Charge ordering in \( \theta-(\text{BEDT-TTF})_2\text{X} \) materials

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We investigate theoretically charge ordered states on the anisotropic triangular lattice characteristic of the \( \theta-(\text{BEDT-TTF})_2\text{X} \) materials. Using exact diagonalization studies, we establish that the charge order (CO) pattern corresponds to a “horizontal” stripe structure, with \( \ldots 1100 \ldots \) CO along the two directions with larger electron hopping (p-directions), and \( \ldots 1010 \ldots \) CO along the third direction (c-direction). The CO is accompanied by co-operative bond dimerizations along all three directions in the highest spin state. In the lowest spin state bonds along the p-directions are tetramerized. Our theory explains the occurrence of a charge-induced high temperature transition as well as a spin gap transition at lower temperature.

KEYWORDS: charge ordering, charge-density wave, BEDT-TTF, spin gap, superconductivity

Ground states involving spatially inhomogeneous charge distributions have in recent years been observed in a wide range of novel electronic solids, particularly in reduced dimensions. In the case of the organic charge-transfer solids (CTS), it has been suggested that the appearance of charge-order (CO) may be related to superconductivity.\textsuperscript{1,2} In the present Letter, we focus on CO within one particular class of the CTS, the \( \theta-(\text{ET})_2\text{X} \) materials (here ET is short for BEDT-TTF). The \( \theta-(\text{ET})_2\text{X} \) materials are particularly interesting for several reasons: (i) many detailed experimental studies have been performed; (ii) some members (e.g., the \( X = I_3 \text{ salt} \)) of this class of CTS are superconducting; and (iii) the structure of the ET conducting layer is fully two dimensional (2D), implying that standard single-particle theories of broken symmetry based on nesting are invalid. In this Letter we present exact numerical many-body calculations establishing that the CO within the \( \theta-(\text{ET})_2\text{X} \) materials is a combined bond-charge density wave (BCDW) state exhibiting a 2D extension of the “\( \ldots 1100 \ldots \)” type CO and BCDW that we have previously shown exist in a wide variety of quasi-one dimensional CTS.\textsuperscript{1} The 2D bond distortions of this state also explain the spin gap seen at low temperatures in the \( \theta-(\text{ET})_2\text{X} \).

The structure of the 2D conducting layer in the \( \theta \)-type materials is shown in Fig. 1. We briefly review the experimental results, focusing on the most widely investigated \( \theta-(\text{ET})_2\text{MM}'(\text{SCN})_4 \) materials. Here M is any of the monovalent cations Rb, Tl and Cs, while M’ is one of the divalent cations Co and Zn. Slowly cooled \( \theta-\text{RbZn} \) exhibits a metal-insulator (M-I) transition at 190 K that is accompanied by a period doubling along the c-direction.\textsuperscript{5,6} Direct evidence for CO was found from NMR studies in this material, although the actual pattern of CO was not discussed.\textsuperscript{7} From analysis of the \( ^{13}\text{C} \) NMR line shapes, Chiba et al. have concluded that the CO in \( \theta-\text{RbZn} \) corresponds to the horizontal stripe structure (see Fig. 2(c)).\textsuperscript{8} A similar conclusion was reached also from the analysis of the reflectance spectrum.\textsuperscript{9} The 190 K transition has no effect on the magnetic susceptibility, but a spin-singlet phase is obtained in this material below 30 K.\textsuperscript{5,7,10} The lower temperature transition has been widely referred to as a spin-Peierls (SP) transition.\textsuperscript{6}

In \( \theta-\text{RbCo} \), the M-I transition also occurs at 190 K and again there is a second transition (below about 40 K) to a spin singlet state.\textsuperscript{5,6} Crystal structure analysis gave clear evidence of dimerization along the c-direction\textsuperscript{11} below this temperature. Importantly, since the dimerization in the c-direction has already occurred at the M-I transition this dimerization cannot itself be the origin of the spin gap.

The \( \theta-\text{TIZn} \) material is already semiconducting at room temperature, but a resistive anomaly is seen at 165 K that may be accompanied by a lattice dimerization along the c-direction.\textsuperscript{5} Evidence for short-range dimerization has been also found in \( \theta-\text{CsCo} \) at the resistive transition, which, however, occurs at a much lower temperature of 20 K.\textsuperscript{11,12} In \( \theta-\text{CsZn} \), NMR measurements have suggested a phase transition to a CO state near 20 K.\textsuperscript{13} Finally, a different \( \theta-(\text{ET})_2 \) material, \( \theta-(\text{ET})_2\text{Cu}_2(\text{CN})_2[\text{N(CN)}_2]_2\), is also of interest in the present context. This material shows a semiconductor to semiconductor transition at 220 K that is accompanied by a weak lattice dimerization along the c-direction.\textsuperscript{14} No magnetic anomaly is seen at this temperature. Below
about 50 K there is a rapid drop in the spin susceptibili-
ity, while the lattice dimerization along the c-direction gets stronger.\textsuperscript{14}

Summarizing the experimental data, the most notable features are (a) the existence of two transitions, one in-
volving charge at high temperatures and the other in-
volving spin at low temperatures; (b) where clear ev-
idence exists, the horizontal stripe charge order (see Fig. 2(c)) is found; and (c) lattice dimerization along the c-direction occurs already at the M-I transition and therefore involves the charge degrees of freedom. We emphasize that the dimerization along the c-direction must necessarily involve distortions of intermolecular distances, and not just charge modulation, since ordinary (as opposed to anomalous) X-ray scattering experiments determine only bond modulations and not site charge modulations.\textsuperscript{15} The origin of the magnetic transition remains an open question, since the dimerization that appears at high temperature cannot itself produce a spin gap at lower temperature.

Both Seo\textsuperscript{16} and McKenzie et al.\textsuperscript{17} have proposed models for the charge ordering in \( \theta \)-ET (ET). Following these authors and our own previous work,\textsuperscript{1} we investigate the electronic properties of the ET layer using the extended Hubbard model:

\[
\begin{align*}
H &= H_0 + H_{ee} \\
H_0 &= - \sum_{\langle ij \rangle, \sigma} t_{ij} c_{i,\sigma}^\dagger c_{j,\sigma} \\
H_{ee} &= U \sum_i n_{i,\uparrow} n_{i,\downarrow} + V \sum_{\langle ij \rangle} n_i n_j
\end{align*}
\]

In the above, \( i, j \) are site indices, \( \cdots \) implies nearest neighbors, \( n_{ij} = n_{i,\uparrow} + n_{j,\downarrow} \), and \( \sigma \) is spin. The average number of electrons (or holes) per site \( \rho \) equals \( \frac{1}{2} \) for these \( \frac{3}{2} \)-filled materials. In accordance with extended Hückel calculations,\textsuperscript{5} we consider \( t_c < 0, t_p > 0 \), and \( |t_c| \ll |t_p| \) within Eq. 1. However, we expect \( V_p \) and \( V_c \) to be roughly the same size, since while the hopping integrals depend upon the relative orientations of the molecules, the Coulomb integrals depend only on the distances between them. Hence one must include both \( V_p \) and \( V_c \). We have not included explicitly either intra- or inter-site electron-phonon couplings in Eq. 1. We will argue below that the signatures as well as the effects of such couplings can be anticipated from accurate solutions to the static extended Hubbard Hamiltonian for the ET lattice.

Seo\textsuperscript{16} has examined three possible CO patterns within the lattice of Fig. 1 at quarter-filling. All of these involve “stripes”, which can be vertical, diagonal, or horizontal stripes, as shown in Figs. 2 (a), (b), and (c). The lattice of Fig. 1 may also be thought of as a square lattice, with the essential proviso that hopping and Coulomb interactions along one of the diagonals must be included. In the square lattice picture, the bonds along the two directions occur along the \( x \) and \( y \) directions, respectively, and the intrastack bond along the \( c \)-direction in this case corresponds to one of the two diagonals of the square lattice. In this picture, the vertical stripe struc-
ture becomes the simple checkerboard pattern of site oc-
cupancy. Similarly, the diagonal stripe structure has al-
ternate fully occupied and vacant rows along the \( x \) di-
rection. Hence, both the vertical and diagonal stripe charge orderings are based on \( ...1010... \) CO in different lat-
tice directions. In contrast, the horizontal stripe corresponds to a \textit{2D version of} \( ...1100... \) CO\textsuperscript{1}, with the \( ...1100... \) orderings occurring along both \( x \) and \( y \) di-
rections \( \cdots \text{and} \cdots 1010... \) CO occurring along the diagonal correspond to the original \( c \)-axis. In nearly all cases that Seo studied using Hartree-Fock (HF)/Hartree solutions of Eq. 1, he found the vertical stripe to be the ground state, competing occasionally with the diagonal stripe. Only by introducing unequal intersite Coulomb correlations \( V_p < V_c \) and bond alternation along the \( c \)-direction did Seo find a CO pattern that is not vertical. In this specific case, the ground state was \textit{either} the diagonal stripe \textit{or} the horizontal stripe, but these were so close in energy that it was difficult to distinguish between the two cases (see Fig. 15 of reference\textsuperscript{16}). McKenzie et al. studied the square lattice \textit{without} \( t_c \) or \( V_c \) in the \( U \to \infty \) limit within the slave-Boson approximation,\textsuperscript{17} and for finite \( U \) with exact diagonalization.\textsuperscript{18} Ignoring \( V_c \) ob-
viously strongly favors the checkerboard pattern CO in the square lattice (see Fig. 2(d)) which corresponds to the vertical stripe order (see Fig. 2(a)), and unsurpris-
ingly these authors find vertical stripe CO in their model and assert that this is what is observed in the \( \theta \)-ET CTS.

Several important issues remain unresolved from these studies. Seo’s work was done within the mean field ap-

![Fig. 2. Different possible CO patterns in the \( \theta \)-ET materials. (a) vertical stripe (b) diagonal stripe, and (c) horizontal stripe. Filled (unfilled) circles correspond to molecular site with greater (smaller) charge density. Corresponding stripe orders within a rotated rectangular lattice with hopping \( t_p \) along the \( x \) and \( y \)-axes, and \( t_c \) along the \( -x+y \) diagonal are shown in (d), (e), and (f). The hopping along the other diagonal is zero.](image-url)
proximation,\textsuperscript{16} which is known to give erroneous behavior for the Hamiltonian of Eq. 1; for instance, in 1D, the critical $V$ for ...CDW formation within HF theory is much too small, and the behavior of this transition as a function of $U$ is incorrect.\textsuperscript{19,20} McKenzie et al.’s calculation\textsuperscript{17,18} ignores the Coulomb interaction $V_c$ completely. While the hopping $t_c$ is indeed small and might legitimately be neglected, $V$ is of similar magnitude in both $p$ and $c$ directions (because the distances are similar), and $V_c/t_c$ is actually much larger than $V_p/t_p$. Importantly, previous theories\textsuperscript{16–18} have failed to explain (a) the $c$-axis dimerization (since the vertical stripe CO exhibits neither charge nor bond dimerization in the $c$ direction), and (b) the low temperature spin gap transition. It is argued in reference\textsuperscript{16} that inclusion of e-ph interactions would lead to bond alternation among the occupied sites along individual 1D stripes (i.e. along the ...1-1-1... bonds in Fig. 2), as in a normal 1D spin-Peierls transition. Alternatively, Seo and Fukuyama have proposed a frustrated spin model to account for the spin gap.\textsuperscript{21} However, it is not clear how the frustrated and CO states could coexist.

To go beyond the previous approximations and assumptions, we have performed exact diagonalization studies for a 16-site lattice with 8 electrons, for the lattice structure of Fig. 1 (see Fig. 3 for the actual finite-size lattice that was investigated). We choose boundary conditions that are periodic along $t_c$ and both the $t_p$ directions, such that all three CO patterns of Fig. 2 are well-defined and can be studied in an unbiased manner (i.e., the classical energies of the three stripe patterns obtained by setting $t_{ij} = 0$, are identical). We consider all hoppings $t_p$ to be identical, and similarly all hoppings $t_c$ are taken to be the same. Since finite periodic systems do not exhibit broken symmetry, we follow our previously established procedure\textsuperscript{1} and add a site energy component $\sum_i \epsilon_i n_i$ to the Hamiltonian of Eq. (1), where $\epsilon_i$ is negative for the “occupied” sites and positive for the “unoccupied” sites. This is equivalent to including on-site electron-phonon (e-ph) coupling effects (within the classical approximation), with fixed spring constants for all three stripe structures. We then calculate the lowest energy corresponding to each specific CO for the smallest $\epsilon_i$ that still gives measurable energy differences between the three stripe structures. As the spring-constant phonon energy is the same for on-site e-ph interactions for all stripe orders considered, the electronic energies in the static limit for small $\epsilon_i$ provide correct measures of the relative stabilities of the different CO patterns in the limit of $0^-\text{eV}$ on-site e-ph coupling.

We have chosen parameters similar to those in reference\textsuperscript{16} and our results below are for $U = 0.7$ eV, $t_c = -0.01$ eV and $t_p = 0.14$ eV (note the overall minus sign in $H_0$ in Eq. (1)), with $V$ ranging from $0.15 - 0.35$ eV and $|\epsilon_i| = 0.01$ eV. Our range of $V$ covers the entire realistic region $V < \frac{1}{2}U$, given the fixed value of $U = 0.7$ eV. We have confirmed that increasing $t_c$ by a factor of 2–3 or decreasing $|\epsilon_i|$ further does not lead to any modification of the phase diagram shown below. As we have discussed extensively in our previous work,\textsuperscript{1} finite-size calculations tend to overemphasize the ...1010... CO and under-emphasize the ...1100... CO. Thus the relative energy of the horizontal stripe CO in the present case is an upper limit, and the actual phase space region where this CO dominates in the thermodynamic limit is larger than what we find below.

In Fig. 4 we have plotted the energy gained upon stripe formation, $\Delta E = E(\epsilon_i = 0) - E(\epsilon_i \neq 0)$ for the vertical, diagonal and horizontal stripe phases, respectively, versus $V$ for the parameters given above. We find that in all cases the ground state contains either the diagonal stripe or the horizontal stripe. Importantly, the horizontal stripe CO dominates over a broad region of the phase space ($V > 0.18$ eV), despite the isotropic intersite Coulomb integrals and uniform $t_c$.

In addition to the energies, we have calculated the charge densities $n_j$ and bond orders, the latter defined as the expectation value of $b_{ij} = \sum_{\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma})$. We find that the order parameter $\Delta n$ here can be very large (~0.3), for $|\epsilon_i| = 0.01$ eV, although this value will depend on the actual strength of the on-site e-ph coupling. However, the bond orders in a given direction are uniform within both the vertical and diagonal stripe phases. On the other hand, within the horizontal CO, the bond orders alternate along the c-direction, while along the two p-directions there occurs a tetramerized periodicity. This is shown in Fig. 3. There is thus a strong tendency to spontaneous bond distortions in the horizontal CO phase in all three directions: the differences in the bond orders in Fig. 3 suggest that for arbitrarily small inter-site e-ph coupling there would occur bond dimerizations along the c-direction and bond tetramerizations along the two diagonal p-directions in the horizontal stripe phase. The tendency to bond distortion
in the θ-ET lattice is a consequence of the co-operative BCDW nature of the horizontal stripe phase.\textsuperscript{1} If finite intra- and/or inter-site e-ph couplings are included, the cooperative nature of the BCDW accompanying horizontal stripe phase will further lower its energy. It is then likely that even in the small V\textsuperscript{-} region of Fig. 4 that the horizontal stripe will dominate.

We have performed similar calculations for the ferromagnetic spin configuration (total spin S = S\textsubscript{max} = 4), and have determined that the bond dimerization in the c-direction persists even here, although the magnitude of the dimerization is smaller. Thus, lattice dimerization in the c-direction is expected at the M-I transition, as this work is based on the incorrect assumption of a checkerboard vertical stripe CO.

horizontal stripe CO in the θ-ET materials for a substantial region of parameter space. This result contradicts the previous results of Seo\textsuperscript{16} and McKenzie et al\textsuperscript{17,18} and is consistent with experiments. In both the ferromagnetic state and the low spin state the CO produces bond dimerization along the c-direction, with the amplitude of the dimerization larger in the low spin state. This explains the observed appearance of c-axis dimerization at the M-I transition\textsuperscript{5,6,11–14} as well as its increase at low temperatures,\textsuperscript{14} where the free energy is dominated by the low spin state. In the two p-directions, bonds are dimerized in the ferromagnetic state but tetramerized in the low spin state. Our work thus explains naturally two distinct transitions in the θ-ET materials, a high temperature transition\textsuperscript{5,11–14} that occurs as soon as the charge-occupancies correspond to the horizontal stripe CO, and a low temperature magnetic transition\textsuperscript{6,7,10}.

The spin gap transition is different from the usual SP transition, which is due to bond alternation in the 1D half-filled spin system. The formation of a spin gap in 2D in the absence of frustration is a unique feature of the strongly correlated 2D \frac{1}{2}\text{-}filled band. Finally, our results raise questions regarding the theory of charge-fluctuation mediated superconductivity proposed by Merino et al.,\textsuperscript{2} as this work is based on the incorrect assumption of a checkerboard vertical stripe CO.

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Fig. 4. The energy gained upon stripe formation, for the three stripe patterns of Fig. 2. Circles, squares and diamonds correspond to vertical, diagonal and horizontal stripe patterns, respectively. For V > 0.18 eV, the ground state has the horizontal stripe CO.

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