Phonon-induced electronic relaxation in a strongly correlated system: the Sn/Si(111) $(\sqrt{3} \times \sqrt{3})$ adlayer revisited

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The ordered adsorbate layer Sn/Si(111) $(\sqrt{3} \times \sqrt{3})$ with coverage of one third of a monolayer is considered as a realization of strong electronic correlation in surface physics. Our theoretical analysis shows that electron-hole pair excitations in this system can be long-lived, up to several hundred nanoseconds, since the decay into surface phonons is found to be a highly non-linear process. We combine first-principles calculations with help of a hybrid functional (HSE06) with modeling by a Mott-Hubbard Hamiltonian coupled to phononic degrees of freedom. The calculations show that the Sn/Si(111) $(\sqrt{3} \times \sqrt{3})$ surface is insulating and the two Sn-derived bands inside the substrate band gap can be described as the lower and upper Hubbard band in a Mott-Hubbard model with $U = 0.75$ eV. Furthermore, phonon spectra are calculated with particular emphasis on the Sn-related surface phonon modes. The calculations demonstrate that the adequate treatment of electronic correlations leads to a stiffening of the wagging mode of neighboring Sn atoms; thus, we predict that the onset of electronic correlations at low temperature should be observable in the phonon spectrum, too. The deformation potential for electron-phonon coupling is calculated for selected vibrational modes and the decay rate of an electron-hole excitation into multiple phonons is estimated, substantiating the very long lifetime of these excitations.

I. INTRODUCTION

Quantum systems defined on a lattice have received attention because they allow one to investigate quantum correlations in a well-controlled way and hence are of recent interest in the context of Quantum Simulators [1-5]. In condensed matter, ordered layers of atoms, several lattice constants apart, on an insulating surface come close to realising a lattice system with well-defined electronic correlation. For instance, atoms of group-IV form ordered structures on the Si(111) surface at sub-monolayer coverage. The electronic bands inside the principal band gap of silicon formed by dangling bond orbitals of the adatoms remain narrow if neighboring atoms in the structure are placed several Angstroms apart. This narrowness of the band is a prerequisite for electronic correlation effects to become noticeable. From electron counting arguments, one could expect a surface band on Si(111) to be half-filled in case of group-IV adatoms (Si, Ge or Sn). There are two complimentary (as we will discuss below) ways of stabilizing the system that both result in a gapped electronic structure: the adatoms may undergo a Jahn-Teller-like distortion leading to a superstructure with inequivalent dangling bond orbitals, or Mott-Hubbard physics may open a gap between the filled and the unoccupied part of the electronic structure. Recently, not only the ground state of strongly correlated systems, but also their dynamics on ultra-short time scales has come into focus of experimental investigations [4,5]. Therefore, understanding the elementary excitations and their interplay, which determines the lifetime of excited states, has become an issue of current interest.

For the system Sn/Si(111) $(\sqrt{3} \times \sqrt{3})$, the prevailing experimental and theoretical view asserts that Mott-Hubbard physics is responsible for the formation of a gap in the electronic spectrum [6-8]. This is in contrast to the related system Sn/Ge(111) $(\sqrt{3} \times \sqrt{3})$ where both experiments and first-principles calculations point to a Jahn-Teller like mechanism that stabilizes the system in a $(3 \times 3)$ superstructure with Sn adatoms at different adsorption heights. While the Jahn-Teller instability makes itself noticeable in the softening of the corresponding phonon mode, the effect of strong electronic correlations on the phonon spectrum has received little attention so far. We will show that electronic correlations in Sn/Si(111) $(\sqrt{3} \times \sqrt{3})$ favor a planar geometry and lead to a stiffening of the associated phonon mode.

We briefly summarize the present understanding of the physics at the Sn/Si(111) surface that has been gained from experimental studies: Experiments using scanning tunneling spectroscopy (STS) indicate that the Sn/Si(111) $(\sqrt{3} \times \sqrt{3})$ system undergoes a metal-to-insulator transition below 30 K. Below this temperature, the pseudo-gap near the Fermi energy develops into a sharp gap [9] whose width is reported to be 35 meV according to recent measurements [8]. Below and above the Fermi energy $E_F$, experiments using angle-resolved photoemission (ARPES) [9] or inverse photoemission (KIRPES) [10] show pronounced quasiparticle peaks. These peaks have an estimated separation on the energy scale of roughly 200 meV (see also the discussion in Ref. [7]). According to recent studies, the most likely candidate for the spin ordering on the Sn/Si(111) $(\sqrt{3} \times \sqrt{3})$ surface is a row-wise antiferromagnetic structure [7,11] in a $(2\sqrt{3} \times \sqrt{3})$ supercell.

In this work, we performed DFT calculations using the semilocal PBE functional to obtain the surface phonon spectrum. These are complemented by hybrid-functional calculations of the electronic band structure and the electron-phonon coupling for selected phonon modes with out-of-phase motions of the Sn atoms. We show that the data extracted from these DFT calculations can be used as input to a model Hamiltonian that allows us to estimate the lifetime of excitons due to phonon emission in a non-linear process. While the electron-phonon coupling is found to be sizable, the decay of the exciton is exponentially suppressed due to the very large number of phonons involved in this process.
II. METHODS

A detailed understanding of the electronic structure of correlated systems requires special methods, for instance the Dynamical Cluster Approximation applied in Ref. [2]. However, these methods, as well as the calculation of phonon spectra, rely on input from density functional theory (DFT). If applied with care, DFT calculations can already reveal salient features and allow us to address the various energy scales in the problem. While local or semi-local density functionals find the Sn/Si(111) (\(\sqrt{3} \times \sqrt{3}\)) to be metallic, the HSE hybrid functional [12, 13] correctly reproduces the insulating ground state [11]. Technically speaking, electronic correlations are treated in the HSE functional as part of the (screened) electronic exchange. Therefore, despite their failure to yield the proper electronic excitation spectrum, HSE calculations can still be used to estimate the basic parameters (on-site Coulomb interaction, electronic exchange). Therefore, despite their failure to yield the proper electronic excitation spectrum, HSE calculations can still be used to estimate the basic parameters (on-site Coulomb interaction, electronic exchange) that are required as input to model Hamiltonians (cf. Ref. [13] employed to describe the electronic relaxation.

In our numerical modeling, the Sn/Si(111) surface with a coverage of \(1/3\) is described by a repeated slab geometry. The supercell was built with 10 Å of vacuum in between the slabs. The Si lattice constant \(a_0 = 5.445\) (5.468 Å) for the HSE (PBE) calculation was used. In order to sample the Brillouin zone of the \(\sqrt{3} \times \sqrt{3}\) and \(2\sqrt{3} \times \sqrt{3}\) unit cells, we used a \(8 \times 8 \times 1\) and \(4 \times 8 \times 1\) Monkhorst-Pack [15] k-point mesh, respectively. The Si dangling bonds on the rear side of the slab were saturated by hydrogen atoms while one Sn atom in \(\sqrt{3} \times \sqrt{3}\) (two tin atoms in \(2\sqrt{3} \times \sqrt{3}\)) were placed on the front surface in the \(T_4\) site. The position of Sn atoms, as well as of the Si atoms in the first eight layers, were relaxed, while the two layers of Si atoms at the rear side are held fixed together with the hydrogen atoms. The residual force components were less than 0.01 eV/Å.

Calculation of phonons and electron-phonon coupling of this system are interesting for us, so the PHONOPY [16] package in conjunction with the VASP [17, 18] code was used for calculating the phonon band dispersion. Finite atomic displacements were used together with a large supercell obtained by doubling the size of the initial supercell in both lateral directions. Atomic forces were calculated for 48 displaced configurations in case of the \(\sqrt{3} \times \sqrt{3}\) structure.

For the electronic band structure, density functional theory calculations were performed by using the FHI-AIMS [19, 20] code, which is an accurate all-electron full-potential electronic structure package based on numeric atom-centered orbitals, with so-called "tight" computational settings. In this part of the work, the screened hybrid functional HSE06 with the mixing factor \(\alpha = 0.25\) and screening parameter \(\omega = 0.11\) bohr\(^{-1}\) was used for the exchange-correlation energy.

III. RESULTS

A. Phonon band structure from GGA-PBE calculations

We start by confirming previous calculations that had demonstrated that a non-spinpolarized PBE calculation of the Sn/Si(111) (\(\sqrt{3} \times \sqrt{3}\)) leads to a metallic surface band. Despite the lack of proper electronic correlations in this approximative method, it is instructive to calculate the phonon spectrum to get a first idea of the surface vibrational properties. Phonon spectra \(\omega_i(q)\) obtained with the PBE functional in the non-magnetic (NM) ground state with the finite-displacement method implemented in PHONOPY are presented in Fig 1. The phonon modes related to Sn appear in two groups: There is one mode in which both the Sn atom and the top-most layer of Si atoms move in phase (\(\omega(q = 0) = 4.00\) THz). Lower-lying modes involve out-of-phase motions of the Sn atom and the neighboring Si atoms. These comprise motions of the Sn atom within the surface plane, leading to two bands with small dispersion (\(\omega = 1.75\) THz at K in the NM calculation), and a more dispersive band corresponding to a vertical motion of the Sn atom relative to the Si atoms (\(\omega = 1.30\) THz at K in the NM calculation). The latter mode shows a slight softening at the edge of the Brillouin zone at the point K. Here, Sn atoms in neighboring unit cells are moving with opposite phase. These Sn atoms are connected by a Si–Si bond lying in the surface plane. The whole group of atoms, Sn–Si–Sn–Sn, performs a ‘wagging’ motion. In agreement with previous studies [21], we interpret the mode softening as a first indication of a possible instability of the (metallic) PBE band structure with respect to Jahn-Teller distortions. However, this finding is not confirmed by the hybrid functional calculations (see below).

In order to investigate to which extent the AFM spin ordering can already account for the correlated electronic features, we performed PBE calculations with the \((2\sqrt{3} \times \sqrt{3})\) unit cell where the magnetic moments of the Sn atoms were frozen in the AFM state. In these calculations, the occupied and the...
unoccupied surface states still overlap in energy, yielding a metallic surface, as seen in Fig. 2. However, the band width of 275 meV of the unoccupied band along $\bar{\Gamma} \bar{M}$ is reduced relative to the non-spinpolarized PBE calculation.

Figure 2. The electronic band structure for AFM spin ordering obtained with the PBE functional including spin-orbit coupling. Calculations are performed in a $(2\sqrt{3} \times \sqrt{3})$ unit cell with two Sn atoms. The red and blue bands are related to different superpositions of spin wave functions.

The calculations of phonon frequencies at $q = 0$ with the PBE functional were repeated in the $(2\sqrt{3} \times \sqrt{3})$ unit cell. Due to the smaller Brillouin zone compared to the $(\sqrt{3} \times \sqrt{3})$ unit cell, back-folding of the phonon modes onto the $\Gamma$ point is observed. Interestingly, the ‘wagging’ mode of the Sn atoms has now moved to higher frequency $\omega(q = 0) = 1.62$ THz compared to the NM calculation ($\omega = 1.30$ THz). Thus, taking into account the electronic correlation at the Sn atoms results in a stiffening of this mode. Freezing the spin density at the Sn atoms prevents the Jahn-Teller effect previously predicted for the metallic, non-magnetic surface. In addition, there is a slightly higher mode at $\omega(q = 0) = 1.77$ THz involving opposite motion of the Sn atoms. By analyzing the mode eigenvector, it can be characterized by a torsion of the Sn–Si–Si–Sn groups mainly within the plane of the surface. Its frequency is almost unchanged (compared to $\omega(q = 0) = 1.75$ THz in the NM calculation); i.e. it is insensitive to the electronic correlations at the Sn atoms.

B. Hybrid functional calculations of electron-phonon coupling

For the calculations with the hybrid functional HSE, a larger $(2\sqrt{3} \times \sqrt{3})$ unit cell with two Sn atoms was used. The ground state is found to be a spin-polarized state in which the magnetic moments at the two Sn atoms are pointing in opposite direction, i.e. they show row-wise antiferromagnetic (AFM) ordering.

The electronic structure displays an indirect band gap of 540 meV including spin-orbit coupling (SOC) and 430 meV if SOC is neglected. This value is in line with similar theoretical work [11] reporting a gap of 328 meV, but is much larger than the experimental value of $\sim 40$ meV obtained from STS [9]. Instead, it is closer to the value of $\sim 200$ meV obtained from ARPES [7]. The width of the occupied (unoccupied) band along $\bar{\Gamma}M$ is $w = 140$ meV ($w = 200$ meV); i.e. smaller than in the PBE ground state. The ferromagnetic solution is $E_{\text{FM}} - E_{\text{AFM}} = 25$ meV per Sn atom higher than the AFM ground state. Calculations including spin-orbit coupling show a splitting of the occupied surface band being largest at the K point ($E_{\text{SOC}} = 22$ meV).

For the ‘wagging’ mode of the Sn atoms, we performed total-energy calculations with finite displacements of both the Sn and Si atoms along the mode eigenvectors. The results
for displacements of varying magnitude are shown in Fig. 5. While the HSE data points fall onto a parabola, as expected for a harmonic vibration, the PBE curve shows strongly anharmonic behavior. Only for small displacements, the stiffening of the mode is observed, while the restoring forces are considerably smaller at larger displacements. This means that the electronic correlations can be destroyed by large displacements in the PBE calculations, while this is not possible in the HSE calculations due to the opening of a band gap. Weak restoring forces after break-down of the electronic correlations cause the Sn atoms to spend relatively long time near the turning points of their oscillatory motion. This could explain why in photoelectron spectra [22] of the surface recorded at a temperature of 70K two distinct peaks associated with two Sn atoms at different adsorption height have been observed. By fitting the HSE data points, the phonon energy $\hbar \omega_{\text{HSE}} = 11$ meV ($\omega_{\text{HSE}} = 2.65 \text{THz}$) is obtained.

Figure 5. Energy as function of displacement along the wagging mode at $q = 0$ for $(2\sqrt{3} \times \sqrt{3})$ with the AFM ordering of the electron spins taken into account. The displacement is given in units of the oscillator length $(\hbar/m_{\text{Sn}}\omega)^{1/2}$. 

Hence, the stiffening of the 'wagging' mode observed already in the AFM spin-polarized PBE calculations is even more pronounced in the HSE calculations. Due to the gap in the HSE band structure, a transfer of spin density between the two Sn atoms is no longer possible. Thus, in the correlated electronic state, the geometrical structure in the AFM state is no longer prone to Jahn-Teller instability. In conclusion, stabilization by spin-ordering and displacive rearrangements of the atoms must be considered as competing stabilization mechanisms excluding each other.

The electron-phonon coupling is investigated using the frozen-phonon approach. While the mode associated to the Jahn-Teller instability became stiffer in the correlated system, we still expect a sizable contribution to electron-phonon coupling from this mode. Therefore, for the phonon modes that involve substantial displacements of the Sn atoms normal to the surface plane in opposite directions (Fig. 3 (a) and (c)), we carry out HSE calculations of the electronic structure for various displaced atomic geometries. The corresponding eigenvector of the dynamical matrix, scaled with the dimensionless atomic mass factor $\sqrt{m_{\text{Sn}}}$ ($j$ stands for Sn or Si, $m_{\text{Sn}} = 109$, $m_{\text{Sn}} = 28$), is used to generate the atomic displacements. Fig. III B a) and b) show the electronic band structure after the displacements have been applied. It is seen that each of the two surface bands splits up into two subbands. The upper (blue) subband has its wavefunction amplitude mostly at the Sn atom that is geometrically closer to the surface plane ('down' atom), while the lower (red) band has its wavefunction amplitude mostly at the Sn atom higher above the surface ('up' atom). The origin of this effect can be traced back to changes in orbital hybridization caused by the displacements: The surface state has a substantial contribution from the Sn $p_z$ orbital pointing perpendicular to the surface plane. The Sn 'up' atom is in a pyramidal coordination and therefore comes close to $p^3$ hybridization; hence the dangling orbital has an increased $s$ orbital character and moves down in energy. The Sn 'down' atom moves towards the surface plane and comes closer to $sp^2$ hybridization; hence the $p_z$ character of the dangling orbital becomes enhanced, and it moves upward in energy. Displacements along the 'wagging' mode involve larger components perpendicular to the surface, and thus have a much stronger effect on the band positions, compared to the 'torsion' mode.

Using deformation potential theory [23], one can determine quantitatively the electron-phonon coupling parameter $\lambda$ from the energetic shifts (relative to the ground state) of the bands caused by the displacements. Specifically, we calculate

$$\lambda = \left( \frac{\hbar}{2m_{\text{Sn}}\omega_{\text{HSE}}} \right)^{1/2} \frac{\Delta \varepsilon}{\Delta x} = \frac{\Delta \varepsilon}{\sqrt{2}}$$

where $\Delta \varepsilon$ is the energy shift of the highest occupied band in the HSE calculation and $\Delta x$ is a displacement of one oscilla-
tor length. Using the band energies at the the K point, we obtain from Fig. IIIA the values $\lambda = 49$ meV and $\lambda = 13$ meV for the ‘wagging’ and the ‘torsion’ mode, respectively. Considerable mode stiffening, in particular of the wagging mode, is observed when AFM spin correlations for a) the wagging mode and b) the torsional mode are taken from Fig. IIIA the values $\lambda = 49$ meV and $\lambda = 13$ meV respectively. By comparing to the band positions to the undistorted structure, Fig. 3, one concludes that the energy difference between the FM and AFM state is given by

$$E_{\text{AFM}} - E_{\text{FM}} = 6J - (-2J) = 8J.$$ 

The presence of spin-orbit interaction would require the generalization to an anisotropic Heisenberg model in which the excitation of spin waves requires a minimum energy. We speculate that this gap in the spin wave spectrum may be responsible for the experimentally observed opening of a tiny gap at low temperatures in the STS experiments [8,9], but do not attempt to estimate it quantitatively.

The charged excitations are given by AFM spin waves. At half filling, every site is occupied by one electron, and the MH Hamiltonian can be approximately transformed onto a Heisenberg model

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j,$$

with the exchange coupling constant given by $J = -4t^2/U$. By counting the number of antiparallel and parallel spin pairs in the row-wise antiferromagnetic and the ferromagnetic state, respectively, one concludes that the energy difference between the FM and AFM state is given by $E_{\text{AFM}} - E_{\text{FM}} = 6J - (-2J) = 8J$. The presence of spin-orbit interaction would require the generalization to an anisotropic Heisenberg model in which the excitation of spin waves requires a minimum energy. We speculate that this gap in the spin wave spectrum may be responsible for the experimentally observed opening of a tiny gap at low temperatures in the STS experiments [8,9], but do not attempt to estimate it quantitatively.

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the two surface bands in the HSE calculation. Taking the direct gap at the K point in the Brillouin zone in Fig. 2, this yields $U = 0.75 \text{eV}$. On the other hand, the total energy difference between the FM and the AFM can be used to obtain an estimate for $J = -3.1 \text{meV}$, and hence, within the large-$U$ limit of the Hubbard model, also an estimate for $U$. Combining the data from the band width $t = 25 \text{meV}$ and from $J = (E_{\text{AFM}} - E_{\text{FM}}) / 8$, we obtain $U = -4t^2 / J = 0.81 \text{eV}$. Hence we conclude that $U \approx 0.75 \text{eV}$, as obtained from the HSE band structure, is indeed a reasonable estimate.

If we disregard the Coulomb interaction between electron and hole, assuming that it is screened, the excitonic energy scale is the same as for charged excitations, i.e., of the order of a few tenth of eV. In principle, these excitations can decay by dissipating their energy to spin waves or to phonons. The relative importance of both processes depends on the spin structure of the excited many-particle states, as discussed in Ref. [24]. Since the excitation energy is sizable, several magnons or phonons need to be generated simultaneously in a highly non-linear process.

In the following, we assume that decay into phonons is the dominating process. The energy scale of the magnons, set by $J = -3.1 \text{meV}$, is even smaller than the vibrational energy scale, and thus an even higher number of magnons as compared to phonons would be required. Thus, the electron-phonon coupling, expressed by the deformation potential $\lambda$, is the decisive parameter. Lenarčič and co-workers [14] have presented a MH model coupled to a phononic Hamiltonian that allows them to estimate the lifetime of the exciton due to decay into phonons by a Zener-type expression. In their approach, the basic time scale for the decay is set by the ratio of the phonon frequency and the band width, $\tau_0 = \hbar^2 \omega_{\text{HSE}} / t^2$. However, the actual decay rate $\tau^{-1}$ is exponentially suppressed with respect to $\tau_0^{-1}$. The dimensionless parameters entering this suppression factor are the order of the process, given by $n = U / (\hbar \omega_{\text{HSE}})$, and the scaled electron-phonon coupling parameter $\xi = \lambda^2 / (\hbar \omega_{\text{HSE}})^2$. According to Lenarčič and co-workers [14], the expression for the lifetime has the form

$$\tau = \tau_0 \sqrt{n} \exp \left( n \left( \ln \frac{n}{2\xi} - 1 \right) \right). \quad (1)$$

From our calculations, we can give a rough estimate for the phonon-related exciton lifetime using the above expression. For the prefactor, $\tau_0 \sim 12 \text{fs}$ is obtained. Typical values for the parameters in the suppression factor are $n = U / (\hbar \omega_{\text{HSE}}) = 68$ and $\xi = 10$. In estimating $\xi$, we used the average of the electron-phonon coupling in the ‘wagging’ and ‘torsion’ modes. Inserting these values into eq. (1), we find that the suppression factor is very significant, of the order of $3.3 \times 10^7$. Thus, the basic time scale of $\tau_0 = 12 \text{fs}$ is extended to $\tau = 400 \text{ns}$. In other words, if the decay into phonons is the only decay channel of the exciton in this system, our calculations predict a very long lifetime which should be easily accessible in experiments. This finding is likely to be generic for systems with strongly correlated surface states: Since the energy scales of surface phonons, typically a few tens of meV, and of the on-site Coulomb repulsion $U$, typically of the order of eV, are very different, decay of the inter-band excitation into phonons is a highly non-linear process. This results in a huge suppression of the phononic decay channel, and a very long lifetime.

### IV. CONCLUSION

Using DFT calculations with the HSE06 hybrid functional, the Sn/Si(111) surface with 1/3 ML coverage was found to be an insulating surface with bands inside the substrate band gap that can be interpreted as upper and lower Mott-Hubbard bands. The phonon spectrum and deformation potentials for electron-phonon coupling in the antiferromagnetic ground state were calculated. Stiffening of the wagging mode of neighboring Sn atoms is predicted from the calculations if electronic correlations are taken into account. Therefore, we conclude that the Jahn-Teller effect, which would be indicated by a mode softening, and the antiferromagnetic ordering of the spin system are two complementary ways of stabilizing group-IV adsorbates on Si(111). The Mott-Hubbard gap is found to be much larger than the typical phononic quanta; therefore the relaxation of electron-hole pairs into the ground state is possible only by a multi-phonon process. A very long lifetime of the excitations, in the order of hundreds of nanoseconds, is predicted.

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