Modeling of networks and globules of charged domain walls observed in pump and pulse induced states.

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Experiments on optical and STM injection of carriers in layered MX₂ materials revealed the formation of nanoscale patterns with networks and globules of domain walls. This is thought to be responsible for the metallization transition of the Mott insulator and for stabilization of a “hidden” state. In response, here we present studies of the classical charged lattice gas model emulating the superlattice of polarons ubiquitous to the material of choice 1T – TaS₂. The injection pulse was simulated by introducing a small random concentration of voids which subsequent evolution was followed by means of Monte Carlo cooling. Below the detected phase transition, the voids gradually coalesce into domain walls forming locally connected globules and then the global network leading to a mosaic fragmentation into domains with different degenerate ground states. The obtained patterns closely resemble the experimental STM visualizations. The surprising aggregation of charged voids is understood by fractionalization of their charges across the walls’ lines.

INTRODUCTION

Major anticipations for the post-silicon electronics are related to materials which demonstrate a layered structure with a possibility for exfoliation down to a few and even a single atomic layer, akin to the graphene. The latest attention was paid to oxides and particularly dichalcogenides of transition metals M₂X₄ with M = Nb, Ta, Ti and X = S, Se, see e.g.¹,² for reviews.

These materials show a very rich phase diagram spanning from unconventional insulators of the so called Peierls and Mott types to the superconductivity³. The transformations among these phases involve formation of superstructures like several types of so called charge density waves (CDW) and/or of hierarchical polaronic crystals. Recent studies of these materials fruitfully overlapped with another new wave in solid state physics. This is the science of controlled transformations of electronic states or even of whole phases by impacts of strong electric fields and/or the fast optical pumping. A super goal is to attend “hidden” states which are inaccessible and even unknown under equilibrium conditions. In relation to this article subjects, the success came recently from observations of ultrafast (at the scale of picoseconds) switching by means of optical⁴,⁵ and voltage⁶,⁷ pulses, as well by local manipulations⁸,⁹. The registered ultrafast switching is already discussed as a way for new types of RAM design, see¹⁰ and rfs. therein.

Most challenging and inspiring observations have been done in studies by the scanning tunneling microscopy (STM) and spectrometry (STS)⁷,⁹,¹¹. They have shown that the switching from an insulating to a conducting state proceeds via creation of local globules or extended networks of domain walls enforcing fragmentation of the insulating electronic crystal into a conducting mosaics of domains with different multiply degenerate ground states.

Most important observations have been done upon very popular nowadays layered material 1T – TaS₂ which is a still enigmatic “polaronic Wigner-crystalline Mott insulator”. The rich phase diagram of 1T – TaS₂ includes such states as incommensurate, nearly commensurate, and commensurate CDWs which unusually support also the Mott insulator state for a subset of electrons. Recently, new long-lived metastable phases have been discovered: a “hidden” state created by laser⁴,⁷ or voltage⁵ pulses, and a most probably related “metallic mosaic” state created locally by STM pulses⁸,⁹.

1T – TaS₂ is a narrow-gap Mott insulator existing unusually on the background formed by a sequence of CDW transitions which have gaped most of the Fermi surface of the high temperature metallic (with 1 electron per Ta site) parent phase². Incomplete nesting leaves each 13-th electron ungaped which in a typical CDW would give rise to a pocket of carriers. Here, each excess carrier is self-trapped by inwards displacements of the surrounding atomic hexagon (forming the “David star” unit) which gives rise to the intragap local level accommodating this electron. Exciting the self-trapped electron from the intragap level deprives the deformations from reasons of existence, the David star levels out in favor of a void in the crystal of polarons. The charged voids are expected to arrange themselves into a Wigner crystal subjected to constraints of commensurability and packing with respect to the underlying structure.

A major question arises: why and how the repul-
sive voids aggregate into the net of walls leaving micro-
crystalline domains in-between? In this paper, we answer
this and related questions by modeling the superlattice
of polarons upon the 2D triangular basic lattice of all Ta
atoms by a classical charged lattice gas with a screened
repulsive Coulomb interaction among the particles. The
external pulse injecting the voids was simulated by in-
roducing a small random concentration of voids reduc-
ing the particles concentration \( \nu \) below the equilibrium
\( \nu_0 = 1/13 \) (some other experimentally relevant concen-
trations are briefly described in the Supplementary Ma-
terial, Sec. III). The subsequent evolution of the sys-
tem, including the passage through the thermodynamic
first order phase transition, was studied by means of the
Monte Carlo simulation. Surprisingly, this minimalistic
model is already able to capture the formation of domain
walls in a close visual resemblance with experimental ob-
servations and also to explain the effect qualitatively as
an intriguing result of the charge fragmentation.

THE MODEL

We model the system of polarons by a lattice gas of
charged particles on a triangular lattice. Each particle
represents the self-trapped electron in the middle of the
David star, thus the effective charge is \(-e\), which is com-
pensated by the static uniform positive background.

The external pulse is simulated by a small concentra-
tion of randomly seeded voids reducing the particles’ con-
centration below the equilibrium: \( \nu = \nu_0 - \delta \nu \). The inter-
action of polarons located at sites \( i, j \) is described by an
effective Hamiltonian \( H = \sum_{i,j} U_{ij} n_i n_j \) with repulsive
interactions \( U_{ij} \). Here the sum is over all pairs of sites
\( i \neq j; n_i = 1 \) (or 0) when particle is present (or absent)
at the site \( i \), and we choose \( U_{ij} \) as the screened Coulomb
potential

\[
U_{ij} = \frac{U_0 a}{|\mathbf{r}_i - \mathbf{r}_j|} \exp \left( -\frac{r - a}{l_s} \right),
\]

where \( U_0 = e^2 \exp(-a/l_s)/a \) is the Coulomb energy of
interaction of particles at neighboring sites in the Wigner
crystal state with the distance \( a = \sqrt{13}b \) between them
\( b \) is the lattice spacing of the underlying triangular lattice,
Fig. 1a), \( l_s \) is the screening length. We keep in mind also
the background uniform neutralizing positive charge.

SUPERLATTICE AND ITS CHARGED DEFECTS.

In the ground state, all particles living on the triangu-
lar lattice tempt to arrange themselves in also the trian-
gular superlattice, which is close-packed and most ener-
getically favorable in 2D\(^{12}\) (with some notable exceptions
for more exotic potentials\(^{13}\)). Since the concentration of
particles is 1/13, then the ground state is 13-fold degen-
erate with respect to translations (Fig. 1a). An addi-
tional mirror symmetry makes the ground state to be in
total 26-fold degenerate. But since within a given sam-
ple two mirror-symmetric phases do not coexist both in
the experiment\(^{14}\) and in the modeling for the sufficiently
slow cooling rates (because of the high energy of the cor-
responding twinning wall), then we consider only one of
them.

The simplest lattice defect is a void or a “polaronic
hole” (Fig. 1b) which is formed when the electron from
the intragap level is taken away or excited to the con-
duction band and soon the associated lattice distortions
vanish. The single void has the relative charge \(+e\) (keep-
ing in mind the background neutralizing charge) and the
Coulomb self-energy of the order \( E_{\text{void}} \approx e^2/a \). While
the void is a particular manifestation of a general notion
of vacancies in crystals, in our case there can be also a
specific topologically nontrivial defect – the domain wall
separating domains with a different 13-fold positional de-
egeneracy of the ground state (Fig. 2). The domain wall
cross-section resembles the discommensuration known in
CDW systems\(^{15}\).

Experimentally, the lattice defects can be introduced
via external pulses, by impurity doping or by the field
effect. For example, a laser or STM pulse can excite the
Mott-band electrons residing in the centers of the David
star clusters, creating an ensemble of voids. Since the
voids are charged objects, then at first sight they should
repel each other and form a Wigner crystal themselves.
But our modeling consistent with the experiment shows
that the voids rather attract one another at short dis-
tances and their ensemble is unstable towards formation
of domain walls’ net. Qualitatively, this instability can
be understood from the following argument. Compare

FIG. 1: (a) Underlying triangular lattice (with the period
\( b \)) of all Ta-atoms and the coloring scheme showing its 13
sublattices; in the ground state only one sublattice (with the
period \( a \)) is occupied. (b) Lattice with \( \nu = 1/13 \) con-
centration of polarons at presence of one void (the emptified "David
star"). The occupied polaronic sites, marked by red circles,
are surrounded by filled "David stars" which perimeters pass
through neighbors which positions are actually displaced in-
wards (not shown here).
energies of the isolated void and of the domain wall segment carrying the same charge. The minimal charge of domain wall per the translation vector \( \mathbf{a}_1 \) is \( +e/13 \) (Fig. 2a), and the energy of the wall’s segment carrying the charge \( +e \) can be estimated as for a uniformly charged line:

\[
E_{wall} \approx 13 \times \frac{(e/13)^2}{a} \ln(l_s/a),
\]

(2)

For moderate screening lengths \( l_s \), it is lower than the void’s self-energy \( E_{void} \), making energetically favorable to decompose the voids into fractionally-charged domain walls. The local effects beyond our model can also favor domain walls with other charges: for the single-step \( +e/13 \) domain wall there are anomalous sites where David stars intersect (Fig. 2a) which raises its energy and can make the double-step \( +2e/13 \) domain walls (Fig. 2b) to be energetically favorable.

\[\text{FIG. 2: Positively charged domain walls with charges per unit cell length } \mathbf{n}: (a) +e/13 ; (b) +2e/13. \text{ The whole sequence of domain walls can be obtained by consecutive displacements of the blue domain by the vector } \mathbf{b}_i \text{ as indicated in (a). In (a), the sites are encircled where David stars within the wall share the corners. Black asterisks designate the sites not belonging to any star.}\]

**NUMERICAL MODELING**

We simulated the cooling evolution of the classical lattice gas with the interaction potential (1) via Metropolis Monte Carlo algorithm (see Methods). We perform slow cooling from \( T = 0.07U_0 \), which is above the detected ordering phase transition (see below), down to \( T = 0.01U_0 \) with a step \( \Delta T = -0.0002U_0 \), reaching either a ground state or a very close in energy metastable state. Below we, first, consider undoped systems (where particles concentration \( \nu \) is exactly \( \nu_0 = 1/13 \)), and then systems doped by voids (with \( \nu = \nu_0 - \delta \nu = \nu_0 (1-\nu_{\text{voids}}) \)), where \( \nu_{\text{voids}} = \delta \nu/\nu_0 \) is the voids’ concentration. Results for another sign of doping are briefly presented in the Supplementary Material, Sec. III.

As a reference system we chose the sample with \( 91 \times 104 \) sites with the total a number of particles \( N_p = 728 \), which corresponds to the concentration \( \nu_0 = 1/13 \).

On cooling, the order-disorder phase transition takes place at \( T_c \approx 0.056U_0 \), below which the triangular superlattice is formed confirming the expectations for the Wigner crystal. Temperature dependencies of the order parameter \( M = \sqrt{\sum (m_i - 1/13)^2/13 \cdot 12} \), where \( m_i \) is the fraction of particles at \( i \)-th sublattice (Fig. 3a) and of the mean value of energy per particle (Fig. 3b) indicate that the transition is of the first order. The insets in the Fig. 3a show a plenty of defects just above \( T_c \), while only two displaced positions are left just below \( T_c \).

On heating, the order-disorder phase transition takes place at \( T \approx 0.063U_0 \), which agrees with our mean field analysis (see Supplementary Sec. II). With increasing \( l_s \), the temperature hysteresis and the tendency to overcooling become more pronounced. An overcooling or even freezing into a glass state feature is known for electronic systems with either a frozen disorder or a Coulomb frustrations\(^{16}\); however in the present model these both factors are absent – the effect is presumably due to only the long-range Coulomb interactions under the lattice constraints.

\[\text{FIG. 3: Temperature dependencies of integrated characteristics for the undoped system. (a) The order parameter; the insets show snapshots of configurations of the system just above and below the phase transition; (b) mean energy per particle. Blue symbols are for cooling and red symbols are for heating simulations.}\]

**Doped system.**

We emulate the doping (the charge injection) by seeding voids at random places and following the subsequent evolution. By global characterizations like those in Fig. 3, the order-disorder transition is preserved, while at a lower temperature. But locally the new mosaic ground
state with the net of domain walls is formed as we will demonstrate below.

Seeding at $T < T_c$ a small number of voids, down to two defects per sample, we observe that the single-void states are unstable with respect to their binding and progressive aggregation. Seeding more voids initiates their gradual coalescence into a globule of interconnected segments of domain walls. The resulting globule performs slowly a random diffusion over the sample while keeping closely its optimal shape and the structure of connections (the Supplementary Video of the system evolution under cooling and its description are presented in Supplementary Sec. I).

Figure 4a shows the low-$T$ configuration of system $130 \times 156$ system, where initially $N_p = 1544$ of particles (with the the corresponding concentration of voids $\nu_{\text{voids}} \approx 1.0\%$) were randomly seeded and then the system was slowly cooled from $T = 0.07U_0 > T_c$ down to $T = 0.01U_0$. In spite of the initial random distribution of particles over the whole sample, finally the voids aggregate into a single globule immersed into a connected volume of the unperturbed crystal. We compare the results of our modeling in Fig. 4a with the experimental picture in Fig. 4b. Similar patterns have been observed also in other experiments.\footnote{FIG. 4: Globule structures. (a) The present modeling for $\nu_{\text{voids}} \approx 1.0\%$ in the domain walls representation, $T = 0.01U_0$; (b) from experiments in\textsuperscript{8}.}

With a further increase of doping, the globule size grows over the whole sample, and finally the branched net of domain walls divides the system into the mosaics of randomly shaped domains (Fig. 5a,c). The comparison of the modeling with the experiment on injection by the STM pulses is shown between panels (a) and (b) in Fig. 4, between panels (a) and (b), (c) and (d) in Fig. 5. The figures visualize a spectacular resemblance of our pictures in Fig. 4a with the experimental results (see Supplementary Sec. III) and corresponding, for example, to the $\sqrt{3} \times \sqrt{3}$ surface CDW observed in the lead coated germanium crystal.\footnote{Note that similar “irregular honeycomb network” structures were predicted for incommensurate phase of krypton on graphite with $\nu_0 \approx 1/3$ and short-range interaction, but with less topological restrictions here.}

**DISCUSSION AND CONCLUSIONS**

Our simulations have shown an apparently surprising behavior: some effective attraction of voids develops from the purely repulsive Coulomb interactions. The coalescence of single voids starts already at their small concentration. For several voids seeded, we observe a gradual fusion of point defects into the globule of the domain walls. Increasingly branched net develops with augmenting of the voids concentration.

That can be understood indeed by noticing that the walls formation is not just gluing of voids but their fractionalization. The domain wall is fractionally ($q = \nu_0 e$) charged per its crystal-unit length, thus reducing the Coulomb self-energy in comparison with the integer-charged single void. Being the charged objects, the domain walls repel each other, but as topological objects they can terminate only at branching points, thus forming in-plane globules. Their repulsion at adjacent layers meets no constraints, hence the experimentally observed alternation of the walls’ patterns among the neighboring layers.\footnote{A similar while simpler doping induced phase transition to the state patterned by charged domain walls was predicted for for quasi-1D polycetylene-like systems with 2-fold degeneracy, see\textsuperscript{18}.}

Our modeling can be straightforwardly extended to other values of concentration $\nu_0$: like $\nu_0 = 1/3$ which is the minimal value where the pattern formation appears with qualitatively similar to the presented here results (see Supplementary Sec. III) and corresponding, for example, to the $\sqrt{3} \times \sqrt{3}$ surface CDW observed in the lead coated germanium crystal.\footnote{For another experimentally known case of $2H - \text{TaSe}_2$ where $\nu_0 = 1/9$ the modeling results are quite different: in some doping range we see a “stripe” phase (see Supplementary Sec. III), which indeed was experimentally observed in this material. The exception of the case $\nu_0 = 1/9$ is rather natural, because here the basis vectors of the superlattice and of the underlying triangular lattice are parallel to each other, which allows for the existence of neutral elementary domain walls.}

It is also possible to study the doping by electrons by seeding the interstitials rather than voids; here the new David stars substantially overlap with their neighbors giving rise to stronger lattice deformations, which may require for a more complicated model. The fragmentation with formation of walls is always confirmed while details of patterns can differ (see Supplementary Fig. 7).

The encouraging visual correspondence of our pictures with experimentally obtained patterns in different regimes of concentrations ensures a dominant role of the
universal model.

Methods

For numerical simulation of the classical lattice gas with interaction potential (1) we employed the Metropolis Monte Carlo method. We used the screening parameter $l_s = 4.5b \approx 1.25a$ and truncated the interactions to zero for sufficiently large interparticle distances (outside the hexagon with the side 24b). At each temperature we performed $\sim 10 - 40$ millions of Monte Carlo steps depending on the numerical experiment. Temperature was linearly lowered from $T = 0.07U_0$ down to $T = 0.01U_0$ with a step $\Delta T = -0.0002U_0$. The following system sizes and numbers of particles were chosen: size $91 \times 104$ and $N_p = 728$ for undoped system; size $130 \times 156$ and $N_p = 1544$, $\nu_{voids} \approx 1.0\%$ for the globule system (Fig. 4a); size $142 \times 164$ and $N_p = 1758$, $\nu_{voids} \approx 1.9\%$ for the net system (Fig. 5a,c). Periodic boundary conditions were imposed.

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Author contributions

S.B. and P.K. together formulated the theoretical concept, designed the model, analyzed results, and wrote the paper: P.K. performed the numerical computations. Correspondence and requests for materials should be addressed to P.K.

Additional information

The authors declare no competing financial interests.

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[1] Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazyev, O. V. & Kis, A. 2D transition metal dichalcogenides. Nat. Rev. Mater. 2, 17033 (2017).
[2] Rossnagel, K. On the origin of charge-density waves in select layered transition-metal dichalcogenides. J. Phys. Condens. Matter 23, 213001 (2011).
[3] Sipos, B., Kusmartseva, A. F., Akrap, A., Berger, H., Forro, L. & Tutis, E. From Mott state to superconductivity in 1T−TaS2. Nat. Mater. 7, 960-965 (2008).
[4] Stojchevska, L. et al. Ultrafast switching to a stable hidden quantum state in an electronic crystal. Science 344, 177-180 (2014).
[5] Vaskivskyi, I. et al. Fast electronic resistance switching involving hidden charge density wave states. Nat. Commun. 7, 11442 (2016).
[6] Yoshida, M. et al. Controlling charge-density-wave states in nano-thick crystals of 1T−TaS2. Scientific Reports 4, 7302 (2014).
[7] Gerasimenko, Y. A., Vaskivskyi I. & Mihailovic, D. Long range electronic order in a metastable state created by ultrafast topological transformation. arXiv:1704.08149 (2017).
[8] Ma, L. et al. A metallic mosaic phase and the origin of Mott-insulating state in 1T−TaS2. Nat. Commun. 7, 960-965 (2016).
[9] Cho, D. et al. Nanoscale manipulation of the Mott insulating state coupled to charge order in 1T−TaS2. Nat. Commun. 7, 10453 (2016).
[10] Svetin, D., Vaskivskyi I., Brazovskii S. & Mihailovic D. Three-dimensional resistivity switching between correlated electronic states in 1T−TaS2. Scientific Reports 7, 46048 (2016).
[11] Cho, D. et al. Correlated electronic states at domain walls of a Mott-charge-density-wave insulator 1T−TaS2. Nat.
[12] Bonsall, L. & Maradudin, A. A. Some static and dynamical properties of a two-dimensional Wigner crystal. *Phys. Rev. B* **15**, 1959 (1977).

[13] Jagla, E. A. Minimum energy configurations of repelling particles in two dimensions. *Journ. Chem. Phys.* **110**, 451-456 (1999).

[14] Shiba, H. & Nakanishi, K. in “Structural Phase Transitions in Layered Transition Metal Compounds”, ed. K. Motizuki (D. Reidel Publishing Company, Dordrecht, 1986).

[15] McMillan, W.L. Theory of discommensurations and the commensurate-incommensurate charge-density-wave phase transitions. *Phys. Rev. B* **14**, 1496-1502 (1976).

[16] Mahmoudian, S., Rademaker, L., Ralko, A., Fratini, S. & Dobrosavljevic V. Glassy Dynamics in Geometrically Frustrated Coulomb Liquids without Disorder. *Phys. Rev. Lett.* **115**, 025701 (2015).

[17] Villain, J. Commensurate-incommensurate transition of krypton monolayers on graphite: a low temperature theory. *Surface Science* **97**, 219-242 (1980).

[18] Karpov, P. & Brazovskii, S. Phase transitions in ensembles of solitons induced by an optical pumping or a strong electric field. *Phys. Rev. B* **94**, 125108 (2016).

[19] Carpinelli, J. M., Weitering, H. H., Plummer, E. W. & Stumpf, R. Direct observation of a surface charge density wave. *Nature* **381**, 398-400 (1996).

[20] Fleming, B. M., Moncton, D. E., McWhan, D. B. & DiSalvo F. J. Broken Hexagonal Symmetry in the Incommensurate Charge-Density Wave Structure of 2H – TaSe2. *Phys. Rev. Lett.* **45**, 576 (1980).
Supplemental Material.

Modeling of networks and globules of charged domain walls observed in pump and pulse induced states.

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The movie (https://www.dropbox.com/s/wv1eblnys3bm0da/suppl-movie.mp4) reflects the process of Monte Carlo (MC) cooling of the system, after several voids have been added to the ordered state below the transition temperature. This procedure differs from the one exploited to obtain the final states reported in the main text. There we always started from a random disordered state at $T > T_c$ in order to reach a better equilibration. The movie demonstrates two regimes in the course of the cooling: (1) merging of voids into a single big cluster seen as the globule of domain walls; (2) random diffusion of the cluster.

We start the simulation from the ordered system where 4 voids have been seeded by hands. (Fig. 1a shows the initial position) and cool it from $T = 0.036U_0$ down to $T = 0.010U_0$ with step $\Delta T = -0.0001U_0$, making at each temperature 10000 MC steps for higher temperatures ($T \geq 0.0310U_0$) or 50000 MC steps for lower temperatures ($T < 0.0310U_0$).

First, each of 4 voids very quickly disintegrates into a small cluster ("1-cluster"), and then begins a random diffusion (note, that periodical boundary conditions are imposed). Being the charged objects, the 1-clusters are repelled from each other. Nevertheless, if two 1-clusters overcome a potential barrier, they merge into a stable 2-cluster, this which lowers
the system energy (the qualitative explanation of this counterintuitive effect is given in the
main body of the paper). The first event of two 1-clusters merging happens at $T = 0.03548U_0$
after $\sim 52000$ MC steps (5-th second of the video).

After several collisions and unsuccessful coalescence attempts, the 2-cluster merges with
a 1-cluster at $T = 0.03407U_0$ (after $\sim 193000$ MC steps, 19-th second of the video). Final
merging to a single cluster happens shortly after that at $T = 0.03378U_0$.

Afterwards, the resultant big cluster performs a random diffusion through the sample.
After the 50-th second, the video is speeded up by the factor of 50. Figure 1b shows the
final position of the simulation.

We conclude that it is indeed energetically favourable and dynamically sustainable for
separate holes to merge into a single cluster.

II. ORDER-DISORDER PHASE TRANSITION: MEAN FIELD THEORY

In this section we present the mean field theory for the order-disorder phase transition for
an undoped system. Since the interactions are of the long-range nature and many particles
affect the given one, we expect mean-filed theory to be a good approximation.

At $T = 0$, perfectly ordered state is observed, where all particles occupy the same sublattice
(one of the 13 equivalent sublattices, not counting for the mirror symmetry, as discussed
in the main text). With gradually increasing the temperature, at some critical temperature
$T = T_c$ order momentarily breaks.

In order to determine $T_c$ we consider a simplified version of the model, dividing the whole
system into closely packed David stars, and allowing for each particle to occupy only one of
13 sites of its David star (Fig. 2). This simplification will lead to a slight overestimation for
$T_c$.

Since the energy $\Delta_1$ ("gap") to excite a particle from its regular position in the David
star center to the first coordination sphere is several times less than the analogous energy
for the second coordination sphere $\Delta_2$ (for example, for the studied in the main text case
$l_s = 4.5b$ we have found $\Delta_1 \approx 0.442U_0$, $\Delta_2 \approx 1.993U_0$). Then taking into account only 1-st
coordination sphere seems to be a reasonable first approximation and we arrive at a simpler
model with only 7 possible states for each particle.

Consider a particle in the mean field of other particles. Let $(s_0, s_1)$ be the occupation
One of the ground states of the system, where particles (red circles) occupy the same sublattice. 1-st, and 2-nd coordination spheres for a given particle (“0”) are shown.

numbers of the 0-th and the 1-st coordination spheres respectively. In the ground state we have \( s_0 = 1, s_1 = 0 \); in the excited state \( s_0 = 0, s_1 = 1 \). Introduce the order parameter

\[
m = \frac{7}{6} \langle s_0 - \frac{1}{7} \rangle,
\]

so in the ordered phase \( m = 1 \), in the disordered phase \( m = 0 \). Since on average only those particles that occupy the given sublattice try to keep the particle in the same sublattice, we use the following “temperature-dependent gap” \( \Delta(T) = \Delta_1 \cdot m(T) \). The one-particle mean-field Hamiltonian \( H = s_1 \Delta_1 m(T) \), gives rise to the partition function \( Z(T) = 1 + 6e^{-\Delta_1 m/T} \).

From the self-consistency condition (1), we get

\[
m = \left( 1 - \frac{7}{6} e^{-\Delta_1 m/T} \right) / Z \text{ or }
\]

\[
m = \frac{1 - e^{-m\Delta_1/T}}{1 + 6e^{-m\Delta_1/T}}
\]

Expanding RHS of (2) to the first order in \( m \) we get \( m = m\Delta_1/7T + o(m) \), which yields to the critical temperature

\[
T_c = \frac{\Delta_1}{7}.
\]

For \( l_s = 4.5b \) we have \( \Delta_1 \approx 0.442U_0 \), and formula (3) gives us \( T_c \approx 0.0631U_0 \), which is very successfully compared with the Monte Carlo simulation result on heating: \( T_c \approx 0.0630U_0 \).

We conclude that the mean field theory is in a very good agreement (within 0.5%) with the results of the simulation. This is rather natural because for the screened Coulomb long-range interaction many coordination spheres of particle’s neighbors contribute to the mean field for a given particle (this fact is incorporated into the definition of the excitation energy \( \Delta_1 \)).
III. RESULTS FOR DIFFERENT VALUES OF CONCENTRATION \( \nu_0 \)

First we give the classification of filling factors on a triangular lattice, and then analyze some representative cases. Figure 3 shows ordinal numbers of neighbors for a given particle (black) – 1 corresponds to the nearest neighbor, 2 to the next-nearest neighbor etc. Knowledge of where the particle’s nearest neighbor sits determines the whole superstructure. Table I presents the correspondence between the number of the occupied sublattice and the concentration of the particles. The third column of the table shows, whether the superlattice possesses only charged domain walls or not: this is connected to the fact, whether the basis vectors of the superlattice are parallel to the basis vectors of the underlying triangular lattice. This is the key factor, determining the domain walls’ patterns in doped systems. The forth column shows, whether the superlattice possesses two different sectors of ground states, which can not be obtained one from another by only a translation – in this case the mirror symmetry is also needed.

In the further subsections we briefly discuss several experimentally accessible cases, with the concentrations \( \nu_0 = 1/3, 1/9, \) or \( 1/13. \)

| # of neighbor | concentration \( \nu_0 \) | only charged domain walls? | two mirror symmetric sectors? |
|---------------|--------------------------|-----------------------------|-------------------------------|
| 2             | 1/3                      | yes                         | no                            |
| 3             | 1/4                      | no                          | no                            |
| 4             | 1/7                      | yes                         | yes                           |
| 5             | 1/9                      | no                          | no                            |
| 6             | 1/12                     | yes                         | no                            |
| 7             | 1/13                     | yes                         | yes                           |
| 8             | 1/16                     | no                          | no                            |
| 9             | 1/19                     | yes                         | yes                           |
| 10            | 1/21                     | yes                         | yes                           |
A. $\nu_0 = 1/3$

Concentration $\nu_0 = 1/3$ is the minimal case, where we observe qualitatively similar patterns as for $\nu_0 = 1/13$. There is, however, an important distinction: single holes are much more stable here and some threshold holes concentration is necessary for the first globule creation. This case corresponds, for example, to Pb on Ge surface charge density wave\textsuperscript{1}.

B. $\nu_0 = 1/9$

In the case $\nu_0 = 1/9$ the minimal domain walls are neutral, because unit vectors of the superlattice and of the underlying triangular lattice are parallel to each other for this concen-
tration, so the results are qualitatively different from 1/3 and 1/13 cases. Which connectivity is more favorable (stripe or network) depends on the sign of wall-crossing energy. Interestingly the “stripe” phase is experimentally observed on heating of \( \nu_0 = 1/9 \) commensurate charge density wave in \( 2H - \text{TaSe}_2 \), see \(^3\).

**FIG. 5.** \( \nu_0 = 1/9 \): domain representation for the “stripe” phase for with positive doping. Here we use 9-coloring scheme (only 3 of them appear on the figure), analogous to 13-coloring scheme used in the main text.

C. \( \nu_0 = 1/13 \)

The case of positive doping was considered in the main text; Fig. 6a,b shows the full-size version of Fig. 5a,c of the main text.

Here we also extend the results of the main text to the case of the electons’ doping which accumulate into interstitials rather than voids (Fig. 7). For negative doping we still observe the charge fractionalization phenomena and qualitatively similar to the case of positive doping structures. The wall crossings are still favorable (thus no “stripe phase”), but connection of 4 walls is also favorable as of 3 walls, which is presumably governed by the short-range physics. Because of this, visually the pictures look differently.

For higher \( l_s \), the long-range part of the Coulomb interaction will become progressively more important and will favor walls’ 3-crossings, with 120° angle between them because of their repulsion, at least for sparse walls’ networks (when the walls’ structure characteristic period is \( \gg l_s \)). Thus we expect that the metastable states with the lowest lying energies
will represent the “irregular honeycomb network”\textsuperscript{4} as observed for the positive doping.

![Diagram](image)

FIG. 6. $\nu_0 = 1/13$: net structure for positive doping: full-sized version of Figure 5 from the main text. (a) Domain wall representation; (b) domain representation

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\textsuperscript{1} J. M. Carpinelli, H. H. Weitering, E. W. Plummer, and R. Stumpf, Direct observation of a surface charge density wave. \textit{Nature} \textbf{381}, 398-400 (1996).

\textsuperscript{2} P. Bak, Commensurate phases, incommensurate phases and the devil’s staircase. \textit{Rep. Prog. Phys.} \textbf{45}, 587-629 (1982).

\textsuperscript{3} R. M. Fleming, D. E. Moncton, D. B. McWhan, and F. J. DiSalvo, Broken Hexagonal Symmetry in the Incommensurate Charge-Density Wave Structure of $2H$ – TaSe\textsubscript{2}. \textit{Phys. Rev. Lett.} \textbf{45}, 576 (1980).

\textsuperscript{4} J. Villain, Commensurate-incommensurate transition of krypton monolayers on graphite: a low temperature theory. \textit{Surface Science} \textbf{97}, 219-242 (1980).
FIG. 7. $\nu_0 = 1/13$: net structure for negative doping, $\nu_{\text{interst}} \approx 1.8\%$, $l_s = 4.5b$, $T = 0.01U_0$: (a) domain wall representation; (b) domain representation.