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Competing Ground States of a Peierls-Hubbard Nanotube

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Abstract. – Motivated by iodo platinum complexes assembled within a quadratic-prism lattice, $[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_{10}\text{H}_8\text{N}_2)\text{I}](\text{NO}_3)_8$, 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, $[\text{Pt}(\text{ea})_4\text{Cl}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (ea = ethylamine = $\text{C}_2\text{H}_7\text{N}$), well-known as Wolfram’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, $R_4[\text{Pt}_2(\text{pop})_4X] \cdot n\text{H}_2\text{O}$ [$X = \text{Br}, \text{I}$; pop = diphosphonate = $\text{P}_2\text{O}_5\text{H}_2$; $R = \text{K}, (\text{C}_2\text{H}_5)_2\text{NH}_2$] [13, 14], have a ground state with halogen-sublattice dimerization, which is reminiscent of the MX conventional, while their analog without any counter ion, $\text{Pt}_2(\text{dta})_4\text{I}$ (dta = dithioacetate = CH_3CS_2) [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, $(\mu\text{-bpy})[\text{Pt}(\text{en})X]_2(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}$; en = ethylenediamine = $\text{C}_2\text{H}_8\text{N}_2$; $\mu\text{-bpy}$ =

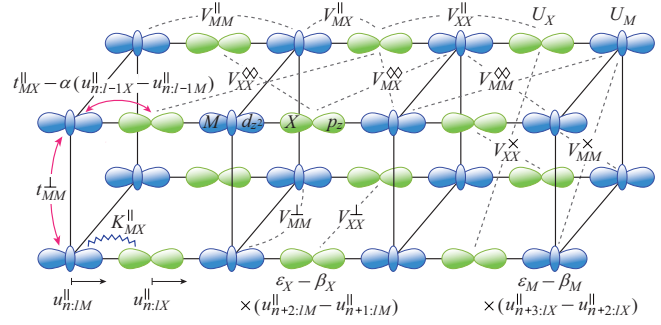


Fig. 1: (Color online) Modelling of an MX quadratic prism, where heavily and lightly shaded clouds denote $M d_{z^2}$ and $X p_z$ orbitals, the electron numbers on which are given by $n_{n:LMs} \equiv a_{n:LMs}^\dagger a_{n:LMs}$ and $n_{n:LXs} \equiv a_{n:LXs}^\dagger a_{n:LXs}$, respectively. The on-site energies of isolated atoms are given by ϵ_M and ϵ_X , while the electron hoppings between these levels are modelled by $t_{MX}^||$ and $t_{MM}^||$. The on-site Coulomb interactions are labelled as U_A ($A = M, X$), whereas the interchain and intra-chain different-site Coulomb interactions as $V_{AA'}^\perp$, $V_{AA'}^{\perp\perp}$, $V_{AA'}^\times$, and $V_{AA'}^\parallel$ ($A, A' = M, X$). The leg-direction displacements of metal and halogen ions, $u_{n:LM}^||$ and $u_{n:LX}^||$, interact with electrons through intersite (α) and intrasite (β_M, β_X) coupling constants at the cost of elastic energy $\propto K_{MX}^||$.

2, 2'-bipyrimidine = $\text{C}_8\text{H}_6\text{N}_4$) and $(\text{bpy})[\text{Pt}(\text{dien})\text{Br}]_2\text{Br}_4 \cdot 2\text{H}_2\text{O}$ (dien = diethylenetriamine = $\text{C}_4\text{H}_{13}\text{N}_3$; bpy = 4, 4'-bipyridyl = $\text{C}_{10}\text{H}_8\text{N}_2$), 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, $[\text{Pt}(\text{en})(\text{bpy})\text{I}]_4(\text{NO}_3)_8$. Tubed metal complexes are scarcely preceded and serve as a new laboratory distinct from sp^2 -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,

$$\begin{aligned}
\mathcal{H} = & \sum_{l,n,s} \left\{ [t_{MX}^{\parallel} - \alpha(u_{n+1:lM}^{\parallel} - u_{n:lX}^{\parallel})] a_{n+1:lMs}^{\dagger} a_{n:lXs} \right. \\
& - [t_{MX}^{\parallel} - \alpha(u_{n:lX}^{\parallel} - u_{n:lM}^{\parallel})] a_{n:lXs}^{\dagger} a_{n:lMs} \\
& \left. - t_{MM}^{\perp} a_{n:l+1Ms}^{\dagger} a_{n:lMs} + \text{H.c.} \right\} \\
& + \sum_{l,n,s} \left\{ [\varepsilon_M - \beta_M(u_{n:lX}^{\parallel} - u_{n-1:lX}^{\parallel})] n_{n:lMs} \right. \\
& \left. + [\varepsilon_X - \beta_X(u_{n+1:lM}^{\parallel} - u_{n:lM}^{\parallel})] n_{n:lXs} \right\} \\
& + \sum_{l,n} \frac{K_{MX}^{\parallel}}{2} [(u_{n:lX}^{\parallel} - u_{n:lM}^{\parallel})^2 + (u_{n+1:lM}^{\parallel} - u_{n:lX}^{\parallel})^2] \\
& + \sum_{A=M,X} \sum_{l,n,s,s'} \left\{ \frac{U_A}{4} n_{n:lAs} n_{n:lA-s} + V_{AA}^{\parallel} n_{n:lAs} n_{n+1:lAs'} \right. \\
& + V_{AA}^{\perp} n_{n:lAs} n_{n:l+1As'} + \frac{V_{AA}^{\times}}{2} n_{n:lAs} n_{n:l+2As'} \\
& \left. + V_{AA}^{\diamond\diamond} (n_{n:lAs} n_{n+1:l+1As'} + n_{n:l+1As} n_{n+1:lAs'}) \right\} \\
& + \sum_{l,n,s,s'} \left\{ V_{MX}^{\parallel} (n_{n:lMs} n_{n:lXs'} + n_{n:lXs} n_{n+1:lMs'}) \right. \\
& + V_{MX}^{\diamond\diamond} (n_{n:lMs} n_{n:l+1Xs'} + n_{n:l+1Ms} n_{n:lXs'} \\
& \left. + n_{n:lXs} n_{n+1:l+1Ms'} + n_{n:l+1Xs} n_{n+1:lMs'}) \right\}, \quad (1)
\end{aligned}$$

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

$\check{D}(X)$	Axial isotropy subgroup	Fixed-point subspace
A_{1g}	$\mathbf{D}_{4h}\mathbf{L}_2\mathbf{ST}$	$h_{XA_{1g}[1,1]}^{00}$
A_{2g}	$(1 + C_{2xl})\mathbf{C}_{4h}\mathbf{L}_2\mathbf{ST}$	$h_{XA_{2g}[1,1]}^{00}$
B_{1g}	$(1 + C_{2al})\mathbf{D}_{2h}\mathbf{L}_2\mathbf{ST}$	$h_{XB_{1g}[1,1]}^{00}$
B_{2g}	$(1 + C_{2xl})\mathbf{D}_{2ah}\mathbf{L}_2\mathbf{ST}$	$h_{XB_{2g}[1,1]}^{00}$
$E_g^{(1)}$	$(1 + C_{2zl})\mathbf{C}_{2xh}\mathbf{L}_2\mathbf{ST}$	$h_{XE_g[1,1]}^{00}$
$E_g^{(2)}$	$(1 + C_{2zl})\mathbf{C}_{2ah}\mathbf{L}_2\mathbf{ST}$	$\sum_{i,j=1}^2 h_{XE_g[i,j]}^{00}/2$
A_{1u}	$(1 + Il)\mathbf{D}_4\mathbf{L}_2\mathbf{ST}$	$h_{XA_{1u}[1,1]}^{00}$
A_{2u}	$(1 + Il)(1 + IC_{2x})\mathbf{C}_4\mathbf{L}_2\mathbf{ST}$	$h_{XA_{2u}[1,1]}^{00}$
B_{1u}	$(1 + Il)(1 + IC_{2a})\mathbf{D}_2\mathbf{L}_2\mathbf{ST}$	$h_{XB_{1u}[1,1]}^{00}$
B_{2u}	$(1 + Il)(1 + IC_{2x})\mathbf{D}_{2a}\mathbf{L}_2\mathbf{ST}$	$h_{XB_{2u}[1,1]}^{00}$
$E_u^{(1)}$	$(1 + Il)(1 + IC_{2y})\mathbf{C}_{2x}\mathbf{L}_2\mathbf{ST}$	$h_{XE_u[1,1]}^{00}$
$E_u^{(2)}$	$(1 + Il)(1 + IC_{2b})\mathbf{C}_{2a}\mathbf{L}_2\mathbf{ST}$	$\sum_{i,j=1}^2 h_{XE_u[i,j]}^{00}/2$

as is illustrated with Fig. 1, where *MX* chain legs and M_4X_4 units of rectangular parallelepiped are numbered by $l = 1, \dots, 4$ and $n = 1, \dots, N$, respectively, while electron spins are indicated by $s, s' = \uparrow, \downarrow$.

When we consider normal states, the symmetry group of any lattice electron system may be written as $\mathbf{G} = \mathbf{P} \times \mathbf{S} \times \mathbf{T}$, where $\mathbf{P}$, $\mathbf{S}$, and $\mathbf{T}$ are the groups of space, spin rotation, and time reversal, respectively. The space group is further decomposed into the translation and point groups as $\mathbf{L} \wedge \mathbf{D}$. For the present d_{z^2} - p_z quadratic prism, $\mathbf{L}$ and $\mathbf{D}$ read as $\{E, l\} \equiv \mathbf{L}_1$ and $\mathbf{D}_{4h}$, respectively, where l is the unit-cell translation in the z direction. Defining the Fourier transformation as $a_{k:lAs} = N^{-1/2} \sum_n e^{-ik(n+\delta_{AX}/2)} a_{n:lAs}$ and $u_{k:lA}^{\parallel} = N^{-1/2} \sum_n e^{-ik(n+\delta_{AX}/2)} u_{n:lA}^{\parallel}$ with the lattice constant along the legs set equal to unity and composing Hermitian bases of the gauge-invariant operators $\{a_{k:lAs}^{\dagger} a_{k:l'A's'}^{\dagger}\}$, we investigate irreducible representations of $\mathbf{G}$ over the real number field, which are referred to as $\check{G}$. Actions of $l \in \mathbf{L}_1$ and $t \in \mathbf{T}$ on the electron operators are defined as $l \cdot a_{k:lAs}^{\dagger} = e^{-ikl} a_{k:lAs}^{\dagger}$ and $t \cdot a_{k:lAs}^{\dagger} = (-1)^{\delta_{s\uparrow}} a_{-k:lA-s}^{\dagger}$. Those of $p \in \mathbf{D}_{4h}$ are calculated as $p \cdot a_{k:lMs}^{\dagger} = [A_{1g}(p)]_{11} a_{pk:lMs}^{\dagger}$ and $p \cdot a_{k:lXs}^{\dagger} = [A_{2u}(p)]_{11} a_{pk:lXs}^{\dagger}$, where $[\check{D}(p)]_{ij}$ is the (i, j) -element of the $\check{D}$ representation matrix for p . Those of $u(\mathbf{e}, \theta) = \sigma^0 \cos(\theta/2) - i(\boldsymbol{\sigma} \cdot \mathbf{e}) \sin(\theta/2) \in \mathbf{S}$ read as $u(\mathbf{e}, \theta) \cdot a_{k:lAs}^{\dagger} = \sum_{s'} [u(\mathbf{e}, \theta)]_{s's} a_{k:lAs'}^{\dagger}$, where σ^0 and $\boldsymbol{\sigma} = (\sigma^x, \sigma^y, \sigma^z)$ are the 2×2 unit matrix and a vector composed of the Pauli matrices, respectively. Any representation $\check{G}$ is expressed as $\check{G} = \check{P} \otimes \check{S} \otimes \check{T}$. Once a wave vector Q is fixed, the relevant little group $\mathbf{D}(Q)$ is given. $\check{P}$ is therefore labelled as $Q\check{D}(Q)$. The relevant representations of $\mathbf{S}$ are given by $\check{S}^0(u(\mathbf{e}, \theta)) = 1$ (singlet) and $\check{S}^1(u(\mathbf{e}, \theta)) = O(u(\mathbf{e}, \theta))$ (triplet), where $O(u(\mathbf{e}, \theta))$ is the 3×3 orthogonal matrix satisfying $u(\mathbf{e}, \theta) \boldsymbol{\sigma}^{\lambda} u^{\dagger}(\mathbf{e}, \theta) =$

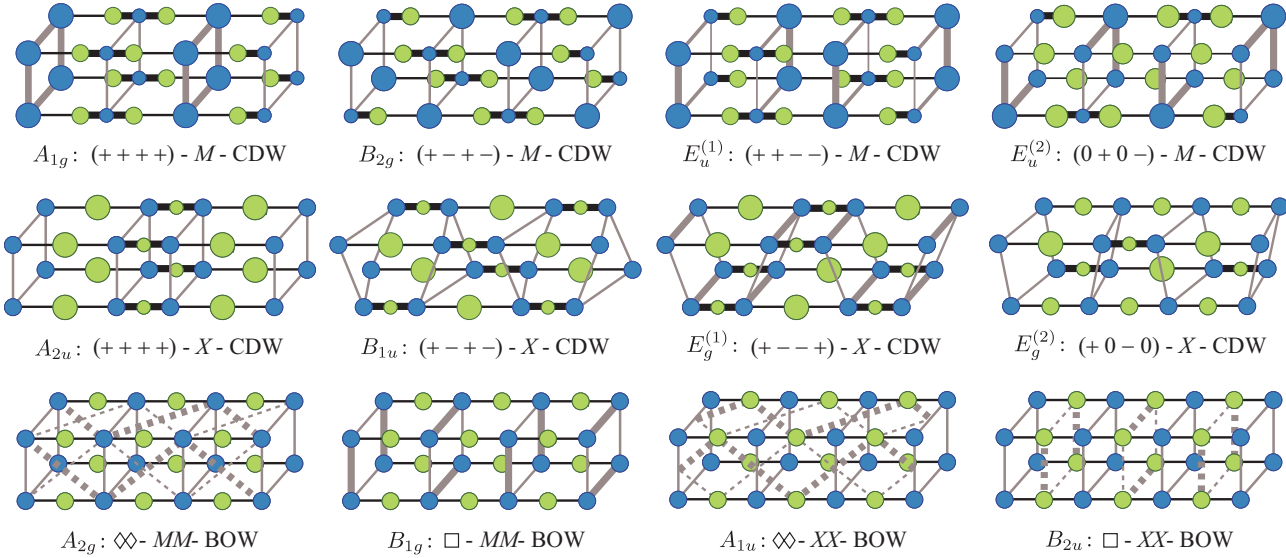


Fig. 2: (Color online) Possible density waves of the $X\check{D}(X) \otimes \check{S}^0 \otimes \check{T}^0$ type, where varied circles and segments represent oscillating electron densities and bond orders, respectively, while irregularly arranged circles denote lattice distortion. Various M (X)-CDW states are referred to as $(\sigma_1, \sigma_2, \sigma_3, \sigma_4)$, where the signatures $\sigma_l = \pm, 0$ denote the charges relative to M^{3+} (X^-) on adjacent metal (halogen) sites forming a square section of the quadratic prism.

$\sum_{\mu=x,y,z} [O(u(e, \theta))]_{\lambda\mu} \sigma^\mu$ ($\lambda = x, y, z$), while those of $\mathbf{T}$ by $\check{T}^0(t) = 1$ (symmetric) and $\check{T}^1(t) = -1$ (antisymmetric). Halogen-bridged platinum complexes are describable with moderately correlated electrons, where neither magnetically ordered phase nor current-wave state has ever been observed without any external field applied. The relevant d and p bands of an as-grown platinum-iodide quadratic-prism compound are of 3/4 electron filling. Thus and thus, we discuss nonmagnetic solutions labelled $\Gamma\check{D}(\Gamma) \otimes \check{S}^0 \otimes \check{T}^0$ and $X\check{D}(X) \otimes \check{S}^0 \otimes \check{T}^0$, where Γ and X denote $Q = 0$ and $Q = \pi$, respectively, and their space groups read as $\mathbf{L}_1 \wedge \mathbf{D}_{4h}$ [35] and $\mathbf{L}_2 \wedge \mathbf{D}_{4h}$ [36], respectively, with $\mathbf{L}_1 \equiv \{E, I\}$ and $\mathbf{L}_2 \equiv \{E, 2I\}$.

Then the Hamiltonian (1) may be rewritten within the Hartree-Fock scheme as

$$\mathcal{H}_{\text{HF}} = \sum_{l,l'} \sum_{A,A'} \sum_{Q=\Gamma,X} \sum_{k,s,s'} \sum_{\lambda=0,x,y,z} x_{lAl'A'}^\lambda(Q; k) \times a_{k+Q;lAs}^\dagger a_{k;l'A's'} \sigma_{ss'}^\lambda \equiv \sum_Q \sum_\lambda h_Q^\lambda, \quad (2)$$

where the order parameters $x_{lAl'A'}^\lambda(Q; k)$, as well as the lattice distortion $u_{Q;lA}^\parallel$, should be determined so as to minimize the free energy at every temperature given. Employing the projection operators

$$P_{\check{D}[i,j]}^\tau = \frac{d_{\check{D}}}{2g} \sum_{t \in \mathbf{T}} \check{T}^\tau(t) \sum_{p \in \mathbf{D}_{4h}} [\check{D}(p)]_{ij}^* t p, \quad (3)$$

where $g (= 16)$ is the order of $\mathbf{D}_{4h}$ and $d_{\check{D}} (\leq 2)$ is the dimension of its arbitrary irreducible representation $\check{D}$, we further decompose the Hamiltonian (2) into symmetry-

definite irreducible components [35, 36] as

$$\mathcal{H}_{\text{HF}} = \sum_{Q=\Gamma,X} \sum_{\check{D}(Q)} \sum_{\lambda=0,x,y,z} \sum_{\tau=0,1} h_{Q\check{D}(Q)}^{\lambda\tau}. \quad (4)$$

We list in Table 1 the irreducible representations $X\check{D}(X) \otimes \check{S}^0 \otimes \check{T}^0$ whose isotropy subgroups are axial, together with their fixed-point subspaces $h_{X\check{D}(X)}^{\lambda\tau}$, where $h_{X\check{D}[i,j]}^{\lambda\tau} = P_{\check{D}[i,j]}^\tau \cdot h_X^\lambda$. All the one-dimensional isotropy subgroups are proved to give stable solutions [37]. Considering that the density matrices $\rho_{l'A'lA}^\lambda(Q; k) = \sum_{s,s'} \langle a_{k+Q;lAs}^\dagger a_{k;l'A's'} \rangle_T \sigma_{ss'}^\lambda / 2$, where $\langle \cdots \rangle_T$ denotes 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 $\sum_s \langle a_{n;lAs}^\dagger a_{n;lAs} \rangle_T$ and bond orders $\text{Re} \sum_s \langle a_{n;lAs}^\dagger a_{n';l'A's} \rangle_T$. The consequent density-wave solutions of $Q = X$ are shown in Fig. 2. While we have analyzed and calculated those of $Q = \Gamma$ as well, none of them but the paramagnetic metal of the full symmetry $\mathbf{D}_{4h} \mathbf{L}_1 \mathbf{ST}$, labelled as $\Gamma A_{1g} \otimes \check{S}^0 \otimes \check{T}^0$ and referred to as PM, plays the ground state under any realistic parametrization.

The $X\check{D}(X) \otimes \check{S}^0 \otimes \check{T}^0$ 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 $\mathbf{D}(X)$ 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 $M d_{z^2}$ orbitals are half filled and lie higher in energy than the fully occupied $X p_z$ orbitals, π -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 $\bar{U}/\kappa\sqrt{1 + [4\pi\epsilon_0\bar{U}r_{n:lA;n':l'A'}/e^2]^2}$, where $\bar{U}$ is the averaged on-site Coulomb repulsion $(U_M + U_X)/2$, $r_{n:lA;n':l'A'}$ the distance between the two sites under no deformation, e the electron charge, ϵ_0 the vacuum dielectric constant, and κ the relative permittivity. Considering x-ray diffraction measurements on the quadratic-prism compound $[\text{Pt}(\text{en})(\text{bpy})\text{I}]_4(\text{NO}_3)_8$ [32], we stand on $r_{n:lM;n+1:lM} = 2r_{n:lM;n:lX} = 6 \text{ \AA}$ and $r_{n:lM;n:l+1M} = r_{n:lX;n:l+1X} = 11 \text{ \AA}$, whereas referring to optical investigations on the analogous ladder compound $(\text{bpy})[\text{Pt}(\text{dien})\text{Br}]_2\text{Br}_4 \cdot 2\text{H}_2\text{O}$ [30, 31], we assume that $t_{MX}^{\parallel} = 1.5 \text{ eV}$, $t_{MM}^{\perp} = 0.32 \text{ eV}$, $U_M = 1.2 \text{ eV}$, $U_X = 1.0 \text{ eV}$, $\epsilon_M - \epsilon_X = 1.2 \text{ eV/\AA}$, $\alpha = 0.84 \text{ eV/\AA}$, $\beta_M = \beta_X = 2.3 \text{ eV/\AA}$, and $K_{MX}^{\parallel} = 8.0 \text{ eV/\AA}^2$. 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 κ 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 $(++++)$, $(+-+-)$ and $(+ + - -)$ are stabilized with increasing $V_{MM}^{\diamond}$, $V_{MM}^{\perp}$, and $V_{MM}^{\times}$, respectively. Interchain electron transfers also bring about energy gains in all but the first. The phase boundaries are roughly given by $V_{MM}^{\perp} = 2V_{MM}^{\diamond} \pm V_{MM}^{\times}$ under slight correction $\propto (t_{MM}^{\perp})^2$. X -CDW states are of occurrence with p electrons strongly correlating against the relative electron affinity $\epsilon_X - \epsilon_M$. The present parametrizations both suggest an M -CDW ground state of the $(+ + - -)$ type closely

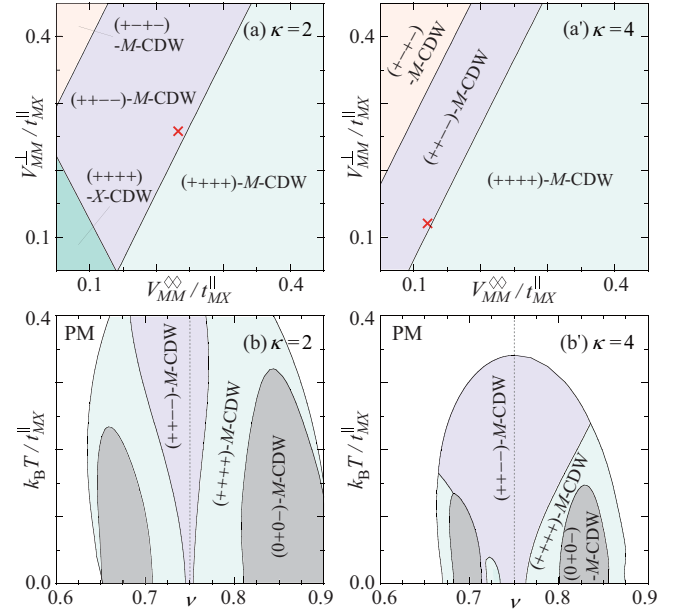


Fig. 3: (Color online) Ground-state phase diagrams on the $V_{MM}^{\perp}$ - $V_{MM}^{\diamond}$ square, where the crosses indicate the Ohno-type parametrizations with $\kappa = 2$ (a) and $\kappa = 4$ (a'), and we move away from these points tuning only $V_{MM}^{\perp}$ and $V_{MM}^{\diamond}$, and thermal phase diagrams with varying electron occupancy ν under the $\kappa = 2$ (b) and $\kappa = 4$ (b') Ohno-type parametrizations, where the dotted lines are guides for eyes, separating the hole- and electron-doped regions.

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, $(+ + + +)$ - M -CDW and $(+ - + -)$ - 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 $[\text{Pt}(\text{en})(\text{bpy})\text{I}]_4(\text{NO}_3)_8$.

Figure 3(b) stimulates another interest in platinum-halide prism compounds. The $(+ + - -)$ -to- $(++++)$ transition with the electron occupancy ν moving away from $3/4$ is caused by activated interchain electron hopping. Under the present Coulomb parametrizations, $(+ + - -)$ - M -CDW and $(+ + + +)$ - 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 π -modulated Peierls distortion and induces a quite interesting phase, $(0+0-)$ - M -CDW, which is derived from another two-dimensional represen-

tation, $XE_u^{(2)} \otimes \tilde{S}^0 \otimes \tilde{T}^0$. 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 $t_{MX}^{\parallel}$ 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 into vacant sites, whereas holes into fully occupied sites. In $(0+0-)$ - M -CDW, the metallic chains 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

$$\frac{E^{(++--)}}{N} = 2(1 + \delta^2)U_M + 8\delta(2V_{MM}^{\parallel} + V_{MM}^{\times}) + 4(1 + \delta)^2(V_{MM}^{\perp} + 2V_{MM}^{\infty}) - \frac{4\beta_M^2}{K_{MX}^{\parallel}}(1 - \delta)^2, \quad (5)$$

$$\frac{E^{(++++)}}{N} = 2(1 + \delta^2)U_M + 16\delta(V_{MM}^{\parallel} + 2V_{MM}^{\infty}) + 4(1 + \delta^2)(V_{MM}^{\times} + 2V_{MM}^{\perp}) - \frac{4\beta_M^2}{K_{MX}^{\parallel}}(1 - \delta)^2, \quad (6)$$

$$\frac{E^{(0+0-)}}{N} = \left(\frac{3}{2} + 2\delta + 2\delta^2\right)U_M + (1 + 2\delta)^2(2V_{MM}^{\parallel} + V_{MM}^{\times}) + 4(1 + 2\delta)(V_{MM}^{\perp} + 2V_{MM}^{\infty}) - \frac{2\beta_M^2}{K_{MX}^{\parallel}}, \quad (7)$$

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 cor-

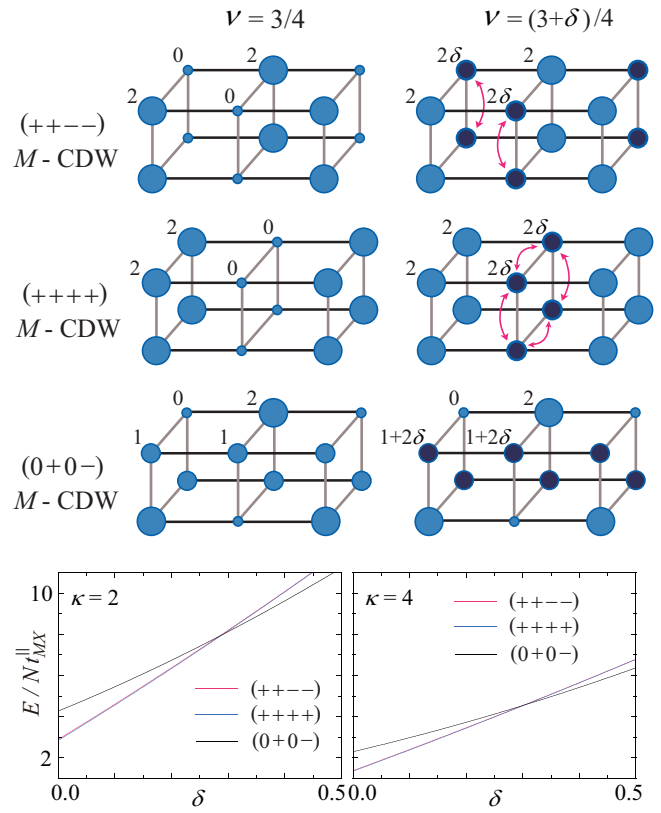


Fig. 4: (Color online) Electron occupancy of the $\text{Pt } d_{z^2}$ orbitals under electron doping in the strong-intrasite-coupling limit. Doped electrons are evenly distributed among the four chains in $(++++)$ - M -CDW and $(++--)$ - M -CDW, whereas they are predominantly put into the two valence-delocalized paramagnetic chains in $(0+0-)$ - M -CDW. The bent arrows signify doping-induced energy gains $\propto t_{MM}^{\perp}$. Energy estimates (5)-(7) are plotted as functions of $\delta \geq 0$ at $\kappa = 2$ and $\kappa = 4$.

relations 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 in 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 $\propto \beta_M / \sqrt{t_{MX}^{\parallel} K_{MX}^{\parallel}}$

decreases in the order $\text{Cl} > \text{Br} > \text{I}$ [52], while the IP-CDW ground states [30] of similar ladder compounds $(\mu\text{-bpym})[\text{Pt}(\text{en})\text{X}]_2\text{X}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ 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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