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First principles calculations of charge and spin density waves of $\sqrt{3}$-adsorbates on semiconductors

S. Scandolo [a,b,*,1], F. Ancilotto [b,c,1], G.L. Chiarotti [b,1], G. Santoro [b,1], S. Serra [b,1], E. Tosatti [a,b,1]

[a] *International Centre for Theoretical Physics (ICTP), I-34014 Trieste, Italy*
[b] *International School for Advanced Studies (SISSA), Via Beirut 4, I-34014 Trieste, Italy*
[c] *Dip. di Fisica, Universitá di Padova, Via Marzolo 8, Padova, Italy*

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Abstract

We present ab-initio electronic structure results on the surface of $\sqrt{3}\times\sqrt{3}$ adsorbates. In particular, we address the issue of metal–insulator instabilities, charge-density waves (CDWs) or spin-density waves (SDWs), driven by partly filled surface states and their 2D Fermi surface, and/or by the onset of magnetic instabilities. The focus is both on the newly discovered commensurate CDW transitions in the Pb/Ge(111) and Sn/Ge(111) structures, and on the puzzling semiconducting behavior of the Pb/Ge(111), K/Si(111):B and SiC(0001) surfaces. In all cases, the main factor driving the instability appears to be an extremely narrow surface state band. So far, we have carried out preliminary calculations for the Si/Si(111) surface, chosen as our model system, within the gradient corrected local density (LDA+GC) and local spin density (LSD+GC) approximations, with the aim of understanding the possible interplay between 2D Fermi surface and electron correlations in the surface+adsorbate system. Our spin-unrestricted results show that the $\sqrt{3}\times\sqrt{3}$ paramagnetic surface is unstable towards a commensurate density wave with periodicity 3×3 and magnetization 1/3.

Keywords: Adatoms; Density functional calculations; Low index single crystal surfaces; Magnetic phenomena (cyclotron resonance, phase transitions, etc.); Semiconducting surfaces; Silicon; Surface relaxation and reconstruction

1. Introduction

Semiconductor surfaces are generally believed to belong to the realm of solid state problems where electron correlations are not too important. Very recently, however, a new phase transition has been observed on Ge(111), when this surface is covered with 1/3 of a monolayer of Pb adatoms [1]. The $\sqrt{3}\times\sqrt{3}$ room-temperature α-phase of Pb/Ge(111) has been observed to transform reversibly into a new phase, with 3×3 periodicity, below 250 K, with noticeable changes in the electronic structure [2,3]. The same phenomenon has been reported for Ge(111) covered with Sn ([4,5]; G. Le Lay et al., pers. commun.), at a slightly lower (210 K) transition temperature. Reconstructions are ubiquitous in semiconductor surfaces, but the finding of a continuous, reversible phase transition as a function of temperature, plus the close agreement of the low-temperature surface periodicity with a calculated Fermi surface "nesting" vector of Pb/Ge(111), is new, and it is

* Corresponding author. Fax: (+39) 40 3787528.
[1] Istituto Nazionale di Fisica delle Materia (INFM), Italy.

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suggested that the transition might be a clear example of a surface-state driven charge-density wave [6,7]. However, there are clear problems with this picture in its simplest form. First, we note that the true nesting cannot be very good, given one electron/adatom. Second, the 3×3 state still contains an odd electron number/cell and should be very metallic, whereas strikingly, EELS evidence suggests, at least for Pb/Ge(111), a small but finite gap or pseudogap [1]. Much larger and clearer insulating gaps have moreover been found recently on other isoelectronic $\sqrt{3} \times \sqrt{3}$ surfaces, such as K/Si(111):B [8], and Si-terminated SiC(0001) [9,10], where electron counting arguments would similarly predict band metallicity. No structural data are available, however, for K/Si(111):B and SiC(0001). In all the above systems, the surface band arising from the half-filled adatom dangling bond orbital [pointing outward from the (111) surface] displays a weak dispersion over the surface Brillouin Zone (SBZ), with typical calculated bandwidths ranging between 0.35 in SiC(0001) and 0.5–0.6 eV in Pb- or Sn- covered Ge(111). The adatoms in fact sit very widely apart, the only source of electron hopping between them requiring higher order hops through the back bonds and the substrate. If such a small bandwith is compared with a relatively large on-site Coulomb repulsion for two electrons when occupying the same dangling bond orbital, or even two neighboring ones, then it could be supposed that strong correlations might play a role in determining the true electronic surface ground state, along with the detailed equilibrium atomic geometry [11]. In particular, K/Si(111):B and SiC(0001) would correspond in this picture to Mott–Hubbard insulators. Strongly correlated electron systems are, strictly speaking, not tractable with effectively one electron methods, such as Hartree–Fock, or local density (LDA) approximations. This is all the more lamentable since these approximations are very good at describing the basic bulk chemistry of these semiconductors, and we have nothing of comparable simplicity and accuracy to replace them, once their validity is impaired by correlations, as it is in Mott insulators. There is, however, at least one well-known trick that one can resort to, which may be successful, provided that one does not forget its deep limitations. The idea is to make use of the fact that Mott insulators are dominated by magnetic correlations. If we extend the one-electron methods to include the possibility of developing static magnetic order parameters, we can hope to recapture, if not the full strongly correlated state, at least a mimic of its local aspects, which may be energetically close enough to the truth [12]. Hence, a further important step to move before abandoning these systems is to switch from restricted Hartree–Fock to unrestricted Hartree–Fock, or from local density to local spin density (LSDA) approximations. Here, long-range magnetic order is permitted, and can both lower the energy and yield insulating states in a half-filled band. If that should happen, it will of course not necessarily follow that the true system must have long-range magnetic order, since in the Mott phenomenon, the insulator precedes the magnet, and not vice versa. All the same, such a calculation is none the less quantitative (i.e. variational), and it may in fact teach us a great deal. In this work, we present a preliminary study of the basic physics of these systems, conducted by comparing LDA with LSDA calculations of a model $\sqrt{3} \times \sqrt{3}$ surface. We focus our interest on Si/Si(111) $\sqrt{3} \times \sqrt{3}$, chosen as a prototype case, for two reasons:

(1) Among the structures displaying "unconventional" behavior, the K/Si(111):B surface (which should closely resemble Si/Si(111)) is the one in which the correlations are larger, surpassed only by SiC(0001).
(2) The availability of accurate theoretical and experimental structural data on the atomic configuration of Si/Si(111) allows us to focus on the electronic issues rather than on the more complex interplay between electronic and atomic degrees of freedom, that will instead form the subject of future investigations.

We performed extensive electronic structure calculations for this surface, both in the local density approximation (LDA) and in the local spin density approximation (LSDA), and we supplemented both types of calculations with gradient corrections

(GC) to the energy functional. We employed a plane-wave basis set with a 9 Ry energy cutoff, and we used a maximum of about 1000 k-points to sample the full SBZ of the $\sqrt{3}\times\sqrt{3}$ phase. In Section 2, we discuss the properties of the undistorted Si/Si(111) $\sqrt{3}\times\sqrt{3}$ surface, and show that in fact correlations do make this surface unstable towards a magnetic state. We also show that a state where the surface band is 2/3 filled with spin-up electrons and 1/3 with spin-down electrons (i.e. where the magnetization $M=1/3$), displays a much stronger tendency to develop a 3×3 density wave than the $M=0$ paramagnetic case. In this case, it transpires that nesting is made strong—nearly perfect—by the fractional magnetization. In Section 3, we present preliminary results of a calculation performed with a 3×3 surface unit cell, where we confirm that a state with $M=1/3$ and 3×3 charge and spin periodicity develops. Conclusions and prospects for future work will be given in Section 4.

2. The unreconstructed surface

The Si/Si(111) $\sqrt{3}\times\sqrt{3}$ unreconstructed surface was modeled with a slab containing two Si bilayers plus a Si adatom that was placed in the T_4 position of the upper surface. All atomic positions were fixed to the values calculated by Northrup [13]. The bottom surface (fourth atomic layer), which is not planar, was saturated with H atoms. With this choice, our calculated Hellmann–Feynman forces were smaller than 0.05 eV Å^{-1} on all atoms of the slab, indicating a reasonably stable starting state. We initially carried out a paramagnetic calculation (LDA+GC) in order to determine the surface band dispersion and the Fermi surface that originates from half-filling this surface band.

The surface band was located in the middle of the bulk-projected energy gap, and had a width of about 0.6 eV. As stated in the Introduction, the nesting vector connecting two parallel portions of the Fermi surface (see Fig. 1) is clearly larger than the value required to justify a commensurate charge-density wave with 3×3 periodicity, which corresponds to twice the $\Gamma\rightarrow M_3$ distance in Fig. 1.

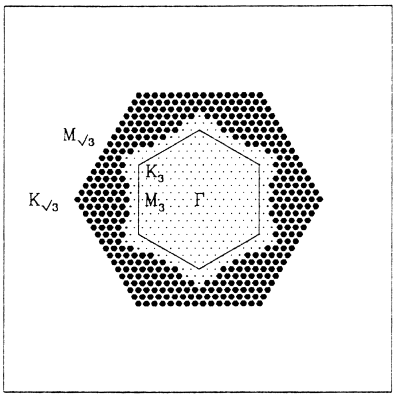

Fig. 1. Fermi surface obtained by half filling the surface band of Si/Si(111); the Brillouin zone of the 3×3 surface is also reported.

This is in agreement with recent calculations reported for the Sn/Ge(111) [4] surface and disagrees with earlier claims for Pb/Ge(111) [1]. Since a low temperature transition to a 3×3 phase has been observed on both Sn/Ge(111) and Pb/Ge(111), the role of a Fermi surface nesting as the driving force of the transition remains to be clarified. A possible low-temperature transition to a 3×3 phase has not been investigated experimentally for the K/Si(111):B system, or for SiC(0001). However, our paramagnetic calculation suggests discarding the nesting argument in all of these systems.

The above calculations have been carried out within the LDA+GC approximation, and are thus inclusive of electron correlations only at a mean field level. This approximation is well-known to be sufficiently accurate only for those systems where the band width, W, is not too small with respect to the on-site Coulomb repulsion, U, and nearest-neighbor repulsion, V. A crude estimate of U and of V in our surface can be obtained by constructing the Wannier function associated with the surface band (see Fig. 2), evaluating its Coulomb integrals U_o, and V_o, and screening them by the electronic response of semi-infinite bulk Si, so that $U\simeq U_o(2)/(\epsilon+1)\simeq U_o/6$, and the same for V. Evaluation of U_o for the Wannier function of Fig. 2 gives $U_o=3.6$ eV, $V_o=1.8$ eV and $U\simeq0.6$ eV, $V\simeq0.3$ to be compared with a band width $W\simeq0.5$ eV. This shows that correlations will

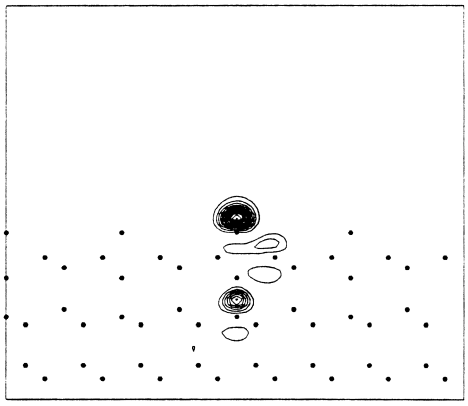

Fig. 2. Density contours of the Wannier function associated with the Si/Si(111) surface band: dots correspond to atomic positions.

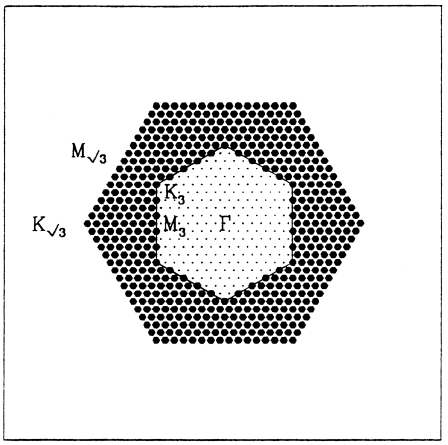

Fig. 3. Fermi surface obtained from the surface band of Si/Si(111) with a fractional filling of 2/3. The Brillouin zone of the 3×3 surface is also reported. Notice the strong nesting properties of the Fermi surface.

indeed be strong, as was surmised. This estimate of U, for example, suggests that the system violates the Stoner criterion for the stability of the paramagnetic state. In fact, estimating a density of states at the Fermi level as $n(E_F)\simeq 2/W$ [this estimate holds for a flat density of states of width W; the calculated $n(E_F)$ is slightly larger], we obtain $n(E_F)U\simeq 2.4>1$. In other words, the Stoner criterion strongly suggests that the paramagnetic state considered so far is unstable with respect to a magnetic state whose character remains to be determined. Because of this, it will be instructive, as explained in the Introduction, to switch to LSDA calculations. We have carried out a spin-polarized calculation of Si/Si(111) within the LSD+GC approximation. For simplicity, we only considered the state with magnetization $M=1/3$, obtained by filling the surface band with 2/3 of spin-up electrons and 1/3 of spin-down electrons. In agreement with what suggested by the Stoner criterion, we found that the $M=1/3$ state is favored, by about 10 meV adatom^{-1} with respect to the unpolarized case. Whereas this calculation is only representative of the fact that a magnetic instability has to set in, the "true" ground state of the system that is yet to be determined, it can be observed that the Fermi surface for spin-up electrons in the $M=1/3$ calculation (see Fig. 3) now displays an exceedingly strong nesting in correspondence to the 3×3 reciprocal vector. In other words, although the $M=1/3$ state may not be the ground state for a $\sqrt{3}\times\sqrt{3}$ periodicity, such a magnetization could be strongly stabilized by a concomitant 3×3 density wave.

3. The 3×3 distorted surface

In order to verify the hypothesis that a 3×3 density wave can stabilize a $M=1/3$ state, we carried out a preliminary study of the electronic ground state in a 3×3 surface unit cell, within the LSD+GC. In this calculation, we did not impose a value of $M=1/3$, but we allowed the magnetization to reach its optimum value in a self-consistent manner. The resulting magnetic moment spontaneously converged to $M=1/3$. At the same time, the system developed a spin density wave such that one of the three adatoms was mainly occupied by spin-down electrons, whereas the remaining two adatoms were mainly of spin-up character. This spin density wave was accompanied by a very small charge density wave ($\Delta\rho/\rho\sim10^{-2}$ in the surface region), so that the total charge approximately preserved the "unreconstructed" $\sqrt{3}\times\sqrt{3}$ periodicity, at variance with what is suggested by the STM data on Sn/Ge(111) and Pb/Ge(111). The resulting band structure (see Fig. 4) was semiconducting, and developed an indirect gap of about 0.2 eV, with an average direct gap of about 0.5 eV.

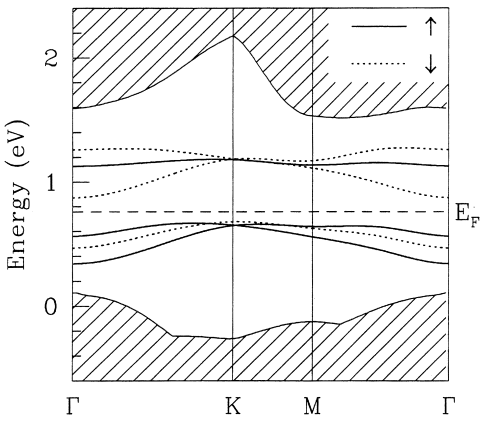

Fig. 4. Surface band structure of the 3x3 reconstructed surface, calculated in the LSD approximation. Solid line, spin-up electrons; dotted line, spin-down electrons. Shaded regions, projected bulk bands.

4. Discussion

Within LSDA, we have obtained a surface energy lowering in going from a paramagnetic, metallic $\sqrt{3}\times\sqrt{3}$ state, to a magnetic, SDW (and in principle also CDW) state with 3×3 periodicity and an insulating gap. This is, therefore, a natural candidate for the ground state of K/Si(111):B. Because of the limitations discussed above, and also because of Mermin–Wagner's theorem, it remains unclear whether long-range magnetic order could ever really develop on this surface. Among other things, a knowledge of spin–orbit coupling and of magnetic anisotropy will be needed. None the less, we believe that we have obtained a static picture of what the local correlations should be. More work is now in progress to extend this work in order to obtain a more detailed picture, as well as understanding to what extent correlations, even if surely weaker, might play a role also on Pb/Ge(111) and Sn/Ge(111). The inclusion of lattice distortions will also be considered, along with the possibility of spin non-collinearity, where the $M=1/3$ might eventually turn into a 120° magnetic structure [11].

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