Wigner crystallization in Na₃Cu₂O₄ and Na₈Cu₅O₁₀ chain compounds

P. Horsch, M. Sofin, M. Mayr, and M. Jansen

1Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

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We report the synthesis of novel edge-sharing chain systems Na₃Cu₂O₄ and Na₈Cu₅O₁₀, which form insulating states with commensurate charge order. We identify these systems as one-dimensional Wigner lattices, where the charge order is determined by long-range Coulomb interaction and the number of holes in the d-shell of Cu. Our interpretation is supported by X-ray structure data as well as by an analysis of magnetic susceptibility and specific heat data. Remarkably, due to large second neighbor Cu-Cu hopping, these systems allow for a distinction between the (classical) Wigner lattice and the 4k_F charge-density wave of quantum mechanical origin.

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The role of strong electron correlations and the concomitant appearance of spatially modulated charge structures constitutes a central issue in current solid state physics. The most prominent example are charge stripes in high-T_c superconductors, which have been discovered first as static modulations in the CuO₂ planes of La₁₋ₓNdₓSrₓCuO₄. The high-T_c enigma has at the same time stimulated the flourishing field of low-dimensional cuprates composed of Cu-O chains and ladders with the hope to gain new insights overlooked so far in the layered cuprates. One important aspect is the role of long-range Coulomb interaction in strongly correlated systems, which gives rise to metal/insulator stripe structures in organic charge-transfer compounds. Following a recently discovered new route in the synthesis of alkalioxometallates, we were able to synthesize several members of a new class of quasi-1D cuprates Na₁₊ₓCuO₂. These intrinsically doped edge-sharing chain systems provide a unique opportunity to study the condensation of charge order (CO) at high temperature and the formation of spatially modulated Heisenberg spin systems at low temperature. Edge-sharing chains are also building blocks of the intensively studied Sr₁₋ₓCaₓCu₂O₄₊₁ system; due to exchange of electrons with ladders, however, the degree of doping is difficult to determine. Here, we argue that these doped chains can be understood as realizations of one-dimensional Wigner lattices (WL), as introduced by Hubbard in the late 70’s in connection with TCNQ charge transfer salts. He suggested that the distribution of electrons is controlled by the Coulomb interaction rather than by the kinetic energy (band width), such that they form a generalized Wigner lattice on the underlying TCNQ chain structure. This view suggests a strikingly different nature of charge excitations, namely as domain walls with fractional charge rather than particle-hole excitations as in common metals and semiconductors. Hubbard’s proposal, however, can be challenged on the grounds that the resulting periodicity of charge modulation can alternatively be explained by a 4k_F charge density wave (CDW) arising from short-range interactions alone and an instability of the Fermi surface, where k_F denotes the Fermi momentum.

The edge-sharing arrangement of CuO₂ squares meets the WL criterion of small band width in an optimal way due to the almost 90° Cu-O-Cu bonds (Fig.1). Unexpected complexity is added because, apart from a small nearest-neighbor hopping matrix element t₁, there is also a second neighbor hopping t₂, which is larger as a consequence of the structure. While this unusual feature does not affect the classical WL order imposed by the Coulomb interaction, it changes the Fermi surface topology, and thereby allows to distinguish the WL from the CDW on the basis of the modulation period.

These systems provide a first example where an unambiguous distinction between the generalized WL and a Fermi surface related 4k_F CDW is possible. We also show that for these edge-sharing compounds even the magnetic and thermodynamic properties can only be explained by invoking a WL ground state emerging from the truly long-ranged Coulomb interaction.

Samples were prepared by the azide/nitrate route. As a source for the alkalimetal component, mixtures of the respective alkali azides and nitrates (or nitrites) are used instead of the alkalioxides. Conveniently, besides the metals’ ratio, also the oxygen content and thus the degree and kind of doping of the desired product can be effectively controlled using the weighed portions of the starting materials. Following this procedure the title compounds Na₃Cu₂O₄ (x = 1/2) and Na₈Cu₅O₁₀ (x = 3/5) have been prepared as microcrystalline, pure phases in gram-amounts. The new oxocuprates (II/III) belong to the compositional series Na₁₊ₓCuO₂, with the end members NaCuO₂ and the still elusive Na₂CuO₂. The most prominent structural feature, common to all representatives known thus far, is a one-dimensional polyanion CuO₂⁻ constituting of CuO₂-square units sharing edges in trans-position. These anionic entities are embedded by sodium ions which achieve coordination numbers of 4-6 with Na-O bond lengths ranging from 227 to 279 pm. The geometric data as determined by single crystal structural analyses give clear evidence for a
CO at the Cu sites (Fig. 1). Based on the Cu to O bond lengths, one can unambiguously distinguish Cu$^{3+}$ and Cu$^{2+}$ sites. The way of linking the primary structural units together with the variations of the copper to oxygen distances inevitably leads to deviations of the O-Cu-O angles from the ideal 90°. As monitored by differential scanning calorimetry measurements CO disappears above the WL melting temperature $T_m = 455$ and 540 K for Na$_3$Cu$_2$O$_4$ and Na$_3$Cu$_2$O$_{10}$, respectively. DC and AC conductivity measurements show also a clear transition from an Arrhenius behaviour below $T_m$ to an almost temperature independent conductivity regime above $T_m$.

For a theoretical analysis one has to recognize that Cu$^{2+}$ is in a $d^9$ configuration with spin 1/2, while Cu$^{3+}$ is in a $d^8$-ligand hole ($d^0L_h$) state, also known as Zhang-Rice singlet state [13]. In contrast to high-$T_c$ cuprates the edge-sharing geometry (Fig. 1(a,b)) leads to strongly reduced hopping matrix elements. This sets the stage for the long-range Coulomb force as dominant interaction

$$H_{Coul} = U \sum_i n_{i,\uparrow} n_{i,\downarrow} + V \sum_{i,j} n_{i,\sigma} n_{j,\bar{\sigma}},$$

where the on-site interaction $U$ suppresses charge fluctuations involving Cu$^{1+}$ ($d^{10}$) configurations. Here we associate the $d^0L_h$ ($d^9,d^{10}$) ionization state with 0 (1,2) electrons, respectively, and $n_{i,\sigma}$ ($\sigma = \uparrow, \downarrow$) counts the number of electrons with spin $\sigma$, while $n_i = n_{i,\uparrow} + n_{i,\downarrow}$. The Coulomb interaction $V_l$ in general is screened by the polarization of neighbouring chains as well as by core electrons [8]. Here we assume a generic Coulomb law $V_l = \frac{\lambda}{r_l^3}$, $l = 1, 2, ..., L$. Crucial for the following is that the interaction is long ranged and convex, i.e., $V_{l''} = V_{l-1} - 2V_l = V_{l+1} > 0$.

![FIG. 1: Structure of edge-sharing copper-oxygen chains along $b$-direction in Na$_3$Cu$_2$O$_4$ (a) and Na$_3$Cu$_2$O$_{10}$ (b), where Cu$^{2+}$ and Cu$^{3+}$ are marked by green and red circles, and O$^{2-}$ (Na$^+$) by large blue (grey) circles, respectively. (c) View on the a-c plane of Na$_3$Cu$_2$O$_4$. For convenience we introduce a cartesian system $a', b' || b, c'$ in addition to crystallographic coordinates.](image)

For commensurate doping concentration $x = m/n$ the interaction $V_l$ selects a particular CO pattern [8]. This pattern is immediately obvious for filling fractions $x = 1/2$ and 3/4 (Fig. 2(a-d)), which involve an equidistant arrangement of the Cu$^{3+}$ sites (red circles in Fig. 2). For a general ratio $x = m/n$ this leads to complex structures with unit cell size $n$ (in units of the Cu-Cu distance $b' = 1$). In case of $x = 3/5$ we encounter in Fig. 2(b) the charge order observed for Na$_3$Cu$_2$O$_{10}$. Charge localization, however, is not perfect in Wigner insulators as electrons still undergo virtual transitions to neighboring sites (Fig. 2(a,b)) in order to retain partially their kinetic energy. The energy of the lowest excitations and the impact of kinetic energy depend strongly on $x$, e.g., the energy of the excitation in Fig. 2(a) relative to the ground state Fig. 2(a) is $V''_1$ while the excitation for $x = 3/5$ in Fig. 2(b) is $V''_5$ about an order of magnitude smaller. To investigate the role of kinetic energy we explore the dynamics of electrons starting from the 1D Hubbard-Wigner model $H_{HW} = H_{Coul} + H_{Kin}$ [8], where

$$H_{Kin} = - \sum_{i,l,\sigma} t_l (c_{i+l,\sigma}^+ c_{i,\sigma} + c_{i,\bar{\sigma}}^+ c_{i+l,\bar{\sigma}})$$

describes the hopping of an electron with spin $\sigma$. Due to the almost 90° Cu-O-Cu angle the hopping $t_1$ between nearest neighbor Cu sites results mainly from direct $d-d$ exchange, while $t_2$ originates from hopping via a Cu-O-Cu path [15] (Fig. 1), leading to the remarkable fact $|t_2| > |t_1|$. We adopt here as typical values $t_1 \sim 63$.
lead to a singularity in the charge susceptibility

can be determined by disregarding spin degrees of fre-

\[ q_w = 1.2\pi \] (solid line as guide to the
eye). Inset shows the temperature dependence of \( S_c(q_w) \). (b) Comparison of
electron dispersions for a system with nearest
neighbor hopping \( t_1 = 1 \) (dashed line) and for \( t_1 = 1, t_2 = 1.5 \) (solid line) with the Fermi energy indicated by
a horizontal line. (c) While the charge susceptibility \( \chi^c(q) \)
for noninteracting spinless fermions in the \( t_1 \) model shows a
logarithmic divergence at \( 2k_{SF} = q_w \), the singularities of
the \( t_1-t_2 \) model are at different momenta.

FIG. 3: (color online) (a) Static charge structure factor \( S_c(q) \)
calculated for interacting spinless fermions and \( t_1 = 0.04\text{V},
\ t_2 = 0.06\text{V at } x = 0.6 \) indicates the instability towards WL
ordering with modulation \( q_w = 1.2\pi \) (solid line as guide to the
eye). Inset shows the temperature dependence of \( S_c(q_w) \). (b)
Comparison of electron dispersions for a system with nearest
neighbor hopping \( t_1 = 1 \) (dashed line) and for \( t_1 = 1, t_2 = 1.5 \) (solid line) with the Fermi energy indicated by
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the \( t_1-t_2 \) model are at different momenta.

meV, \( t_2 \approx 94 \text{ meV} \), derived from ab-initio band structure
calculations for the Cu\( ^{2+} \) edge-sharing reference system
Li\( _2\)CuO\( _2 \)[16]. These values are indeed much smaller than
our estimates for \( U \approx 3.8 \text{ eV} \) and \( V \approx 1.5 \text{ eV} \) based on
optical data for Li\( _2\)CuO\( _2 \)[12].

Using exact diagonalization we have calculated the
static structure factor \( S_c(q) \) for chains up to 25 sites.
The peaks of \( S_c(q) \) at \( q_w = 1.2\pi \) (and at \( 0.8\pi = 2\pi - q_w \))
are characteristic for a WL modulation at \( x = 3/5 \) (Fig.
3(a)). Since the magnetic energy scale is much smaller
than the Coulomb interaction \( V \), the charge structure
can be determined by disregarding spin degrees of free-
don, namely in terms of spinless fermions (SF). The SF-
CDW arises as an instability due to low energy scattering
between the two Fermi points at \( \pm k_{SF} \) which
lead to a singularity in the charge susceptibility \( \chi^c(q) \) at
\( q = 2k_{SF} = 4k_F \). Subsequent inclusion of interactions
is expected to change the character of a singularity, yet
not the momentum at which the singularity occurs. This
explains the origin of the \( 4k_F \) CDW instability in inter-
acting 1D systems and, as \( 4k_F = 2\pi m/n \), the coincidence
with the modulation period \( n \) of the WL.

The equivalence of WL and CDW periodicity disap-
pears when \( t_2 > \alpha t_1 \) (\( \alpha = 0.38 \) at \( x = 0.6 \)); then there are
four instead of two Fermi points leading to new singular-
ities in \( \chi^c(q) \) (Fig.3(b,c)) and to a shift of the original
singularity away from \( 4k_F = q_w \). In this case the stan-
dard tools of many body theory such as bosonization[11]
suggest a change of the modulation period. This, how-
ever, is not reflected in the experiment and is also not ob-
served in our numerical results for \( S_c(q) \) (Fig. 3(a)). In
fact, the singularity remains at \( q_w \) up to a value \( t_2 \approx 4t_1 \), a
striking manifestation that the structure is robust and
controlled by the long range Coulomb interaction[17].
The calculated \( S_c(q) \) shows besides the main peak at \( q_w \)
a weak higher harmonic feature at \( q = 2q_w - 2\pi \), con-
sistent with the relative intensities of structural reflexes
calculated from the experimentally determined Cu ion
positions (vertical bars in Fig. 3(a)). Further results (in-
set Fig.3(a)) reveal that WL correlations persist up to
temperatures \( k_BT \approx 0.05\text{V} \), consistent with experiment.

The magnetic susceptibility \( \chi(T) \) was measured in
the temperature range from 5 K to 350 K using a SQUID
magnetometer. The data (Fig. 4(a)) reveal strikingly dif-
ferent temperature dependences for the two compounds:
\( \chi(T) \) for Na\( _3\)Cu\( _2\)O\( _4 \) displays some similarity with a near-
est neighbor Heisenberg antiferromagnetic chain[13],
whereas the Na\( _6\)Cu\( _6\)O\( _{10} \) data show continuous increase
down to low temperature until its maximum near 25 K is
reached. Both systems reveal antiferromagnetic correla-
tions, yet magnetic order is observed only for Na\( _3\)Cu\( _2\)O\( _4 \)
at \( T_N = 23.5 \text{ K} \). A calculation of \( \chi(T) \) as we assume that
the spins remain fixed at their positions \( \mathbf{R}_i \) as given by
the structural analysis and by \( H_{HW} \) (Fig.2). This leads
to a generalized Heisenberg model

\[ H_{Heis} = \frac{1}{2} \sum_{i,j} J(R_i - R_j)\mathbf{S}_i \cdot \mathbf{S}_j, \]

where the exchange constants depend on the distance
\( |R_i - R_j| \) between the spins and on the direction (paral-
el to the chains or perpendicular). For \( x = 0.5 \) only the
exchange constants \( J_2, J_4, \) along the chains contribute,
while for \( x = 0.6 J_1, J_2, J_3, \ldots \) are relevant. Apart from
the modulated spin pattern, superexchange[13] in WL’s
shows further novel features, namely fluctuations (a) of
spin positions and (b) of antiferromagnetic exchange
integrals \( J_1 \sim 4t_1^2/(U + \Delta(V)) \) due to the low energy charge
fluctuations. The energy shifts \( \Delta(V) \) due to \( V \) depend
on the WL structure, and are in general different for
left (right) scattering processes (see Fig. 2(b)). The ex-
change constants may be estimated from the parameters
specified above. The largest coupling is \( J_2 \approx 100 - 200 \)
K resulting from superexchange via a Cu-O-O-Cu path.
Because of the almost 90° Cu-O-Cu bond angle (13) \( J_1 \)
exchange is smaller. Yet in the case of \( J_1 \) there are addi-
tional exchange contributions, which have to be taken
into account. The most important of these involve O
\( p_\pi \) configurations with Hund interaction on oxygen[20],
such that the total \( J_1 \) may become negative.

We have used finite temperature diagonalization
(FTD) [21] to calculate \( \chi(T) \) for Na\( _3\)Cu\( _2\)O\( _4 \) studying
chains up to \( N = 48 \) sites (24 spins). Good agreement
with experiment was achieved with \( J_2 = 172, J_3 = 17 \text{ K} \)
and 1.97 for the g-factor. The small antiferromagnetic in-
terchain coupling \( J' = 34 \text{ K} \) (Fig. 4(b)) is frustrating as
interpreted as a crossover between two regimes. While chains turn out to be ferrimagnetic, calculation of a double chain was necessary to account for the interchain interactions used in the calculation of $\chi(T)$: For $\text{Na}_8\text{Cu}_5\text{O}_{10}$ (b) the magnetic exchange $J'$ is frustrated due to triangular coordination, while it is not frustrated for $\text{Na}_5\text{Cu}_2\text{O}_4$ both along $a'$-direction (c) and $c'$-direction (d).

The correlations on $b'$ chains are antiferromagnetic. The interaction $J'$ has been taken into account in a mean-field approach. The magnetic exchange $J'$ is the result for a single chain, while $z'$ counts the number of spins on neighboring chains ($z' = 4$). The frustrated geometry implies a spin gap $\Delta_{s}$. For the present parameter set we obtain $\Delta_{s} \sim 4$ K, consistent with our analysis of the specific heat data. A thorough analysis of the Curie contribution, using specific heat and susceptibility data independently, reveals that there are about $\sim 1\%$ impurities per Cu ion present in both $\text{Na}_8\text{Cu}_5\text{O}_4$ and $\text{Na}_5\text{Cu}_2\text{O}_{10}$.

In the case of $\text{Na}_8\text{Cu}_5\text{O}_{10}$ the correlations along the $b'$ chains turn out to be of ferrimagnetic nature. A full FTD calculation of a double chain was necessary to account for the AF interchain exchange $J'$ along $c'$-direction (Fig. 4(d)), while the coupling of chains along $a'$-direction (Fig. 4(c)) was treated within mean-field. This implies ferrimagnetic $a'$-$b'$ planes, which are antiferromagnetically coupled along $c'$-direction. A satisfactory description was found for $J_1 = -22$ K, $J_2 = 113$ K, $J' = 21$ K and $g = 2.0$. The ferromagnetic interaction $J_1$ is the origin of the strong enhancement of $\chi(T)$ in the $x = 0.6$ system. The reduced value of $J_2$ can be explained by low-energy charge fluctuations (Fig. 2(b)), which involve a fluctuation of spin positions, i.e., $J_{2ff}^{m} \approx (1 - p)J_2 + pJ_1$ and a larger probability $p$ than for $x = 1/2$.

The strong variation of $\chi(T)$ in $\text{Na}_8\text{Cu}_5\text{O}_{10}$ should be interpreted as a crossover between two regimes. While at high temperature $\chi(T)$ is controlled by the individual spins, at low temperatures only effective spins 1/2, formed by three spins which are coupled by the largest interaction $J_3$, are relevant (Fig. 2(b)). The composite nature of the effective spins and their internal energy level structure becomes relevant in the intermediate temperature region. The interaction between these effective spins is renormalized to $J_{1ff}^{eff} = \frac{1}{5}[J_1 - J_3 + \frac{3}{4}J_5]$. Thus, the peculiar low-T behavior of $\chi(T)$ is controlled by an interplay of the small $J_{1ff}^{eff}$ between effective spins, resulting from WL order, and the interchain interactions.

Finally, the new compounds provide a unique opportunity to study the competition between two entirely different states, the classical WL dictated by the long-range Coulomb interaction and the CDW of quantum mechanical origin, i.e., resulting from a Fermi surface instability. These materials highlight the importance of long-range Coulomb interaction in strongly correlated systems, and provide a one-dimensional test ground for the study of charge stripe formation.

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![Fig. 4](image-url) (color online) (a) Temperature dependence of susceptibility $\chi(T)$ for $\text{Na}_8\text{Cu}_5\text{O}_4$ and $\chi/T$ for $\text{Na}_8\text{Cu}_5\text{O}_{10}$. Multiplication by $1/3$ in the latter case provides a comparison per spin. Theoretical results calculated by FTD are indicated by lines (exchange constants are given in the text). Sketch of interchain interactions used in the calculation of $\chi(T)$: For $\text{Na}_8\text{Cu}_5\text{O}_4$ (b) the magnetic exchange $J'$ is frustrated due to triangular coordination, while it is not frustrated for $\text{Na}_5\text{Cu}_2\text{O}_4$ both along $a'$-direction (c) and $c'$-direction (d).

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