (cyan/lightgrey) for the 1-band model. Bottom: Derived Wannier-like bands (cyan/lightgrey) for the four-band model.

Note that hence the semicore \(d\) electrons of Ge and Sn are treated as valence in our computations and relativistic effects are included via the scalar-relativistic norm-conserving pseudopotentials. Since usually more appropriate for surface studies than LDA, we employed the GGA in the form of the PBE functional\(^{45}\) to the exchange-correlation term in the density functional.

The density of states (DOS) shown in Fig. 2 displays for both surface systems a prominent structure close to the Fermi level of width \(W \sim 0.4\) eV (slightly larger for Sn/Ge(111)). Two subpeaks are visible, one nearby the Fermi energy and the other at the upper energy edge in the unoccupied region. The major contributions to this low energy part stems from the orbitals of the Sn adatom hybridizing with the orbitals of neighbouring substrate atoms of the first and second layer (see Fig. 2b). It becomes further obvious from the angular-momentum resolved DOS in Fig. 2: that concerning the tin part the Sn(5p\(_x\)) orbital is dominantly responsible for the low-energy weight. Minor contribution to this is also added by the Sn(5s) orbital.

As seen from the band-structure plots in Fig. 3 and Fig. 4 the low-energy DOS is associated with a single surface band within the gap of the bulk system. The so-called fatband resolution for the Sn(5p) orbitals, i.e., the identification of the contribution of a given orbital character to a Kohn-Sham band at each \(k\) point via the width of a broadened coating ‘band’, underlines the dominating \(p_z\) weight on this half-filled surface band. A straightforward MLWF construction may be applied to the single surface bands for both systems. The real-space Wannier function (see Fig. 5) shows not only the \(p_z\)-like lobe but displays additionally the threefold bonding aspects to the substrate atoms. A spread of 14.2 Å\(^2\) for this MLWF was obtained in the case of Sn/Si(111). Albeit a rather similar low-energy state may be identified in the flat Sn/Ge(111) system, it has to be noted that conventional DFT has its problems in describing germanium systems. For the bulk material, there is a nearly vanishing band gap within DFT\(^{46}\) and additionally relativistic effects on the band structure are also important\(^{46,47}\). Still in our PBE-GGA study a single Wannier band may also be extracted in this case (see Fig. 4), however contrary to Sn/Si(111) that band touches occupied levels at the \(\Gamma\) point.

Due to the substrate geometry and the apparent Sn(5s) contribution at the Fermi level, an extended low-energy modeling based on \(sp^2\) hybridized orbitals seems even more adequate for these systems. Indeed as shown in Figs. 3, 4, the effective bands from the corresponding four-band MLWF construction fit well to the full Sn(5p) fatband dispersion (Sn(5s) has nearly exclusively weight on the band at the Fermi level). The chemically more appealing \(sp^2+p_z\) viewpoint yields three of the four orbitals having a dominant in-plane orientation with an 120° angle between them, while a fourth one is now directly reminiscent of the \(p_z\) orbital (see Fig. 6). This latter Wannier-like orbital has indeed major weight on the low-energy band close to \(\varepsilon_F\). Compared to the one-band case, the spread of the Wannier-like functions are
now given as 13.6 Å² for the \(sp^2\)-like orbitals and 20.8 Å² for the remaining \(p_z\)-like orbital.

The hopping integrals for both Wannier constructions are provided in Tab. I In the one-band model the nearest-neighbor hopping with an absolute value \(|t|\sim 45\) meV is negative in accordance with the hole-like dispersion from Fig. (6) around the \(\Gamma\) point. For the Sn/Ge(111) system the more distant hoppings are slightly larger, whereas \(|t|\) is somewhat smaller compared to the Sn/Si(111) case. The onsite energies in the four-band model yield a crystal-field splitting between the \(sp^2\)-like orbitals relative to the \(\sqrt{3}\times\sqrt{3}R30^\circ\) unit cell.

FIG. 5: (Color online) Wannier orbital corresponding to the one-band model. The numbers are references for the PBE-GGA DOS plot in Fig. 4

FIG. 6: (Color online) Left: Wannier-like orbitals of the four-band model. (a-c) \(sp^2\)-like orbitals and (d) \(p_z\)-like orbital. Right: Top view on the spatial orientations of the three \(sp^2\)-like orbitals relative to the \(\sqrt{3}\times\sqrt{3}R30^\circ\) unit cell.

The hopping integrals up to the fourth-nearest neighbours for the minimal one-band case (top) and the 4-band \((sp^2+p_z)\) model (bottom). For the latter case, the last entries of the given 4x4 matrix are associated with the \(p_z\)-like orbital. Note that the values correspond to the entries of the real-space Wannier(-like) Hamiltonian, i.e., a minus sign is included.

TABLE I: Hopping integrals up to the fourth-nearest neighbours for the minimal one-band case (top) and the 4-band \((sp^2+p_z)\) model (bottom). For the latter case, the last entries of the given 4x4 matrix are associated with the \(p_z\)-like orbital. Note that the values correspond to the entries of the real-space Wannier(-like) Hamiltonian, i.e., a minus sign is included.
B. Three-site Sn unit cell

It is believed from experimental studies that the structural ground state of the Sn/Ge(111) system corresponds to a two-down-one-up (2D-1U) distortion of the Sn submonolayer\textsuperscript{[2]}. To be able to account for this reconstruction (cf. Fig. 1), we thus performed electronic-structure calculations using a 3×3 supercell with a difference $\Delta=0.32$ Å between the up-down Sn positions\textsuperscript{[3]}, which we applied to our PBE-GGA structurally relaxed unit cell with the planar submonolayer. In these extended supercell calculations only one orbital per Sn adatom is included in the subsequent MLWF construction. This results in a Kohn-Sham-Wannier hamiltonian which corresponds to a single-orbital problem on a three-site triangular cluster. For comparison, we derived such enlarged hamiltonians also for the flat systems via corresponding larger unit-cell calculations for planar Sn/(Si,Ge)(111). The resulting Wannier-like bands are shown in Fig. 8. Whereas the bands again fit exactly in the Sn/Si(111) case, for the distorted Sn/Ge(111) surface a shift towards lower lying bands at the $\Gamma$-point is visible. The latter feature is again due to the band hybridizations already observed in the single-site Sn unit cell. It may be observed that the 2D-1U surface reconstruction leads to a small splitting of the low-energy bands, affecting mainly the occupied part of these states.

Besides the study of the influence of apparent surface reconstructions, the investigation of the magnetic behavior seems a most important endeavor. As already outlined in the introduction, the quasi-2D triangular Sn submonolayer might be a realistic case for the application of model ideas discussed in the context of 2D quantum magnetism. Therefore we investigated possible magnetic orderings within PBE-GGA, especially for the Sn/Si(111) system where intricate ordering patterns are heavily discussed\textsuperscript{[4,20]}. Although (finite-temperature) magnetism would be very interesting, one has to keep in mind that the constituents (Sn,Si,Ge) are no high-susceptible magnetic materials. The $sp$-bonding (involving large principal quantum numbers) with filled $d$ states renders magnetism from a chemical point of view questionable. Furthermore the rather large Sn-Sn nearest-neighbor distance of $\sim 6.7$ Å asks for a robust exchange path to facilitate the appearance of long-range order. Still the low-dimensional 2D-character might be sufficient to induce delicate magnetic behavior. Note also that the high DOS close to the Fermi level (cf. Fig. 2) might give rise to flat-band ferromagnetism\textsuperscript{[48,49]}.

The results of our investigation of different magnetic orderings on planar Sn/Si(111) 3×3 are summarized in Tab. II. The calculations show that especially the ferromagnetic (FM) order is rather intriguing. One may stabilize a FM solution for Sn/Si(111), resembling previous work by Profetta and Tosatti\textsuperscript{[20]}, however this state is energetically unfavorable compared to the nonmagnetic (NM) solution. The corresponding local energy minimum of this FM state appears to be rather flat, thus already small disturbances drive the DFT self-consistency cycle towards the NM state. This was confirmed within all three utilized band-structure codes, i.e., MBPP, CP-PAW and VASP, whereby the Sn-substrate distance does not influence this qualitative result. Note the rather small local $M_{\text{Sn}}$ moment compared to total FM moment of the supercell. Thus this metastable FM state is far from being originated from pure local Sn moments, but has significant nonlocal character. Since collinear AFM order is impossible due to frustration on the undistorted lattice, a collinear ferrimagnetic ordering (two up spins and one down spin on the minimal triangle) as well as the in-plane noncollinear 120°-AFM state were investigated. Indeed, both latter ordering patterns are found to be stable with respect to the nonmagnetic solution,

\begin{table}[h]
\centering
\begin{tabular}{l|c|c|c}
\hline
magnetic ordering & $E$ [meV] & $M$ [$\mu_B$] & $M_{\text{Sn}}$ [$\mu_B$] \\
\hline
ferromagnetic & 1.5 & 0.80 & 0.031 \\
collinear ferrimagnetic & -1.6 & 0.44 & 0.055 \\
120° antiferromagnetic & -3.6 & 0.00 & 0.058 \\
\hline
\end{tabular}
\caption{Comparison of the different magnetic orderings in the flat Sn submonolayer of the $\sqrt{3}\times\sqrt{3}R30°$ surface with the Si substrate. The energies $E$ and total moments $M$ are given with respect to the nonmagnetic structure in PBE-GGA and correspond to an enlarged 3×3 unit cell. This cell incorporates 66 atoms, namely 54 Si, 3 Sn and 9 H atoms (for saturation of the bottom bulk-like Si layer).}
\end{table}
with the lowest total energy for the 120°-AFM ordering. Though the local Sn magnetic moments \(M_{\text{Sn}}\) are only of the order of \(\sim 0.06 \mu_B\) within PBE-GGA, detailed convergence studies elucidated nonetheless their nonzero value. Note that these local \(M_{\text{Sn}}\) are supplemented by additional spin-polarisation on the remaining sites and the interstitial contribute. Hence again the picture of strictly localized magnetism is not appropriate on the weakly-correlated modeling level, but still local moments with small AFM exchange may exist in these Sn submonolayers. Those may possibly give rise to spin-liquid physics or eventual magnetic long-range order also in the correlated regime.

Similar magnetic PBE-GGA studies for a model planar Sn/Ge(111) 3×3 surface did not result in magnetic long-range order. The stronger hybridization of the Ge(4s4p) states with tin should generally weaken the magnetic tendencies compared to the silicon substrate. We did not investigate the more realistic 2D-1U reconstructed structure in this matter, which is left for further studies.

IV. INVESTIGATION OF ELECTRONIC CORRELATIONS

In order to take the principal effect of electronic correlations into account, we concentrate in the following on the realistic one-band models derived in section III A and their cluster extension from section III B. Furthermore we restrict the investigations to paramagnetic modelings, i.e. do not cover possible magnetic orderings. Since it became clear from the last section III B that the energy scale for magnetic long-range order is rather small, such an analysis shall be postponed to future studies.

A. LDA+DMFT(QMC) study

By combining our Wannier hamiltonians with the DMFT framework we are in the position to reveal the spectral function of the surface systems in the interacting regime. Due to the small bandwidth of \(W \sim 0.4\) eV, already small absolute values for the Hubbard \(U\) may introduce strong correlation effects. Although the low-energy bands of the discussed systems are mainly composed of Sn(5s5p) states, an onsite Coulomb interaction of this order of magnitude may very well be reasonable. Note that also the screening capabilities because of the semiconducting substrate are limited. The results of the paramagnetic single-site DMFT(QMC) calculations for the realistic one-band model are displayed in Fig. 9 for different choices of the Hubbard \(U\). Of course, due to the simplicity of the modeling the spectral function (finally obtained via the maximum-entropy method) follows the usual behavior with increasing \(U\), i.e., a low-energy band narrowing with the additional appearance of Hubbard-band features at higher energies takes place. The Mott transition is reached at a critical value of about \(U_c \sim 0.6\) eV for the Sn/Si(111) surface systems (with a somewhat larger value for planar Sn/Ge(111)). Since this transition shows a weak first-order character in the calculations (see also section IV B critical interactions \(U_{\text{si}}, U_{\text{ge}}\) govern this regime, respectively. However in the present study, due to the simplicity of the one-band modeling, we did not map out the respective hysteresis loops. The energy gap within the insulating Mott state is of the order of \(\sim 0.2\) eV for \(U \sim 0.7\) eV with Hubbard bands at around 0.3 eV above and below \(E_F\) for both Sn/(Si,Ge)(111) sys-
tems. The position of our Hubbard excitations is roughly in line with the region of increased spectral-weight transfer measured in photoemission experiments below 30K. Hence a rather small Hubbard $U$, slightly larger than the single bandwidth, is sufficient to drive the Sn-dominated surface band Mott insulating. This value is however not very surprising since from the involved quantum numbers of the respective states no large value of $U$ (i.e., as for transition-metal and/or $f$ systems) is expected.

In order to study the importance of intersite self-energy effects, especially for the distorted Sn/Ge(111) case, we also performed cluster DMFT (CDMFT) (for recent reviews see e.g. Refs. 50–52) computations within the cellular cluster framework for the basic Sn triangle in the submonolayer. The resulting spectral functions are shown in Fig. 10. Note that we employed a somewhat higher temperature within the QMC solver because of the larger numerical effort in the cluster framework. For the planar Sn/Si(111) case the main differences to the single-site results are given by a slightly smaller $U_c\sim0.55$ eV, smaller energy gap and Hubbard bands in some closer range to the low-energy region. We checked that those observations are not only due to the different temperatures of our computations. One may also observe a stronger asymmetry in the spectrum up and below the Fermi level, with some stronger reduction of low-energy spectral weight below $E_F$. For the site-resolved spectral function of the Sn/Ge(111) $3\times3$ system in the distorted 2D-1U structure it is first important to remark that the two downwards shifted Sn atoms are inequivalent by symmetry due to different hybridization with the ‘up’ atom even assuming the same height for the ‘down’ 2D atom (see section VIII B). The latter are moreover less occupied than the upwards shifted Sn atom. With increasing $U$, this filling imbalance because of the distortion-induced crystal-field shifts becomes smaller and is compensated at the Mott transition (see Fig. 10). However a slightly larger critical $U_c$ compared to the planar cluster for Sn/Ge(111) is necessary to reach this transition (more or less equivalent to the critical $U$ within the planar single-site DMFT). The above noted spectral asymmetry in the occupied and unoccupied part is even larger in the distorted case.

**B. LDA+RISB study**

In addition to DMFT(QMC) computations we have performed slave-boson calculations within the RISB framework to further verify our results and to achieve a better resolution of the qualitative differences in values for the critical $U$ in the various cases. Furthermore we also want to elucidate the intersite spin correlations in the cellular cluster modeling. The RISB results for the quasiparticle weight $Z$ are shown in Fig. 11. In the one-band case, the RISB method yields for both flat systems a first-order transition from the paramagnetic metal to the paramagnetic insulator. The corresponding critical $U$ values are given by $U_c\sim0.75$ eV (0.78 eV) for for Sn/(Si,Ge)(111) $\sqrt{3}\times\sqrt{3}R30^\circ$, hence show the same qualitative trend as DMFT(QMC). A somewhat larger absolute value within RISB is understandable from the saddle-point approximation which is identical to the neglection of quantum fluctuations. The cellular-cluster investigations again verify the reduced critical Hubbard $U$ values (similar to the ones from DMFT(QMC)) due to an increase in the correlation strength via the inclusion of the nearest-neighbor self energies. Also the enhanced $U_c$ for the distorted 2D-1U structure of Sn/Ge(111) is a solid result. Note that the first-order character of the transition is strengthened in the cluster modeling. To allow for a commensurable Mott transition, the correlations have to drive additional charge transfers between the Sn site in the 2D-1U structure. The therefore enhanced charge fluctuations in the latter case may thus account for the larger $U_c$. In Fig. 12 we show the continuous development of the individual site fillings with increasing $U$ for the 2D-1U structure. The corresponding labeling of the different Sn atoms is given in the inset of Fig. 12. As it is clearly seen, the originally enhanced occupation of the low-energy orbital for the upwards shifted Sn atom on the cluster becomes reduced with increasing $U$, while the downwards shifted ones gain electron filling in their respective orbitals. This is in line with the results obtained from the more elaborate QMC solver to DMFT (cf. Fig. 10).

In order to provide some insight into the magnetic behavior with taking into account electronic correlations, Fig. 13 displays the local spin correlations $\langle S_iS_j \rangle$ between the Sn atoms from the low-energy modeling. It is seen that the spin correlations are always negative, i.e., of AFM character, as expected by considering the superexchange induced via $U$. Naturally, the degree of magnetic behavior is therewith increased compared to the noninteracting case. The comparison of the two different substrates with the planar geometry of the Sn submonolayer exhibits the stronger magnetic correlations within the
Sn/Si(111) system. Thus the qualitative result obtained from the weakly-correlated PBE-GGA modeling extends to the strongly correlated treatment. In the 2D-1U structure of Sn/Ge(111), the values of \( \langle S_i S_j \rangle \) for the now different Sn-Sn pairs show interesting behavior. Somewhat counterintuitive, the spin correlations between the two up-down pairs, here denoted Sn(1)-Sn(3) and Sn(2)-Sn(3), scale rather differently with increasing \( U \). While for the Sn(2)-Sn(3) pair \( \langle S_i S_j \rangle \) is most negative, for the Sn(1)-Sn(3) pair the spin correlations become nonmonotonic close to \( U_c \), anticipating tendencies to eventual FM coupling. The remaining Sn(1)-Sn(2) pair of the two down atoms scales inbetween these functions. This result can be explained by the fact that the absolute value of the hopping amplitude \( t \) is maximum between the Sn(2)-Sn(3) pair and is accordingly weakened between Sn(1)-Sn(3). Because of the upward shift of the Sn(3) atom, the lobe from its effective Wannier orbital pointing towards Sn(2) achieves a wider range, leading to stronger overlap with the Wannier orbital of Sn(2).

V. SUMMARY

We have presented a detailed modeling of the Sn/(Si,Ge)(111) surface systems using state-of-the-art band-structure methods combined with many-body techniques. In addition to previous DFT investigations we extracted realistic one- and four-band Wannier-like hamiltonians that are capable of describing the electronic structure close to the Fermi level. The physics of the minimal one-band model is of course restricted, however due to the prominent Sn-dominated half-filled surface band at \( \varepsilon_F \), especially for Sn/Si(111) \( \sqrt{3} \times \sqrt{3}R30^{\circ} \) this is believed to be an adequate modeling viewpoint. The atomic description of the Sn/Ge(111) system still raises some questions concerning the apparent limitations of simplified exchange-correlation functionals in this case. Nonetheless on the present level of investigation and comparison, the PBE-GGA perspective appears sufficient to reveal the essential differences between both surface systems. The hybridization of the Sn submonolayer with the substrate is stronger in the case of Ge, leading there to a more intriguing entanglement of that layer with the supporting atoms below. Consequently, structural reconstructions are more likely and indeed take place as verified in experimental studies.

The magnetic behavior in these systems renders them most fascinating from a fundamental physics point of view in terms of possible low-dimensional quantum magnetism. The (non)collinear spin-polarized DFT calculations revealed that there is indeed the chance for intricate magnetic orderings. In this respect we found the 120°-AFM structure to be the magnetic ground state in the weakly-correlated description. Further theoretical studies, including the effect of true many-body correlations on the magnetism are important and should be motivated by the present work. Although the resulting moments are rather small, maybe advanced experimental techniques are capable of exploring these small energy scales.

Using DMFT(QMC) and RISB techniques, a moderate value of the order of \( U \sim 0.5-0.6 \) eV was found to govern the systems from a one-band Hubbard-like model in a strongly-correlated limit. Because of the small low-energy bandwidth it is reasonable to expect electronic correlations to be important, however sole local Coulomb interactions are surely limited in the description of these systems based on carbon-group elements. Yet already on this rather simple level a delicate interplay between the structural and electronic degrees of freedom, anticipated in other model(-like) framework, was verified on the grounds of an LDA+DMFT approach. Future studies now have to concentrate on including the substrate degrees of freedom explicitly in the modeling of...
the interacting electronic structure, perhaps even allowing for the dynamical structural reconstructions needed for Sn/Ge(111).

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