Correlation-driven charge order in a frustrated two-dimensional atom lattice

F. Adler, S. Rachel, M. Laubach, J. Maklar, A. Fleszar, J. Schäfer, and R. Claessen

1Physikalisches Institut and Röntgen Center for Complex Material Systems (RCCM), Universität Würzburg, D-97074 Würzburg, Germany
2School of Physics, University of Melbourne, Parkville, VIC 3010, Australia
3Institut für Theoretische Physik, Technische Universität Dresden, D-01069 Dresden, Germany
4Institut für Theoretische Physik und Astrophysik, Universität Würzburg, D-97074 Würzburg, Germany

The triangular lattice of localised electrons is the canonical example for a geometrically frustrated spin arrangement. In conjunction with strong local Coulomb interactions, it leads to a competition of antiferromagnetic order and spin liquid behaviour. However, when longer-ranged Coulomb interactions become relevant, charge order might emerge and an even richer phase diagram can be expected. Nevertheless, candidate materials are rare. Here we show that a Pb atom lattice on a silicon substrate is an excellent realisation of an extended Hubbard model. In our study using scanning tunneling microscopy, we detect a charge-ordered state not previously known. The full interacting phase diagram is explored by an extended variational cluster approach, which finds charge order driven by non-local interactions, and in competition with magnetic order. By exploiting the tunability of correlation strength, hopping parameters and bandfilling, this material class represents a promising platform to search for exotic states of matter, in particular, for chiral topological superconductivity.

In a frustrated lattice of uncompensated spins the exchange interactions cannot be saturated completely on every site. This leads to competing groundstates where either a specific magnetic order or a spin liquid phase can emerge [1, 4]. When non-local Coulomb interactions are involved or the system is doped away from half filling, the formation of charge-order is another possibility. These scenarios are often accompanied by superconductivity arising in the vicinity of such ordered phases. Yet, candidate materials are limited to very few bulk solids, such as cobaltates [6, 7] and organic compounds [8, 9]. However, due to the complexity of these materials, the occurrence of particular phases is not fully understood. In contrast, atomic two-dimensional (2D) lattices in triangular geometry, experimentally generated by epitaxial sub-monolayer deposition on an insulating substrate, are intriguingly simple in structure. Thus they provide versatile model systems for the study of strong electron correlations. The generically rich phase diagram of correlated triangular systems has been pointed out in theoretical studies of lattice models [10, 11] and surface systems [12, 13], including charge order (CO) and the possibility of topological superconductivity [14, 20]. In this respect, the atomic architecture allows to tune the interactions by variation of the adatom species as well as the substrate which provides screening and mediates the electron hopping [21]. In addition, dopants such as alkali atoms have been demonstrated to change the band filling [22].

The case in point are group-IV adsorbates (Sn, Pb) on semiconductor surfaces such as Si, Ge or SiC [12, 21, 24]. The key concept here is that unsaturated adsorbate orbitals exist with half filling which are subject to strong local and non-local Coulomb interactions. These surface systems thus represent a rich playground for the investigation of correlation physics in a frustrated lattice, including the formation of unusual symmetry-broken ground states. The experimental system is a triangular array of atoms with a dilute coverage of a 1/3 monolayer, forming a $\sqrt{3} \times \sqrt{3}$ surface reconstruction (Fig. 1a), where the adsorbed Sn or Pb atoms are known to reside in $T_4$ position [21, 24]. This implies that three out of their four valence orbitals are engaged in covalent back-bonds to the substrate. Of relevance for the physics is the fourth orbital (out-of-plane $p_z$-orbital): it remains “dangling”
and contains only one electron. Such half-filled surface band is prone to strong electron correlations, and here the on-site Coulomb repulsion becomes the dominating term due to the weak hopping matrix elements (Fig. 1b). At low temperatures, some systems undergo a phase transition to a $3 \times 3$ superstructure. For Sn and Pb on Ge(111) it was initially interpreted as a Peierls distortion $^{26, 27}$. However, subsequently this was heavily debated due to insufficient nesting conditions in the electron band structure $^{28}$. With the obvious presence of strong electron correlations, a single-particle description must appear insufficient $^{29}$, calling for approaches that account for the relevant many-body interactions.

In this work, we investigate the symmetry-broken ground state of Pb on Si(111). It might be the experimentally least studied system, since it coexists with other surface phases, see Supplemental Information (SI) Fig. S1, thereby prohibiting the use of spatially averaging techniques such as photoemission. The phase with $3 \times 3$ superstructure (Fig. 1b) exists below 86 K $^{29, 30}$, and lacks a clear explanation so far. A theoretical study has pointed to the role of nearest-neighbour interactions $^{13}$, hinting at the formation of CO. Yet, it is crucial to also account for longer-ranged hopping (Fig. 1b), which – in case of Sn/Si(111) – tend to stabilize magnetic order as a competing phase in the electronic phase diagram $^{31}$. For comparison, Sn/Si(111) shows neither a structural phase transition upon cooling down to 2 K $^{32}$, nor any signs of a charge-ordered state down to 4 K (see SI Fig. S2). Instead, one finds a Mott-insulating state with row-wise antiferromagnetic order $^{31}$ (see SI, Section IV). For Pb/Si(111) we employ a local probe, namely low-temperature scanning tunnelling spectroscopy (STS), which is sensitive to CO (Fig. 1b). We connect these data with an advanced theoretical description using an extended variational cluster approach (XVCA). It accurately accounts for non-local Coulomb interactions, and allocates Pb/Si(111) in the CO regime of the phase diagram.

Results

Discovery of charge order. The atomically resolved maps are recorded by scanning tunneling microscopy (STM) on a single ($3 \times 3$)-reconstructed domain of Pb/Si(111). The studies are conducted at $T = 4.3$ K, i.e., deep in the low-temperature phase $^{23, 30}$. In order to disentangle atomic coordinates and spectroscopic features, we have performed topographic STM measurements (at constant tunneling current) at different sample biases, and have simultaneously conducted STS to record the local density of states (LDOS) by a modulation technique (see Methods).

Fig. 2 shows topographic images and the corresponding LDOS maps for selected tunneling biases, all recorded at the exact same location on the sample. In the LDOS maps, we observe a regular large-scale redistribution of the charge over the spatial coordinates, where the atom in the center of the hexagonal Wigner-Seitz (WS) unit cell shows a significantly enhanced LDOS, while the six surrounding atoms in the corner fade into the background and can hardly be resolved individually. A similar behaviour is found for other sample biases, too (see Fig. S3). As illustrated in Fig. S1, charge is accumulated on 1/3 of the adatoms, while it is depleted on the neighbouring ones. This experiment thereby represents the discovery of CO in the Pb atom lattice on Si(111), and in conjunction with the theoretical modelling below this is established as driven by correlations.

Such behaviour can also be detected in the topographic maps, but a more elaborate analysis is required due to the interference of spectroscopic and topographic information. In a topographic STM image, the recorded apparent “height” of an atom at given bias is not only determined by the topographic corrugation, but also by the energy-integrated LDOS (from the Fermi energy to the energy that corresponds to the bias). This effect can be disentangled in a straightforward manner by analysing the bias-dependent signal.

Starting at small negative bias of $U \geq -100$ mV (Fig. 2a) the atom in the center of the WS unit cell appears lower than neighbouring atoms. Since there is only little contribution from the integrated LDOS at low bias voltages, this qualitatively reflects the true corrugation of the sample surface, i.e., Pb atoms are arranged in a “1-down/2-up” configuration. The total height difference we observe between “up” and “down” atoms is only 70 pm (see Fig. S4). With increasing absolute bias voltage the CO state progressively imprints its charge distribution onto the topographic maps, raising the apparent height of the atom in the center of the WS unit cell. Eventually, for $U \leq -150$ meV, this atom appears higher than surrounding atoms (Fig. 2a), rendering the topographic maps completely dominated by LDOS effects.

Extended Hubbard model. For better theoretical insight into the STM results we model the Pb adatom system as an extended Hubbard model with isotropic hopping integrals $t_{ij} \equiv t_{i-j_1} = t_n$ between the nth neighbouring Pb atoms. We perform $ab$ initio calculations to obtain accurate values for the hopping integrals (see SI). Local electron-electron interactions are included as a Hubbard on-site term with amplitude $U_0$ while non-local interactions are accounted for by the nearest-neighbor Coulomb term with amplitude $U_1$. The total Hamiltonian reads

$$
\mathcal{H} = \sum_{ij, \sigma} \left( t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.} \right) + U_0 \sum_i n_{i\uparrow} n_{i\downarrow} + U_1 \sum_{(ij)} n_i n_j.
$$

(1)

Here $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) denotes a fermionic creation (annihilation) operator, $n_{i\sigma} \equiv c_{i\sigma}^\dagger c_{i\sigma}$, and $n_i = n_{i\uparrow} + n_{i\downarrow}$. We consider a filling of one electron per lattice site, in agreement with
FIG. 2. Bias voltage series of Pb/Si(111) in STM/STS. Topography (top) and the corresponding LDOS maps (bottom) of Pb/Si(111) for bias voltages $U = -100$ mV (a), $U = -125$ mV (b) and $U = -150$ mV (c). A 3 x 3 Wigner-Seitz unit cell is marked in each panel. While the LDOS maps show the CO state with a qualitatively unchanged appearance, the contrast in the topographic maps switches due to the interplay of LDOS effects from the CO state with the concomitant topographic buckling.

FIG. 3. $U_0/t_1$ vs. $U_1/t_1$ phase diagram obtained within XVCA. For dominant onsite-repulsion $U_0$ we find an antiferromagnetic insulator with row-wise order, for sufficiently strong nearest-neighbour repulsion $U_1$ a charge ordered insulator. For weaker interactions also metallic regimes are present. Used parameters are $t_2/t_1 = -0.383$, $t_3/t_1 = 0.125$ with $(U_0/t_1,U_1/t_1) = (11,5)$ for PbSi and (15,4) for SnSi. The energy scale for PbSi (SnSi) is set by $t_1 = 58.5$ meV ($t_1 = 52.7$ meV).

However, values for $U_0$, $U_1$, etc. can usually not be obtained from pure ab initio methods; instead we will use them as system parameters to be fitted to the experimental data. For dominating on-site interaction ($U_1/U_0 \ll 1$) one would expect magnetic long-range order, provided that frustration caused by the triangular lattice, hoppings and interactions is not strong enough to trigger spin liquid physics. In contrast, for sufficiently large ratio $U_1/U_0$ one would rather expect some type of CO. We note that there is not only frustration which decreases the magnetic ordering tendencies; also CO is exposed to similar frustration effects due to the nearest-neighbour Coulomb interaction.

In the following, we apply the XVCA [33] (see Methods and SI) and map out the interacting $U_0$–$U_1$ phase diagram for single particle parameters $t_2/t_1 = -0.383$ and $t_3/t_1 = 0.125$. Pb/Si(111) and its sister compound Sn/Si(111) [31] exhibit different hopping integrals; it turns out, however, that the ratios $t_2/t_1$ and $t_3/t_1$ are essentially identical (with negligible $t_4/t_1$) for both compounds allowing for a universal interacting phase diagram containing both the Pb/Si and the Sn/Si system (see Fig. 3).

The phase diagram of Hamiltonian (1) reveals metallic and insulating phases. As speculated earlier we indeed find insulating many-body ground states which either realise antiferromagnetic order (as in the Sn/Si system)
or CO (as in the Pb/Si system, see Fig. 2) depending on the interaction parameters $U_0$ and $U_1$. We did not find any signs of other magnetically or charge ordered phases in the parameter regime covered by Fig. 3. In the insulating regime, we find the first order phase transition from CO to antiferromagnetism (AFM) for $U_1/U_0 \approx 0.43$. The XVCA method allows us to compute LDOS and single-particle spectral functions which can be compared to the experimental data in order to determine the position of Sn/Si(111) (see SI) and Pb/Si(111) in the phase diagram Fig. 3.

Discussion

The $3 \times 3$ patches on the surface of Pb/Si(111) manifesting the CO are too small (see Fig. S1) to permit angle-resolved photoemission. Instead, STS serves as local spectroscopic probe, and in addition to the maps of Fig. 3, LDOS spectra as a function of bias voltage have been recorded at the corner and the central atoms of the unit cell, respectively, in Fig. 4. Within XVCA we can use the spatial resolution on the cluster and compute the LDOS at a central and corner site correspondingly. In the absence of CO, LDOS maps at both sites clearly coincide, but otherwise they must deviate as a manifestation of the CO groundstate.

We simulate LDOS plots on the $(U_0, U_1)$ manifold; comparison with the experimental data, see Fig. 4, allows us to locate Pb/Si(111) in the phase diagram Fig. 3. The best match between STS and XVCA is obtained for interaction parameters $(U_0/t_1, U_1/t_1) = (11, 5)$. Here we take the normalized STS data $dI/dV/(I/V)$ as a measure of the LDOS (for explanation and raw data see Fig. S5). The spectra agree in their main features: a vastly different LDOS in the occupied states, and a congeneric behaviour in the unoccupied states. These criteria are only fulfilled in an area close to the phase boundary, but exclusively in the domain of the CO phase. In looking at the CO amplitude, we find for the occupied states in theory a ratio of charges on a corner atom versus a center atom, i.e., $n(\text{corner})/n(\text{center}) = 0.8/1.4 = 0.57$ (see SI, Eq. S17). In the experiment, the spatial contrast becomes significant above approximately $-0.6\,\text{eV}$, and integrating up to $E_F$ the charge ratio is $\approx 0.60$. This shows that the modelling is qualitatively and also quantitatively in close agreement. The XVCA methodology accurately accounts for non-local Coulomb interactions by exactly including them within the cluster and in a variational scheme between the clusters; thus it represents a major advantage concerning the degree of “material-realistic” modelling.

It is worth emphasising the role of longer-ranged Coulomb interactions also in the light of possible spin liquid formation [3, 5]: Ignoring the presence of $U_1$ for a moment, the tight-binding parameters for Sn/Si and Pb/Si would correspond in the strong coupling limit (i.e., $U_0 \gg t_1$ where a spin-model description is valid) to exchange parameters which realise a quantum spin liquid phase [3, 34]. It might even be possible that $U_0/t_1 = 15$ as found for Sn/Si is already sufficiently large to observe such an interesting phenomenon (in this case, such a spin liquid would be placed in the bottom right corner of the phase diagram Fig. 3). Thus we conclude that not only the longer-ranged hoppings but also the non-local Coulomb interactions stabilise the row-wise AFM state (Sn/Si) or even push the ground state into the CO regime (Pb/Si). This demonstrates how sensitive the many-body ground states of these adatom systems are with respect to competing energy scales.

The possibility of a superconducting regime in the phase diagram of correlated triangular electron systems has been widely addressed [12, 18, 20]. The material system used here is captivating by its simplicity, i.e., the limited number of ingredients and the well-defined correlation parameters which are easy to control, in comparison to the multi-elemental alloys used for the study of high-temperature superconductivity thus far. Notably, correlated 2D triangular lattices are expected to yield either chiral singlet or chiral triplet superconductivity [11, 20]: the latter is known to host exotic Majorana fermions bound to the vortex cores [35, 37]. The 2D lattices discussed here are thus a promising platform to search for these phenomena.

Methods

Preparation of 2D systems. We used p-doped Si(111) substrates with a sheet resistance $\rho < 0.02\,\Omega\,\text{cm}$ to ensure sufficient conductivity for tunneling at low temperatures. The substrates were prepared by repeated flashing at $T = 1650\,\text{K}$ for 10s followed by...
a slow cool-down to room temperature until a sharp 7 × 7 LEED-pattern was observed. The Pb/Si(111) surface was prepared by evaporating ~ 1 ML of Pb on a substrate kept at room temperature followed by an annealing step at \( T = 720 \) K for 5 min. This results in a surface which, at room temperature, is mostly covered with 1 × 1 Pb/Si(111) and small islands of the desired \( \sqrt{3} \times \sqrt{3} \) phase which was in the focus of this study. The Sn/Si(111) surface was prepared by evaporating 1/3 ML of Sn on a substrate kept at room temperature followed by an annealing step at \( T = 820 \) K for 2.5 min.

**Scanning tunneling microscopy (STM) and spectroscopy (STS).** Our experiments were performed with an Omicron LT-STM with a base pressure < 5 × 10^{-11} mbar at \( T = 4.3 \) K. The utilised tungsten tips were tested on a Ag(111) single crystal for sharpness and spectroscopic properties. All STM data shown here was recorded at constant tunneling current with a setpoint \( I = 200 \) pA. LDOS maps were recorded using a modulation spectroscopy technique with a lock-in amplifier. Data were recorded with a modulation voltage \( U_m = 10 \) mV at a frequency of \( \nu = 653 \) Hz.

**Extended Variational Cluster Approach (XVCA).** The XVCA method extends the Variational Cluster Approach (VCA) originally introduced for Hubbard models with local interactions only. This extension takes into account longer-ranged interactions. Both XVCA and VCA provide an efficient scheme to approximately solve the many-body problem, with the single-particle Green’s function \( \mathcal{G}(k, \omega) \) as the central outcome. Using \( \mathcal{G}(k, \omega) \), we can directly compute LDOS and single-particle spectral function \( \mathcal{A}(k, \omega) \). A detailed description and discussion of the XVCA method is given in the SI.

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**Author contributions**

J.S. and R.C. conceived and supervised the experiment. F.A. performed the measurements and analysed the data. S.R. and M.L. performed the the XVCA calculations. A.F. performed the LDA calculations. F.A., S.R., M.L., J.M., J.S. and R.C. wrote the manuscript. All authors discussed the results and implications.