Triangular Mott-Hubbard Insulator Phases of Sn/Si(111) and Sn/Ge(111) Surfaces

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The ground state of Sn/Si(111) and Sn/Ge(111) surface α phases is reexamined theoretically, based on *ab initio* calculations where correlations are approximately included through the orbital dependence of the Coulomb interaction (in the local density + Hubbard U approximation). The effect of correlations is to destabilize the vertical buckling in Sn/Ge(111) and to make the surface magnetic, with a metal-insulator transition for both systems. This signals the onset of a stable narrow gap Mott-Hubbard insulating state, in agreement with very recent experiments. Antiferromagnetic exchange is proposed to be responsible for the observed Γ-point photoemission intensity, as well as for the partial metallization observed above 60 K in Sn/Si(111). Extrinsic metallization of Sn/Si(111) by, e.g., alkali doping, could lead to a novel 2D triangular superconducting state of this and similar surfaces.

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Metal-insulator transitions and strongly correlated states of electrons in the genuinely two-dimensional (2D) ''dangling bond'' surface states of semiconductors have long been sought after [1] but seldom realized and characterized. On these surfaces, band physics usually takes over, driving large structural reconstructions, which remove metallicity with a strong energy gain [2]. The resulting passivation of surface states unfortunately also removes alternative and more interesting phases, including charge density waves (CDW) or spin density waves, Mott-Hubbard insulators (MIs), and possibly 2D superconductivity [3].

Plummer and others [4–8], however, called attention to the α-phase surfaces, obtained by covering an ideal metallic (111) semiconductor surface with a $\sqrt{3} \times \sqrt{3}R30°$ ($\sqrt{3}$) triangular array of group IV adatoms. These systems, where adatoms lie as far apart as $\sim$7 Å, possess a very narrow half-filled adatom surface state band, making them ideally prone to various instabilities and to strong correlations. A low temperature CDW-like reversible 3×3 periodic surface adatom distortion was indeed reported in metallic Pb/Ge(111) and Sn/Ge(111) [5,8], whereas undistorted triangular MI states appeared to prevail in isoelectronic surfaces such as Si/SiC(0001) [7] and K:Si(111)$\sqrt{3} - B$ [6].

Density functional calculations in the local density approximation (LDA) supported this diversity of behavior, indicating that a large $\sim$0.3 Å periodic ''up-down'' distortion [9–11] akin to a valence disproportionation [12] should be the ground state of Sn/Ge(111), against an undistorted magnetic insulator prevailing in a large gap system like Si/SiC(0001) [13–15]. Interestingly, the intermediate case of Sn/Si(111) failed to fall neatly on either side of this divide. Within LDA, this surface is equally close to undistorted magnetism (evolving to an insulator as we shall see later) as it is to a 3×3 distorted metal [10]; but neither state is actually stable in the strain free surface [12]. As we will show presently, $T = 0$ LDA seems paradoxically to describe better the behavior of these surfaces at *nonzero* temperature, whereas a better account of correlations is needed to describe their actual ground state.

Systems realizing in two dimensions a spontaneous transition between these two types of states, namely, the distorted (or undistorted) nonmagnetic band metal and the magnetic undistorted MI, are very interesting to pursue. Among other things, the latter constitute the building block of many important strongly correlated systems, including (in the square lattice version) cuprate superconductors. Model studies do indicate that distorted metal-undistorted MI transitions are to be expected in the present system as a function of parameters [15]. Correlations in Sn/Si(111) and Sn/Ge(111) surfaces were discussed by Flores *et al.* [16], who, however, concluded against a transition to a MI ground state. In fact, until recently no such transition was actually observed in α phases.

Within the last few months that situation changed drastically. Cooling Sn/Ge(111) below 20 K apparently turns it from a 3×3 distorted metal to an undistorted $\sqrt{3}$ insulator, presumably a MI [17]. Equally striking, Sn/Si(111) is now shown by Modesti's group [18] to turn continuously from an undistorted metal to a narrow gap insulator, again presumably a MI, below 60 K. If Sn/Ge(111) is intriguing enough due to the disappearance of structural distortion at low T, the result on Sn/Si(111) is no less puzzling. Low temperature photoemission [18,19] finds Sn-related surface bands below E_F at the Γ point, as though folded over from the K point. This is an intriguing but clear indication of 3×3 periodicity, for in the $\sqrt{3}$ surface there are no such filled surface states at Γ [20]. Structural tools including scanning tunneling microscopy (STM) and photoelectron diffraction show only $\sqrt{3}$ periodicity, so that the

3×3 motif is not structural. For both surfaces therefore, the LDA predictions of metallic ground states turn out to be in error.

Unraveling this situation calls for a renewed theoretical effort. Calculations should at the same time be of first principles quality, so as to permit total energy comparisons, but also treat correlations more accurately than LDA, so as to identify MIs if and when present. The local density approximation + Hubbard U (LDA + U) approach, while still a mean field approximation (thus, for example, replacing a MI with a fictitious magnetic band insulator) does satisfy these criteria [21] and is suitable to describe quantitatively surface MIs [22]. We therefore conducted a series of accurate LDA and LDA + U calculations for Sn/Si(111) and Sn/Ge(111).

The geometries considered were periodic slabs consisting of three (111) semiconductor bilayers, H saturated at the bottom, and with the $1/3$ monolayer of Sn adsorbed at $T4$ sites on the top surface. We used the plane wave implementation of density-functional theory [12,23] in the gradient corrected local spin density approximation (LSDA), extended to include a Hubbard U (LSDA + U). Beginning with an undistorted $\sqrt{3}$ geometry (one Sn per cell), we turned on an increasing electron-electron onsite repulsion U ranging from zero to an estimated full value of $U \simeq 4$ eV [24] for two electrons occupying the same Sn $5p_z$ orbital—this single orbital constituting about 50% of the surface state [11]. The effect of a finite U parameter in LSDA + U is to favor integer occupancy of this orbital, which is the crucial effect of strong correlations.

Figure 1 summarizes the main physical quantities calculated at zero temperature for Sn/Si(111) and Sn/Ge(111), illustratively shown for increasing U values. Sn/Si(111), metallic and weakly magnetic already at $U \simeq 0$, develops a stronger magnetization and eventually a metal-insulator transition $U \simeq 2$ eV, where the spin moment per adatom site saturates to $1\mu_B$. The insulating gap reaches 0.3 eV at

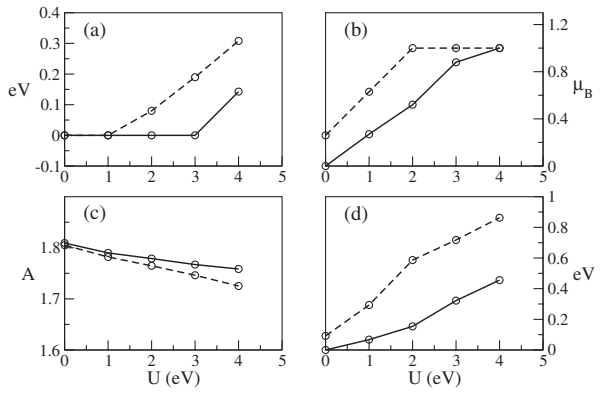

FIG. 1. Sn/Si(111) (dashed lines) and Sn/Ge(111) (solid lines) $\sqrt{3}$ calculations for increasing correlation parameter U: (a) minimum band gap; (b) spin moment per adatom; (c) Sn vertical height measured over the outer semiconductor plane; (d) magnetic exchange splitting. Lines are guides for the eye.

the final realistic value $U \simeq 4$ eV, where the exchange splitting between opposite spins orientations becomes as large as 0.8 eV. The insulating state gains Coulomb energy, but loses band energy relative to the metallic state. This is also reflected indirectly by the predicted downward geometrical relaxation of the Sn adatoms by about 0.06 Å closer to the Si substrate, upon going from metal at to insulator. Vertical adatom positions control hybridization between the $5p_z$ dangling bond orbital and the underlying Si-Si antibonding state [11,25]. That hybridization is strong in the metallic state (and actually modulated in the 3×3 distortion), but counterproductive and thus weaker in the insulating state. Within the artificial $\sqrt{3}$ geometry, results for Sn/Ge(111) are on the whole similar to those in Sn/Si(111), except that magnetism does not develop at $U \simeq 0$, and the metal-insulator transition occurs only for $U \simeq 4$ eV. All gaps and splittings are correspondingly smaller.

We may crudely identify the magnetic 2D insulators near $U \simeq 4$ eV with the actual MI states of the true surfaces, whose measured gaps are qualitatively similar, ranging from zero to hundreds of meV [17,18]. Before taking that identification seriously, we must, however, compare the structural properties of the insulator with those of the competing phases, in particular, with the 3×3 distorted metallic ones. To that end we repeated all LSDA + U calculations in an enlarged 3×3 cell, where both distortive and ferromagnetic order parameters are allowed. The outcome for Sn/Si(111) was uneventful, and identically the same undistorted magnetic states were recovered for all U values. That confirms that a $\sqrt{3}$ MI is indeed the LSDA + U predicted ground state of Sn/Si(111). Apart from magnetism, not yet investigated experimentally, this fully agrees with recent data by Modesti *et al.* [18].

The evolution is different in Sn/Ge(111) where initially at $U \simeq 0$ the ground state is metallic, nonmagnetic, but now 3×3 distorted, one Sn up by $\Delta/2$, two down by $\Delta/2$. The up-down amplitude $\Delta \simeq 0.36$ Å and the energy gain ~ 9 meV/Sn are same as previously found long ago by similar methods [9–12] and hitherto believed to describe the true ground state of this surface. However, as shown in Fig. 2 (obtained by constrained structural optimization along the distortion path) for increasing U the distortion Δ eventually disappears giving way to the same magnetic insulator previously found at $U \simeq 4$ eV. Hence inclusion of correlations strongly modifies the ground state of Sn/Ge(111) from a 3×3 distorted metal to a magnetic insulator with $\sqrt{3}$ structural symmetry. This agrees with the STM and photoemission results of Cortés *et al.* below 20 K [17].

In the MI phase, an unpaired electron is localized near each Sn adatom site. Ignoring anisotropy, these $1/2$ spins form a 2D triangular Heisenberg-like magnet with intersite antiferromagnetic (AF) exchange coupling whose order of magnitude is set by $J \sim t^2/U_{\text{eff}} \sim 5$ meV

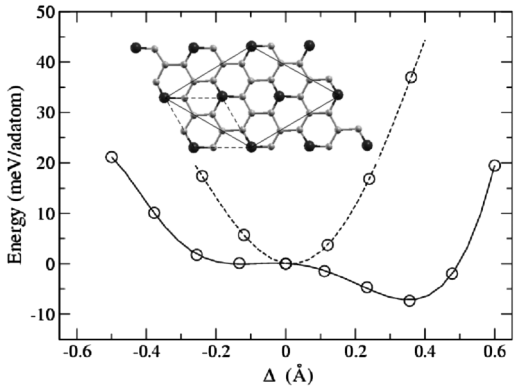

FIG. 2. Sn/Ge(111): Total energy per adatom as a function of 3×3 up-down distortion Δ. LDA (solid line) and LSDA + U, $U = 4$ eV (dashed line). The zero of energy is at $\Delta = 0.0$ Å in both cases. Inset: Schematics of the $\sqrt{3} \times \sqrt{3}R30°$ unit cell (dashed line) and the 3×3 unit cell (solid line). Black spheres represent Sn adatoms, gray spheres Si (Ge) atoms of the first and second layer.

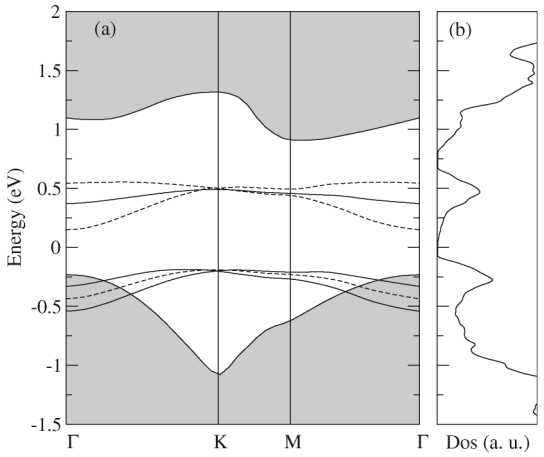

FIG. 3. (a) Sn/Si(111): LDA + U spin-up bands (solid line) and spin-down bands (dashed line) for the ferrimagnetic 3×3 phase. (b) Total density of electronic states (solid line) showing the gap at the Fermi level (zero).

(for $t \sim 0.05$ eV, $U_{\text{eff}} \sim 0.5$ eV [26]). Their ground state could thus be either a 120° noncollinear Néel state [27] or a spin liquid [28]. We made use of collinear LSDA + U to calculate the actual J values for Sn/Si(111) and Sn/Ge(111). We carried out two separate 3×3 unit cell $U = 4$ eV calculations, one fully ferromagnetic ($3\mu_B$ per cell), the other *ferrimagnetic* ($1\mu_B$ per cell), with two adatom spins up, one down [29]. The total energy change per 3×3 cell ΔE amounts to switching 6 bonds from antiferromagnetic to ferromagnetic, which for spins 1/2 implies an energy loss of 9 J. We calculated $\Delta E = 27$ and 42 meV, implying $J \sim 3$ and 5 meV for Sn/Si(111) and Sn/Ge(111), respectively. Because of the better accuracy of the ferromagnetic calculation, these are most likely underestimates, and we conclude that at least up to a hundred Kelvin the MI state of Sn/Si(111) and Sn/Ge(111) is likely to possess AF short range order, probably even outright Néel order, although renormalized by quantum fluctuations [27]. Hole spectral function calculations in the 2D triangular t-J model [30] suggest that purely magnetic 3×3 order will give rise to photoemission features typical of a 3×3 band folding, even in the absence of structural 3×3 periodicities. Figure 3 shows the LSDA + U electronic bands of Sn/Si(111) ferrimagnetic state which exemplify that folding. The photoemission intensity near E_F at Γ [18,19] observed in Sn/Si(111) is thus likely due to 3×3 AF order and consequent folding. The same 3×3 magnetic folding should now be searched and detected at the true Γ point of Sn/Ge(111)'s low temperature MI state.

These results are intriguing, and lead on to a number of interesting questions. First, why do the MI states evolve into metallic phases, beginning near 60 and 20 K, respectively, in Sn/Si(111) and Sn/Ge(111)? Moreover, why do these finite temperature metallic phases resemble the uncorrelated LDA ground states calculated at $T = 0$?

A driving force for the observed T-induced metallization of MI states is, in analogy with V_2O_3 and 2D $k-(ET)_2Cu[N(CN)_2]Cl$ [31], their lack of spin entropy, frozen out by AF short range order. If $\Delta E \sim W(1 - U/U_c)$ represents a typical insulator-metal energy difference per site (for a transition at $U = U_c$), and $T\Delta S(T) \sim \gamma T^2$ the entropy-related free energy difference (assuming AF frozen spins and a charge gap in the MI), then the low-T insulator-metal phase boundary is predicted of the form:

$$T_{\text{im}} = [W(U/U_c - 1)/\gamma]^{1/2}, \tag{1}$$

which is sketched in Fig. 4, and is well brought out experimentally in 3D compounds [31]. Here $W \sim 0.3$ eV is the bare bandwidth, and γ is the electronic specific heat coefficient (perhaps of order 0.01 J/mol K^2, or roughly 0.1 meV/site K^2, as in 2D organics [31]). We thus suggest that quasiparticle entropy may drive these surfaces across the insulator-metal phase boundary, resurrecting the metallic phase, itself only metastable at $T = 0$. Four point

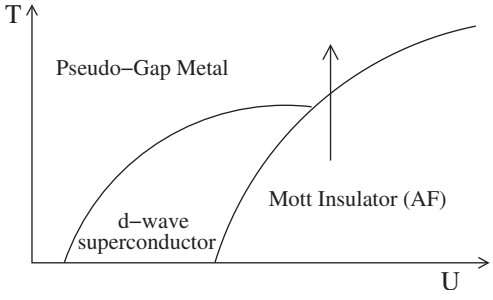

FIG. 4. Schematic phase diagram of Sn/Si(111) in the temperature-interaction plane. The arrow describes the entropy-induced metallization due to AF order in the MI.

conductance measurements [32] could be of great help in ascertaining this scenario.

The next and crucial if still speculative question is whether there is any chance to realize a 2D (power-law ordered) superconducting state in these surfaces [3]. As indicated in Fig. 4, in the general phase diagram of the triangular Hubbard lattice, as realized by organics under pressure [31], there is indeed a low-T d-wave superconductor on the metallic side next to the MI phase. We thus propose that one should try to achieve superconductivity by metallization of Sn/Si(111) below 60 K. Metallization could be attempted by, e.g., reducing U, or by increasing the bandwidth, or by doping surface bands away from half-filling. The latter might be realized by alkali deposition, the former possibly through heavy doping of the Si bulk substrate. We note in passing that the d-wave superconducting state in a triangular lattice would probably break rotational symmetry [33], an event readily observable by STM.

One remaining unknown is the role of spin orbit coupling. While large in Sn, the largely p_z nature of the state will reduce its relevance. Possibly, some amount of magnetocrystalline anisotropy will result. Depending on its sign, the spin $1/2$ sites will turn from Heisenberg to either Ising (out of the surface plane; in this case, the ferrimagnetic state considered above actually corresponds to the true MI ground state) or XY (in the surface plane). This aspect remains open for future investigation.

In conclusion, in this Letter we provide a first theoretical background for the insulating ground state just observed in surface α-phases Sn/Si(111) and Sn/Ge(111), and obtain quantitative indications that the insulating phase observed in both should be of correlation origin. LSDA + U calculations predict a stable magnetic and (Mott-Hubbard–like) insulating $\sqrt{3}$ phase in Sn/Si(111), as well as the disappearance of the 3×3 distortion in Sn/Ge(111), as is experimentally observed. Temperature induced metallization is argued to represent evidence for antiferromagnetism in the Mott state. Should metallization be provoked at sufficiently low temperatures, a 2D d-wave superconducting state could be achieved. A number of experimental approaches, including surface doping, and four point conductance measurements are suggested for the future.

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