Competing Ground States of a Peierls-Hubbard Nanotube

JUN OHARA and SHOJI YAMAMOTO

Department of Physics, Hokkaido University, Sapporo 060-0810, Japan

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Abstract. - Motivated by iodo platinum complexes assembled within a quadratic-prism lattice, [Pt(C₂H₅N₂)(C₁₀H₂₅N₂)]₄(NO₃)₈, we investigate the ground-state properties of a Peierls-Hubbard four-legged tube. Making a group-theoretical analysis, we systematically reveal a variety of valence arrangements, including half-metallic charge-density-wave states. Quantum and thermal phase competition is numerically demonstrated with particular emphasis on doping-induced successive insulator-to-metal transitions with conductivity increasing stepwise.

Quasi-one-dimensional halogen (X)-bridged transition-metal (M) complexes [1–4] are unique optoelectronic materials. A platinum-chloride chain compound, [Pt(ena)₂Cl]Cl₂·2H₂O (ena = ethylenediamine = C₂H₅N₂), well-known as Wolffram’s red salt, exhibits a Peierls-distorted mixed-valent ground state [5], whereas its nickel analog has a Mott-insulating monovalent regular-chain structure [6, 7]. Microscopic electronic-structure calculations demonstrated the robustness [8] and tunability [9] of the Peierls instability. Metal binucleation leads to a wider variety of electronic states [10–12]. Diplatinum-halide chain compounds, R₂[Pt₂(pop)₄X]·2H₂O [X = Br, I; pop = diphenylphosphine = P₂H₂], R = K, (C₂H₅)₂NH [13,14], have a ground state with halogen-sublattice dimerization, which is reminiscent of the MX conventional, while their analog without any counter ion, Pt₂(dta)Cl₂ (dta = dithioacetate = CH₂CS₂) [15,16], possesses a novel ground state with metal-sublattice dimerization, where twisting of the dta ligand possibly plays an essential role [17]. The former exhibits photo- and/or pressure-induced phase transitions [18–21], whereas the latter undergoes successive phase transitions with increasing temperature [22,23]. There are further attempts [24,25] at bridging polynuclear and/or heterometallic units by halogens.

Hundreds of MX compounds have thus been synthesized and studied, but they all have single-chain-assembled structures. In such circumstances, several chemists designed MX ladders [26,27]. Platinum-halide double-chain compounds, (μ-b pym)₂[Pt(en)₂X]Cl₂·2H₂O (X = Cl, Br; en = ethylenediamine = C₂H₅N₂; μ-b pym = 2,2′-bipyrimidine = C₉H₆N₄) and (bpy)[Pt(dien)Br₂]Br₄ · 2H₂O (dien = diethylenetriamine = C₉H₁₈N₃; bpy = 4,4′-bipyridyl = C₁₀H₈N₂), are made in distinct ground states of mixed valence [28,29] and they are optically distinguishable [30,31]. Another chemical exploration is so exciting as to spark renewed interest not only in...
MX materials but also in the modern microelectronics. Otsubo and Kitagawa [32] have patterned MX chains in a nanotube and fabricated a quadratic-prism compound, [Pt(en)(bpy)]I₄(NO₃)₈. Tubed metal complexes are scarcely precedent and serve as a new laboratory distinct from sp²-bonded-carbon nanotubes [33]. The bpy ligands can be replaced in an attempt to tune the inside diameter, while alternative bridging halide ions may enhance the Peierls distortion. Platinum-halide tubes and ribbons potentially reveal fully correlated electrons coupled with phonons on a way from one to two dimensions. The cylindrical structure may yield novel valence arrangements of its own and unlikely in an open plain. A theoretical scenario for quantum, thermal, and possibly photoinduced transitions between them must stimulate extensive experimental explorations of this new MX family.

Thus motivated, we investigate broken-symmetry solutions of a four-legged Peierls-Hubbard tube. A group-theoretical bifurcation theory predicts the variety of ground states in a platinum-halide quadratic prism. Numerical calculations visualize their close competition as a function of temperature, electron occupancy, and Coulomb interactions. Determination of any one-dimensional structure demands an elaborate analysis [34] of the diffuse X-ray scattering intensity. Resonant Raman spectroscopy [14] is potentially eloquent of the valence arrangement. Our systematic analysis based on a symmetry argument will stimulate and serve for such structural investigations.

Metal-halide quadratic prisms are describable with a two-band extended Peierls-Hubbard Hamiltonian,

\[
\mathcal{H} = \sum_{l,n,s} \left\{ t_{\text{MX}}^{\|} - \alpha (u_{n+1,l:M}^{\|} - u_{n,l:X}^{\|}) a_{n+1:l:M}^\dagger a_{n:l:X} + \text{H.c.} \right\} + \sum_{\alpha \neq \beta, \sigma} \left\{ \mathcal{E}_{\alpha X} - \beta M (u_{n,l}^{\|} - u_{n,l}^{\perp}) \right\} n_{\alpha l:n:M}s_{\alpha l:n:X}s_{\alpha l:n:Ms} + \sum_{l,n} K_{\text{MX}} \frac{1}{2} (u_{n,l}^{\|} - u_{n,l}^{\perp})^2 + (u_{n+1,l}^{\|} - u_{n,l}^{\perp})^2 \right\} + \sum_{A=M,X,n,s,s'} \left\{ U_{A} n_{n:A}s_{n+1:A} + V_{A}^X n_{n:A}s_{n+1:A}^s \right\} + \sum_{l,n,s,s'} \left\{ V_{\text{MX}}^{\perp} n_{n:l:M}s_{n+1:l:M}s'_{n+l+1:M} + n_{n:l:M}s_{n+1:l:M}s'_{n+l+1:M} \right\},
\]

as is illustrated with Fig. 1, where MX chain legs and M₄X₄ units of rectangular parallelepiped are numbered by \( l = 1, \ldots, 4 \) and \( n = 1, \ldots, N \), respectively, while electron spins are indicated by \( s, s' = \uparrow, \downarrow \).

Table 1: Axial isotropy subgroups and their fixed-point subspaces for the irreducible representations \( \mathcal{X}(X) \otimes \mathcal{S}^0 \otimes \hat{T}^0 \).

<table>
<thead>
<tr>
<th>( \mathcal{D}(X) )</th>
<th>Axial isotropy subgroup</th>
<th>Fixed-point subspace</th>
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<tbody>
<tr>
<td>( A_1g )</td>
<td>( D_{4h} )</td>
<td>( t_{X A_4s}^{00} )</td>
</tr>
<tr>
<td>( A_2g )</td>
<td>( (1 + C_{2z})C_{4h} )</td>
<td>( t_{X A_4s}^{00} )</td>
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<tr>
<td>( B_1g )</td>
<td>( (1 + C_{2z}) )</td>
<td>( t_{X A_4s}^{00} )</td>
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<td>( E_g^{(1)} )</td>
<td>( (1 + C_{2z})C_{2z} )</td>
<td>( t_{X E_s}^{00} )</td>
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<tr>
<td>( E_g^{(2)} )</td>
<td>( (1 + C_{2z})C_{2z} )</td>
<td>( t_{X E_s}^{00} )</td>
</tr>
<tr>
<td>( A_{1u} )</td>
<td>( (1 + I)D_{2h} )</td>
<td>( t_{X A_4s}^{00} )</td>
</tr>
<tr>
<td>( A_{2u} )</td>
<td>( (1 + I)(1 + IC_{2z})C_{1z} )</td>
<td>( t_{X A_4s}^{00} )</td>
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<tr>
<td>( B_{1u} )</td>
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When we consider normal states, the symmetry group of any lattice electron system may be written as \( G = P \times S \times T \), where \( P \), \( S \), and \( T \) are the groups of space, spin rotation, and time reversal, respectively. The space group is further decomposed into the translation and point groups as \( L \) and \( D \). For the present \( d_{z^2}-p_z \) quadratic prism, \( L \) and \( D \) read as \( \{ L, I \} \cong \mathfrak{L} \) and \( D_{4h} \), respectively, where \( l \) is the unit-cell translation in the \( z \) direction. Defining the Fourier transformation as \( a_{k:l:A}s = N^{-1/2} \sum_{n} e^{-i(k(n + \delta_{AX}/2))} a_{n:l:A}s \) and \( u_{k:l:A} = N^{-1/2} \sum_{n} e^{-i(k(n + \delta_{AX}/2))} u_{n:l:A} \) with the lattice constant along the legs set equal to unity and composing Hermitian bases of the gauge-invariant operators \( \{ a_{k:l:A}, a_{k:l:A}^\dagger \} \), we investigate irreducible representations of \( G \) over the real number field, which are referred to as \( \mathcal{G} \). Actions of \( l \in \mathfrak{L} \) and \( t \in \mathfrak{T} \) on the electron operators are defined as \( l \cdot a_{k:l:A}s = e^{-i\delta_{k:A}s}a_{k+l:A}s \) and \( t \cdot a_{k:l:A}s = (1)^{\delta_{k:A}} a_{k+l:A}s \). Those of \( p \in \mathfrak{D} \) are calculated as \( p \cdot a_{k:l:A}s = [A_1g(p)]_{11} a_{k+l:M}s \) and \( p \cdot a_{k:l:A}s = [A_2u(p)]_{11} a_{k+l:M}s \), where \( \mathcal{D}(p)_{ij} \) is the \((i,j)\)-element of the \( \mathcal{D} \) representation matrix for \( p \). Those of \( u(e, \theta) = \sigma^0 \cos(\theta/2) - i(\sigma \cdot e) \sin(\theta/2) \) read \( u(e, \theta) \cdot a_{k:l:A}s = \sum_{s} [u(e, \theta)]_{s} a_{k+l:A}s' \), where \( \sigma^0 \) and \( \sigma = (\sigma^x, \sigma^y, \sigma^z) \) are the \( 2 \times 2 \) unit matrix and a vector composed of the Pauli matrices, respectively. Any representation \( \mathcal{G} \) is expressed as \( \mathcal{G} = \mathcal{P} \otimes \mathcal{S} \otimes \hat{T} \). Once a wave vector \( Q \) is fixed, the relevant little group \( \mathcal{D}(Q) \) is given. \( \mathcal{P} \) is therefore labelled as \( Q\mathcal{D}(Q) \). The relevant representations of \( \mathcal{S} \) are given by \( S^0(u(e, \theta)) = 1 \) (singlet) and \( S^1(u(e, \theta)) = O(u(e, \theta)) \) (triplet), where \( O(u(e, \theta)) \) is the \( 3 \times 3 \) orthogonal matrix satisfying \( u(e, \theta) \sigma \cdot u(e, \theta) = 1 \).
The relevant quantities have been observed without any external field applied. Thus and thus, we discuss nonmagnetic solutions whose isotropy subgroups are axial, together with their fixed-point subspaces $h_{XD(X)}^{\lambda \tau}$, where $h_{XD(X)}^{\lambda \tau} = P_{D[i,j]}^{\tau} \cdot h_{X}^{\lambda}$. All the one-dimensional isotropy subgroups are proved to give stable solutions [37]. Considering that the density matrices $P_{QD[\pi]}^{\lambda \tau}$ and bond orders $Re \sum_{\lambda} \langle \cdots | Q_{\lambda} \rangle$ denote the thermal average in a Hartree-Fock eigenstate, are of the same symmetry as their host Hamiltonian, we learn the oscillating pattern of charge densities $\sum_{\lambda} \langle \cdots | Q_{\lambda} \rangle$ and bond orders $Re \sum_{\lambda} \langle \cdots | Q_{\lambda} \rangle$. The consequent density-wave solutions of $Q = X$ are shown in Fig. 2. While we have analyzed and calculated those of $Q = X$ as well, none of them but the paramagnetic metal of the full symmetry $D_{4h}L_{1}ST$, labelled as $\Gamma A_{1g} \otimes S^{0} \otimes T^{0}$ and referred to as FM, plays the ground state under any realistic parametrization.

The $XD(X) \otimes S^{0} \otimes T^{0}$ solutions are classified into three groups: charge density waves on the metal sublattice with the halogen sublattice distorted, charge density waves on the halogen sublattice with the metal sublattice distorted, and bond order waves without any charge oscillation, which are abbreviated as $M$-CDW, $X$-CDW, and BOW, respectively. No lattice distortion accompanies BOW within the present Hamiltonian (1). Every BOW state may be stabilized by direct electron transfers on the oscillating bonds and their interactions with phonons, but any is of little occurrence under realistic modelling.
There are twice four kinds of CDW states. Although all the CDW states gain a condensation energy due to their Peierls distortion, they are not necessarily gapped. M- and X-CDW of the \((0 + 0−)\) type are half metallic, where two legs are valence-delocalized, while the rest are valence-trapped. Such states as cell-doubled but partially metallic are generally possible in tubed \(MX\) compounds, including triangular prisms, whose little groups \(D(X)\) all have a two-dimensional irreducible representation of axial isotropy subgroup. All the other CDW states are fully gapped at the boundaries of the reduced Brillouin zone. Since the \(M \, d_{x^2}\) orbitals are half filled and lie higher in energy than the fully occupied \(X \, p_z\) orbitals, \(\pi\)-modulated \(d\)-electron CDW states are most likely to appear in undoped samples at low temperatures.

Now we are eager to observe actual phase competitions. We have many unknown electronic correlation parameters as well as well-established crystallographic ones [32]. Then, extending the Ohno relationship [38] to our heteroatomic system [39], we design, unless otherwise noted, the Coulomb interaction between different sites \(n: lA\) and \(n': l'A'\) as \(\bar{U}/\sqrt{k A/1 + [4\pi e^2U_nA/n' A'/e^2]}/2\), where \(\bar{U}\) is the averaged on-site Coulomb repulsion \((U_M + U_X)/2\), \(r_{nA; n'l'A'}\) the distance between the two sites under no deformation, \(e\) the electron charge, \(\epsilon_0\) the vacuum dielectric constant, and \(\kappa\) the relative permittivity. Considering x-ray diffraction measurements on the quadratic-prism compound \([Pt(en)(bpy)]_4(NO_3)_8\) [32], we stand on \(r_{nA; n+l+1A} = 2r_{nA; n+lX} = 6\,\text{Å}\) and \(r_{nA; n+l+1X} = r_{nA; n+lX} = 11\,\text{Å}\), whereas referring to optical investigations on the analogous ladder compound \((bpy)[Pt(dien)Br]_2Br_4 \cdot 2H_2O\) [30,31], we assume that \(t_{MX} = 1.5\,\text{eV}, t_{MM} = 0.32\,\text{eV}, U_M = 1.2\,\text{eV}, U_X = 1.0\,\text{eV}, \varepsilon_M - \varepsilon_X = 1.2\,\text{eV}, \alpha = 0.84\,\text{eV/Å}, \beta_M = \beta_X = 2.3\,\text{eV/Å}, \text{and} K_{Bl} = 8.0\,\text{eV/Å}^2\). Such a parametrization is consistent with previous model studies [3,4,40], first-principle calculations [41], and photostructural investigations [20,42,43] on \(MX\) and \(MMX\) chains. Under little information about platinum-halide dielectric constants, we set \(\kappa\) two ways, that is, equal to 2, considering the moderate screening in organic semiconductors [44,45], and equal to 4, considering the strong screening in transition-metal complexes [46].

Figure 3(a) demonstrates quantum phase transitions in the low-temperature limit. The competition within \(M\)-CDW states is straightforwardly understandable when we assume the \(X \, p_z\) orbitals to be fully filled and thus inactive. Those of \((+++\cdot++), (-+−−)\) and \((++--)\) are stabilized with increasing \(V_{MM}^{XX}\), \(V_{MM}^{\perp}\), and \(V_{MM}^{\perp}\), respectively. Interchain electron transfers also bring about energy gains in all but the first. The phase boundaries are roughly given by \(V_{MM}^{XX} = 2V_{MM}^{\perp} \pm V_{MM}^{\perp}\) under slight correction \(\times (t_{MM}^{\perp})^2\). X-CDW states are of occurrence with \(p\) electrons strongly correlating against the relative electron affinity \(\varepsilon_X = \varepsilon_M\). The present parametrizations both suggest an \(M\)-CDW ground state of the \((++--)\) type closely competing with that of the \((++++)\) type. From the theoretical point of view, \((++--)\)-\(M\)-CDW is characteristic of a tubed lattice in that it belongs to a two-dimensional representation. On the other hand, \((+++\cdot++\cdot−−)\)-\(M\)-CDW and \((−−++\cdot−−)\)-\(M\)-CDW have good analogy with CDW states of the in-phase (IP) and out-of-phase (OP) types, respectively, found in \(MX\) ladder compounds [30]. We are all excited at the thought of structural investigations of \([Pt(en)(bpy)]_4(NO_3)_8\).

Figure 3(b) stimulates another interest in platinum-halide prism compounds. The \((++−−)\)-to-\((++++)\) transition with the electron occupancy \(\nu\) moving away from \(3/4\) is caused by activated interchain electron hopping. Under the present Coulomb parametrizations, \((++--)\)-\(M\)-CDW and \((+++\cdot++\cdot−−)\)-\(M\)-CDW are almost balanced at \(\nu = 3/4\) and it is the slight energy correction \(\propto (t_{MM}^{\perp})^2\) that stabilizes the former over the latter. There is no interchain electronic communication between phased 3/4-filled CDW chains in the strong-coupling limit. However, slightly doped electrons or holes bring about energy gains \(\propto t_{MM}^{\perp}\) in \((++++)\)-\(M\)-CDW as well as in \((++--)\)-\(M\)-CDW, which are illustrated with bent arrows in Fig. 4, and those in the former are roughly twice as much as those in the latter. That is why \((++++)\)-\(M\)-CDW is quick to replace \((++--)\)-\(M\)-CDW under doping. Further doping destabilizes the \(\pi\)-modulated Peierls distortion and induces a quite interesting phase, \((0 + 0−)\)-\(M\)-CDW, which is derived from another two-dimensional represen-
tation, $X E^{(2)}_{\text{in}} \otimes S^0 \otimes T^0$. There occurs a partially metallic state in between the totally valence-trapped and fully metallic states, where intermediate conductivity should be observed. A thermal transition to PM is hardly realistic considering $t_{\text{MX}}^{\|}$ of eV order, while doping-induced quantum transitions to metallic states may be feasible. Electrochemical doping, by exposing a single crystal to halogen vapor [47], for instance, possibly causes successive phase transitions towards the fully metallic state with conductivity increasing stepwise.

The doping-induced stabilization of the novel half-metallic phase against the fully distorted $M$-CDW states is well understandable within a simple consideration of their electronic correlation energies. Figure 4 gives a single-band description of $M$-CDW states under doping. In $(+ - -)$-$M$-CDW and $(++++)$-$M$-CDW, electrons are doped first, while the Peierls-distorted chains remain half-filled (in the single-band picture), because the metallic Pt$^{3+}$ bands are sandwiched between the bonding Pt$^{2+}$ and antibonding Pt$^{4+}$ bands far apart from them. Their per-unit $d$-electron energies under electron doping are estimated as

$$E^{(+ - -)} = (2 + \delta^2)U_M + 8\delta(2V_{MM}^{\|} + V_{MM}^{\perp}) + 4(1 + \delta^2)(V_{MM}^{\|} + 2V_{MM}^{\perp}) - \frac{4\beta^2}{K_{\text{MX}}} (1 - \delta)^2,$$

$$E^{(++++)} = (2 + \delta^2)U_M + 16\delta(V_{MM}^{\|} + 2V_{MM}^{\perp}) + 4(1 + \delta^2)(V_{MM}^{\perp} + 2V_{MM}^{\perp}) - \frac{4\beta^2}{K_{\text{MX}}} (1 - \delta)^2,$$

$$E^{(0+0-)} = \left(\frac{3}{2} + 2\delta + 2\delta^2\right)U_M + (1 + 2\delta)^2(2V_{MM}^{\|} + V_{MM}^{\perp}) + 4(1 + 2\delta)(V_{MM}^{\perp} + 2V_{MM}^{\perp}) - \frac{2\beta^2}{K_{\text{MX}}^2},$$

and are visualized in Fig. 4. $(+ - -)$-$M$-CDW and $(++++)$-$M$-CDW are indeed closely competing with each other and the most interesting $(+ - +)$-to $(0+0-)$ transition is reproduced well. $E^{(++++)}$ and $E^{(0+0-)}$ are balanced at $\delta \simeq 0.29$ and $\delta \simeq 0.30$ in the cases of $\kappa = 2$ and $\kappa = 4$, respectively. Because of the electron-hole symmetry in the single-band modelling, the transition points under hole doping are simply obtained as $-\delta$.

With respect to the appearance of a partially distorted prism lattice, we should further note that any structural instability is conditional in the present system. Indeed a single $MX$ chain is unconditionally distorted [48, 49], but coupled $MX$ chains, whether tubed or not, are never distorted under infinitesimal coupling. It is the case with organic polymers as well. The Peierls instability in polyacetylene is unconditional, whereas those in polyacene are conditional [45, 50]. It is not only due to Coulomb correlations but also of geometric origin that half the chains remain undistorted in $(0+0-)$-$M$-CDW.

Structural instabilities of longer period may also be mentioned in this context. We have indeed found CDW solutions of $0 < Q < \pi$ under doping. At $\nu = 3/4 \pm 1/16$, for example, there exists a quadratic prism composed of two $3/4$-filled dimerized and two $(3/4 \pm 1/8)$-filled tetramerized chains as well as a wholly octamerized prism. However, they are generally higher in energy than $(0+0-)$-$M$-CDW under the present parametrizations. Besides $2k_F$ instabilities, $4k_F$-CDW states such as all the chains octamerized at $\nu = 3/4 \pm 1/32$ have also been found, but they are inferior to $(++++)$-$M$-CDW energy. All such instabilities are conditional and the critical coupling strength is on the whole an increasing function of the number of constituent chains and the spatial period of oscillation. There is a possibility [51] of long-period ground states appearing with stronger on-site electron-phonon coupling and/or weaker intersite Coulomb interaction. However, it may not be the case with our platinum-halide prisms, especially with iodo complexes. The Peierls gap $\propto \beta_M / \sqrt{t_{\text{MX}}^{\|} K_{\text{MX}}}$.
decreases in the order Cl > Br > I [52], while the IP-CDW ground states [30] of similar ladder compounds (μ-bpym)[Pt(en)X]2X(ClO4)3·H2O demonstrate the relevance of the intersite Coulomb interactions. We are hoping for large-scale measurement and further tuning of tubed MX compounds.

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