Ground-state properties of a Peierls-Hubbard triangular prism

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Motivated by recent chemical attempts at assembling halogen-bridged transition-metal complexes within a nanotube, we model and characterize a platinum-halide triangular prism in terms of a Peierls-Hubbard Hamiltonian. Based on a group-theoretical argument, we reveal a variety of valence arrangements, including heterogeneous or partially metallic charge-density-wave states. Quantum and thermal phase competitions are numerically demonstrated with particular emphasis on novel insulator-to-metal and insulator-to-insulator transitions under doping, the former of which is of the first order, while the latter of which is of the second order.

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I. INTRODUCTION

The success of patterning a graphite sheet into a cylinder stimulated the public interest in the geometric tunability of electronic properties. Carbon nanotubes indeed vary from metals to semiconductors with the inside diameter and the chiral angle. Their nature is fairly describable within the π-electron nearest-neighbor tight-binding model and is relatively insensitive to Coulomb interactions. A tubed vanadium oxide Na₂V₃O₇, consists of strongly correlated d electrons, but they are completely localized. Another transition-metal-based nanotubular compound [Pt(en)(bpy)I]Cl₂ (en = ethylenediamine = C₈H₁₅N₂) also behaves as a Heisenberg magnet. In such circumstances, a platinum-iodide quadratic-prism compound [Pt(en)(bpy)I]Cl₂(NO₃)₈ (en = ethylenediamine = C₈H₁₅N₂; bpy = 4,4′-bipyridyl = C₁₅H₁₂N₂), featured by competing electron-electron and electron-lattice interactions, has sparked a brandnew interest in lattice electron nanostructures.

Quasi-one-dimensional transition-metal (M) complexes with bridging halogens (X) possess unique optoelectronic properties which are widely available according to the constituent metals, halogens, ligand molecules and counter ions. Platinum-halide single-chain compounds such as Wolffram’s red salt [Pt(en)₂Cl₂]·2H₂O (en = ethylenediamine = C₈H₁₅N₂) have a Peierls-distorted mixed-valent ground state, whereas their nickel analogs consist of Mott-insulating mono-valent regular chains. In between are palladium halides, while its analog without any counter ion, [Pt₂(dta)₂]I (dta = dithiocacetic acid = CH₃CS₂), is of metallic conduction at room temperature and undergoes a double transition to a novel Peierls insulator with decreasing temperature (µ-bpy)₂[Pt(en)₂]Cl₂(NO₃)₈·2H₂O (X = Cl; Br; µ-bpym = 2,2′-bipyrimidine = C₈H₆N₄) and (bpy)₂[Pt(dien)Br]Br·2H₂O (dien = diethylentriamine = C₈H₁₅N₃) were synthesized in an attempt to bring a couple of MX chains into interaction. They are made in similar ladder structures but in distinct ground states of mixed valence which are optically distinguishable.

Thus and thus, the MX class of materials have been fascinating numerous chemists and physicists for more than half a century. Much effort is still devoted to elaborating new varieties and the novel porous nanotube [Pt(en)(bpy)]Cl₂(NO₃)₈ has just been fabricated. Diffuse X-ray scattering measurements on it suggest two or more cell-doubled mixed-valent phases compet-
ing with each other in the ground state. Such phases are indeed recognizable as broken-symmetry solutions of a four-legged Peierls-Hubbard Hamiltonian of tetragonal symmetry.  Then we may have an idea of bringing coupled MX chains into geometric frustration. A platinum-halide triangular-prism compound must be a unique charge-frustrated nanotubular system and may exhibit novel valence arrangements which have never been observed in any other material. Thus motivated, we apply a group-theoretical bifurcation theory to a three-legged Peierls-Hubbard Hamiltonian of hexagonal symmetry and reveal its exotic ground states. They are numerically calculated and compared with each other in an attempt to guide future experiments.

II. MODEL HAMILTONIAN AND ITS SYMMETRY PROPERTIES

Metal-halide triangular prisms are describable in terms of a two-band extended Peierls-Hubbard Hamiltonian of hexagonal symmetry,

$$\mathcal{H} = \sum_{l,n,s} \left\{ \left[ t_{lXX} - \alpha \left( u_{l+1,11M} - u_{l+1,11M} \right) \right] a_{l+1,11M}^\dagger a_{l,11M} + H.c. \right\}$$

$$+ \sum_{l,n,u} \left\{ \left[ t_{lXX} - \alpha \left( u_{l,11M} - u_{l-1,11M} \right) \right] a_{l,11M}^\dagger a_{l-1,11M} + H.c. \right\}$$

$$+ \sum_{A,M,X} \left\{ t_{A,M,X} a_{l,11M} a_{n,l,11M,11M} + V_{A,M,X} a_{l,11M} a_{n,l,11M,11M}^\dagger \right\}$$

$$+ \sum_{l,n,s,s'} \left\{ \left[ t_{lXX} - \alpha \left( u_{l,11M} - u_{l,11M} \right) \right] a_{l,11M}^\dagger a_{l,11M} \right\}$$

where $MX$ chain legs and $M_3X_3$ prism units are numbered by $l = 1,2,3$ and $n = 1,2,\cdots,N$, respectively, while electron spins are indicated by $s,s' = \uparrow,\downarrow$. The modeling is visualized and explained in more detail in Fig. 1.

Unless the gauge symmetry is broken, the symmetry group of any lattice electron system can be written as $G = \mathbb{P} \times \mathbb{S} \times \mathbb{T}$, where $\mathbb{P}$, $\mathbb{S}$ and $\mathbb{T}$ are the groups of space, spin rotation, and time reversal, respectively. The space group is further decomposed into the translation and point groups as $L \wedge D$. For $d_2$-$X_p$ triangular prisms, $L$ and $D$ read as $\{E,l\} \equiv L_1$ and $D_{3h}$, respectively, where $l$ is the unit-cell translation in the $z$ direction. Defining the Fourier transformation as $a_{k,l,11M} = N^{-1/2} \sum_n e^{-i(k+\delta_{AX}/2)n} a_{n,l,11M}$ and $u_{k,lA} = N^{-1/2} \sum_n e^{-i(k+\delta_{AX}/2)n} u_{n,lA}$ with the lattice constant along the tube axis set equal to unity and composing Hermitian bases of the gauge-invariant operators $\{a_{k,l,11M}^\dagger a_{k',l'11M}^\dagger\}$, we find out irreducible representations of $G$ over the real number field, which are referred to as $\tilde{G}$. Actions of $l \in L_1$ and $t \in T$ on the electron operators are defined as $l \cdot a_{k,l,11M}^\dagger = e^{-i\delta_{lA}} a_{k,l,11M}^\dagger$ and $t \cdot a_{k,l,11M}^\dagger = (-1)^{\delta_{lA}} a_{k,l,11M}^\dagger$. Those of $p \in D_{3h}$ are calculated as $p \cdot a_{k,l,11M}^\dagger = [A_1(p)]_{11M} a_{k,l,11M}^\dagger$ and $p \cdot a_{k,l,11M}^\dagger = [A_2(p)]_{11M} a_{k,l,11M}^\dagger$, where $[D(p)]_{ij}$ is the $(i,j)$-element of the $D$ representation matrix for $p$. Those of $u(e,\theta) = e^{i\lambda \cos(\theta/2)} - i(\sigma \cdot e)\sin(\theta/2) \in \mathbb{S}$ are represented as $u(e,\theta) \cdot a_{k,l,11M}^\dagger = \sum_{s,s'} [u(e,\theta)]_{s,s'} a_{k,l,11M}^\dagger$, 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 $\tilde{G}$ is expressed as $\tilde{G} = P \otimes S \otimes T$. Once a wave vector $Q$ is fixed, the relevant little group $D(Q)$ is given. $P$ is therefore labeled as $QD(Q)$. The relevant representations of $\mathbb{S}$ 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 $u(e,\theta)\sigma^0 u(e,\theta)^\dagger = \sum_{\lambda = x,y,z} [O(u(e,\theta))]_{\lambda\mu}\sigma^\mu$ ($\lambda = x,y,z$). Those of $\mathbb{T}$ are given by $T^0(t) = 1$ (symmetric) and $T^1(t) = -1$ (antisymmetric). Considering that platinum 5d electrons are moderately correlated, magnetically broken-symmetry solutions are less interesting. Nontrivial current-wave phases, whether of charge or of spin, are of little occurrence unless electrons are well itinerant in both leg and rung directions. Therefore, we discuss density-wave solutions of the $P \otimes S^0 \otimes T^0$ type. Since the relevant $d_2$ and $p_z$ orbitals of constituent MX chains are formally half and fully filled, respectively, we take much interest in cell-doubled mixed-valent states among others. Increasing temperature and/or electrochemical doping may suppress lattice dimerization and induce valence delocalization. Thus we consider the cases of $Q = 0$ and $Q = \pi$, which are described by the translation groups $L_1 \equiv \{E,l\}$ and $L_2 \equiv \{E,2l\}$, respectively, and are hereafter referred to as $\Gamma$ and $X$, respectively. Both $D(\Gamma)$ and $D(X)$ read as $D_{3h}$.

We take the Hartree-Fock scheme of rewriting the Hamiltonian (2.1) into

$$\mathcal{H}_{HF} = \sum_{l,l',A,A'} \sum_{Q,l,k,s,s'} \sum_{\lambda=0,1,2} \sum_{P',Q} x_{l,A'}^\lambda A' (Q;k)$$

$$\times a_{k+Q;A,A'}^\dagger a_{k';l'X}s,s' \sigma_{s,s'}^\lambda \equiv \sum_{Q} \sum_{\lambda} h_{Q,A,A'}^\lambda$$

where the self-consistent fields $x_{l,A'}^\lambda A' (Q;k)$, as well as the lattice distortions $u_{Q;A,A'}^\lambda$, can be described in terms of the density matrices $\rho_{Q,A,A'}^\lambda (Q;k) = \cdots$
TABLE I: Symmetry properties of irreducible representations, $\Gamma \tilde{D}(\Gamma) \otimes \tilde{S}^0 \otimes T^0$ and $X \tilde{D}(X) \otimes \tilde{S}^0 \otimes T^0$, available on the condition of axial isotropy subgroup.

| Irreducible representation | Axial isotropy subgroup | Fixed-point subspace | Broken-symmetry Hamiltonian | Physical character |
|----------------------------|------------------------|---------------------|----------------------------|-------------------|
| $\Gamma A'_1 \otimes \tilde{S}^0 \otimes T^0$ | $D_{3h} L_1 ST$ | $h_{\Gamma A'_1[1,1]}^{\otimes 2}$ | $h_{\Gamma A'_1[1,1]}^{\otimes 2}$ | PM |
| $\Gamma A'_2 \otimes \tilde{S}^0 \otimes T^0$ | $C_{3h} L_1 ST$ | $h_{\Gamma A'_2[1,1]}^{\otimes 2}$ | $h_{\Gamma A'_2[1,1]}^{\otimes 2}$ | V-MX-BOW |
| $\Gamma A''_1 \otimes \tilde{S}^0 \otimes T^0$ | $D_{3h} L_1 ST$ | $h_{\Gamma A''_1[1,1]}^{\otimes 2}$ | $h_{\Gamma A''_1[1,1]}^{\otimes 2}$ | ||-MX-BOW |
| $\Gamma A''_2 \otimes \tilde{S}^0 \otimes T^0$ | $C_{3h} L_1 ST$ | $h_{\Gamma A''_2[1,1]}^{\otimes 2}$ | $h_{\Gamma A''_2[1,1]}^{\otimes 2}$ | (- - -)-MX-BOW |
| $\Gamma E'(1) \otimes \tilde{S}^0 \otimes T^0$ | $D_{3h} L_1 ST$ | $h_{\Gamma E'[1,1]}^{\otimes 2}$ | $h_{\Gamma E'[1,1]}^{\otimes 2}$ | $\triangle$-MM-BOW |
| $\Gamma E''(1) \otimes \tilde{S}^0 \otimes T^0$ | $(1 + \sigma_{1z}) L_1 ST$ | $h_{\Gamma E''[1,1]}^{\otimes 2}$ | $h_{\Gamma E''[1,1]}^{\otimes 2}$ | $\pm$-MX-BOW |
| $\Gamma E''(2) \otimes \tilde{S}^0 \otimes T^0$ | $(1 + C_{2z}) L_1 ST$ | $h_{\Gamma E''[2,2]}^{\otimes 2}$ | $h_{\Gamma E''[2,2]}^{\otimes 2}$ | $(0 - -)-MX-BOW |
| $\Gamma XA'_1 \otimes \tilde{S}^0 \otimes T^0$ | $D_{3h} L_1 ST$ | $h_{\Gamma XA'_1[1,1]}^{\otimes 2}$ | $h_{\Gamma XA'_1[1,1]}^{\otimes 2}$ | $(++)-M-CDW |
| $\Gamma XA'_2 \otimes \tilde{S}^0 \otimes T^0$ | $(1 + C_{21}) L_1 ST$ | $h_{\Gamma XA'_2[1,1]}^{\otimes 2}$ | $h_{\Gamma XA'_2[1,1]}^{\otimes 2}$ | $X-XX-BOW |
| $\Gamma XA''_1 \otimes \tilde{S}^0 \otimes T^0$ | $C_{3h} L_2 ST$ | $h_{\Gamma XA''_1[1,1]}^{\otimes 2}$ | $h_{\Gamma XA''_1[1,1]}^{\otimes 2}$ | $(++)-X-CDW |
| $\Gamma XA''_2 \otimes \tilde{S}^0 \otimes T^0$ | $(1 + C_{21}) L_1 ST$ | $h_{\Gamma XA''_2[1,1]}^{\otimes 2}$ | $h_{\Gamma XA''_2[1,1]}^{\otimes 2}$ | $(++)-X-CDW |
| $\Gamma XE'(1) \otimes \tilde{S}^0 \otimes T^0$ | $C_{2v} L_2 ST$ | $h_{\Gamma XE'[1,1]}^{\otimes 2}$ | $h_{\Gamma XE'[1,1]}^{\otimes 2}$ | $(++)-M-CDW |
| $\Gamma XE''(1) \otimes \tilde{S}^0 \otimes T^0$ | $(1 + C_{21}) L_1 ST$ | $h_{\Gamma XE''[1,1]}^{\otimes 2}$ | $h_{\Gamma XE''[1,1]}^{\otimes 2}$ | $(0 - -)-M-CDW |
| $\Gamma XE''(2) \otimes \tilde{S}^0 \otimes T^0$ | $(1 + C_{21}) L_1 ST$ | $h_{\Gamma XE''[2,2]}^{\otimes 2}$ | $h_{\Gamma XE''[2,2]}^{\otimes 2}$ | $(0 - -)-X-CDW |

\[\sum_{n,s}(\mathcal{A}_{n+k' A \sigma}^{\mathcal{A} \sigma} e^{i n \mathcal{Q} \cdot \mathbf{r}})/2 \text{ with } \langle \cdots \rangle_T \text{ denoting the canonical average and are adiabatically determined at each temperature } T \text{ so as to minimize the free energy.}

Employing the projection operators

\[P_{D[i,j]} = \frac{d_D}{2g} \sum_{t \in T} \tilde{T}^T(t) \sum_{p \in D_{3h}} [\tilde{D}(p)]_{ij}^* t_p, \tag{2.3}\]

where \(g = 12\) is the order of \(D_{3h}\) and \(d_D \leq 2\) is the dimension of its arbitrary irreducible representation \(D\), we further decompose the Hamiltonian \(\mathcal{H}_{HF}\) into its fixed-point subspaces as

\[\mathcal{H}_{HF} = \sum_{Q \in \mathcal{Q}, X \in D(\tilde{Q}), \lambda = 0, x, y, z} \sum_{\mathbf{r} = 0,1} \hbar^{\mathcal{X}}_{Q \tilde{D}(\mathcal{Q})} \otimes \tilde{S}^0 \otimes T^0, \tag{2.4}\]

where \(\hbar^{\mathcal{X}}_{Q \tilde{D}(\mathcal{Q})} = P_{D[i,j]} \cdot h_{\tilde{D}}^Q\). We list in Table I the thus-obtained irreducible representations together with their broken-symmetry Hamiltonians. The two-dimensional representations \(E'\) and \(E''\) are generally available in a variety of isotropy subgroups. Here we consider only the axial ones discarding those of two-dimensional fixed point subspace. Every irreducible representation is guaranteed to yield a stable solution only when its isotropy subgroup possesses a one-dimensional fixed point subspace. Considering that the density matrices are of the same symmetry as their host Hamiltonian, we learn the oscillating pattern of electron densities, \(\sum_{\mathbf{r}} (\mathcal{A}_{n \mathbf{r} n \mathbf{r} A}^{\mathcal{A} \sigma} e^{i n \mathcal{Q} \cdot \mathbf{r}})/\sum_{\mathbf{r}}\), and bond orders, \(\sum_{\mathbf{r}} (\mathcal{A}_{n \mathbf{r} n \mathbf{r} A}^{\mathcal{A} \sigma} e^{i n \mathcal{Q} \cdot \mathbf{r}})/\sum_{\mathbf{r}}\).

In Fig. 2 we draw and name the consequent charge-density-wave (CDW) solutions, including bond-order-wave (BOW) ones which are recognizable as bond-centered CDW states.

Two kinds of axial isotropy subgroups are available from all the two-dimensional representations but \(\Gamma E''\). A single state is derived from each of the second kind, whereas two quantitatively different states can be born to each of the first kind, which are distinguishably named. These symmetrically (qualitatively) degenerate but practically (quantitatively) distinct varieties read as heterogeneous CDW states, where each chain is no longer 3/4-filled, that is, one or two chains are charge-rich, while the rest are charge-poor. Such an interchain charge polarization is common to all the two-dimensional representations, including \(\Gamma E''(1) \otimes \tilde{S}^0 \otimes T^0\). The thus-broken electron-hole symmetry yields an exotic phase diagram. It is the geometric frustration rather than any orbital hybridization that breaks down the electron-hole symmetry in triangular-prism MX complexes. It is not the case with even-legged ladders and prisms where the electron-hole symmetry is kept within any single-band description and the d-electron phase diagram as a function of doping is symmetric with respect to the half occupancy.

All the \(\Gamma \tilde{D}(\Gamma) \otimes \tilde{S}^0 \otimes T^0\) solutions but the paramagnetic metal (PM) of the full symmetry \(D_{3h} L_1 ST\) are characterized as BOW states. There is no lattice distortion in some of them under the present modeling, but even \(\triangle\)-MM-BOW may be accompanied by cell deformation on the assumption that the interchain electron transfer \(t_{\text{MM}}\) can be coupled to phonons. Every BOW may be stabilized by electrons directly hopping on the oscillating bonds and their interactions with phonons, but any is of little occurrence within realistic modeling and parameterization. BOW states are more likely to appear...
in decoupled chains of the $MX_{24,25}$ and $MMX_{27,33}$ types.

The $XD(X)\otimes S^0 \otimes T^0$ solutions are classified into three groups: CDWs on the metal sublattice with the halogen sublattice dimerized, those on the halogen sublattice with the metal sublattice dimerized and BOWs without any charge oscillation. We find twice three irreducible representations assuming a CDW character. There is a one-to-one correspondence between $M$- and $X$-CDWs. $X$-CDW states consist of mixed-valent halogen ions. $p$ electrons may be activated with increasing $\varepsilon_X$ and $U_X$, but platinum-fluorides are hard to fabricate. Although all CDW states gain a condensation energy due to the Peierls distortion, they are not necessarily gapped. Those of the $(0+)$ type are partially metallic, where only two chains are valence-trapped and the rest is valence-delocalized. Such states as cell-doubled but gapless at the Fermi level are never available from $MX$ ladders, but generally possible in $MX$ tubes, whose little groups $D(X)$ necessarily have a two-dimensional irreducible representation of axial isotropy subgroup. All other CDW states are fully gapped at the boundaries of the reduced Brillouin zone.

**III. QUANTUM AND THERMAL PHASE DIAGRAMS**

Now we numerically draw various phase diagrams. We model a trial $MX$ prism on the platinum-halide ladder compound ($\mu$-bpy)₃[Pt(en)₂X₂](ClO₄)₂·H₂O. Assuming that platinum ions are equally spaced in the leg and rung directions, $r_{\parallel MM} = 2r_{\parallel MX} = r_{\parallel MM}$, we set the transfer integrals for $t_{\parallel MM} = 0.4t_{\parallel MX}$. The on-site electronic parameters are taken as $U_M = 0.8t_{\parallel MX}$, $U_X = 0.66t_{\parallel MX}$ and $\varepsilon_M - \varepsilon_X = 2.0t_{\parallel MX}$, while the elastic constants are adjusted to $\alpha = 0.24\sqrt{t_{\parallel MX}K_{MX}^{\parallel}}$ and $\beta_M = \beta_X = 0.65\sqrt{t_{\parallel MX}K_{MX}^{\parallel}}$. Coulomb interactions between different sites are designed as $V_{MX}^{\parallel} = (U_M + U_X)/4$. 

![Diagram](image-url)
ground-state phase diagrams are calculated at a sufficiently low temperature, $k_B T/|\alpha|_{\perp} = 0.001$. In $(\pm + +)-M$-CDW chain, three chains may unequally be distorted, that is, the CDW amplitude of one chain may be larger than those of the rest two. In order to detect such a heterogeneous CDW, we decompose the electron densities $d_{n\pm 1M}$ into net $(\tilde{d}_{n\pm 1M})$ components as

$$d_{n\pm 1M} = \tilde{d}_{n\pm 1M} + d_{n\pm 1M};$$

and calculate the ratios $|\tilde{d}_{n\pm 2M}/\tilde{d}_{n\pm 1M}|$ (Fig. 4). These ratios are independent of the unit index $n$ in any ground state and correspond to unity when three chains are proportionate in charge. $(++ +)-M$-CDW, bifurcating from $(+ + +)-M$-CDW, is possibly of remarkable interchain charge polarization, where the interchain heterogeneity barometer $|\tilde{d}_{n\pm 2M}/\tilde{d}_{n\pm 1M}|$ goes almost down to 0.3, while $(- + +)-M$-CDW, discontinuously replacing $(+ + +)-M$-CDW, is generally of moderate interchain charge polarization, where $|\tilde{d}_{n\pm 2M}/\tilde{d}_{n\pm 1M}|$ is not so far from unity.

Then we may have an idea of describing the $(---)$-to-$(+ + +)-M$-CDW transition in terms of weakly coupled CDW chains of Pt$^{2+}$ and Pt$^{4+}$.

Figure 3(a) demonstrates that $V_{\perp}^\times_{\perp}$ and $V_{\perp}^{\perp}_{\perp}$ are the driving interactions for $(++ +)-M$-CDW and $(+- +)-M$-CDW, respectively. Under strong valence localization, their $d$-electron energies may be expressed as

$$E_{(++ +)-M-CDW} = \frac{3}{N} \varepsilon_M - \frac{3\beta^2_{\perp}}{K_{\perp}^2} + \frac{3U_M}{2}$$

$$E_{(-+ +)-M-CDW} = \frac{3}{N} \varepsilon_M - \frac{3\beta^2_{\perp}}{K_{\perp}^2} + \frac{3U_M}{2}$$

which are balanced at $V_{\perp}^{\perp}_{\perp} = 2V_{\perp}^\times_{\perp}$ and are consistent with numerical findings in Fig. 3(a) to a certain extent. We can refine such an analytic consideration taking account of transfer effects. Decoupled chains, whether in $(+ + +)-M$-CDW or in $(- + +)-M$-CDW, gain the...
same hopping energy on the zeroth-order phase boundary
$V_{\text{MM}}^\perp = 2V_{\text{MM}}^\|$. The interchain contact $t_{\text{MM}}^\perp$ switched on contributes further stabilization energy to the $(+++) -$ arrangement but is of no benefit to the $(+++) +$ one. We obtain a correcter estimate of the phase boundary as

$$V_{\text{MM}}^\perp = 2V_{\text{MM}}^\| - \frac{(t_{\text{MM}}^\perp)^2}{4\beta_\text{M}^2/K_{\text{MM}}^\perp - U_\text{M} + 4V_{\text{MM}}^\| - V_{\text{MM}}^\perp} + V_{\text{MM}}^\perp,$$  \(3.4\)

provided $t_{\text{MM}}^\perp K_{\text{MM}}^\perp / \beta_\text{M}$, and it is indeed in excellent agreement with the numerical calculation. The standard parametrization of $V_{\text{MM}}^\perp = \sqrt{2V_{\text{MM}}^\|}$ applied to decoupled chains results in a $(+++) -$ $-CDW$ to replace $(+++) +$ $-CDW$. The close competition between $(+++) +$ $-CDW$ and $(+++)-CDW$ depends on electron-lattice couplings as well. With increasing $\beta_\text{M}$, $(+++) -$ $-CDW$ loses the advantage of interchain electron hopping $\propto (t_{\text{MM}}^\perp)^2$ and is again replaced by $(+++) +$ $-CDW$, as is demonstrated in Fig. 3(b). In the moderate coupling region $(+++) -$ $-CDW$ generally plays the ground state, while with increasing electron-phonon interactions of the Peierls and/or Holstein types, $(+++) +$ $-CDW$ appears instead.

When we tune the band filling, we find $-CDW$ transitions between the $(+++) +$ and $(+++) -$ types as well as those between the $(+++) +$ and $(+++) -$ types in the electron-doped region [Fig. 3(c)]. The collapse of the electron-hole symmetry results from the frustration-induced interchain charge polarization. Although $(+++) +$ $-CDW$ and $(+++) -$ $-CDW$ are born of the same representation $X^\text{E}(1) \otimes S^0 \otimes T^0$, their boundaries to $(+++) +$ $-CDW$ are different in character. The invariance groups of $(+++) +$ $-CDW$ and $(+++) -$ $-CDW$ are $\text{C}_2\perp \text{L}_2\text{ST}$ and $\text{D}_{3h}\text{L}_2\text{ST}$, respectively. Since the former is a subgroup of the latter, there may be a continuous transition of the second order between them, which is the case with any instability arising from PM of the full symmetry. $(+++) +$-$(+++) -$ $-CDW$ transitions are indeed of the second order, whereas $(+++) -$-$(+++) +$ $-CDW$ transitions are of the first order. A continuous transition between distinct $-CDW$ states is unusual and has never been observed in any other $\text{MX}$ compound. We thus wait eagerly for geometrically frustrated $\text{MX}$ prisms to be fabricated.

Figure 3(b) stimulates another interest in platinum-halide nanotubes. There appears a quite interesting phase, $(0+-) -$ $-CDW$, in the hole-doped region, which consists of Peierls-insulating dimerized chains and a paramagnetic regular chain. Figure 3 elucidates its energy structure, together with those of $(+++) +$ $-CDW$ and $(+++) -$ $-CDW$. $(+++) +$ $-CDW$ and $(+++) -$ $-CDW$ are fully gapped, whereas $(0+-) -$ $-CDW$ is gapless and metallic. The metallic band is essentially composed of trivalent platinum ions [Fig. 3(c)], though there survives a finite contribution from those of trapped valence under the standard parametrization of intermediate electron-lattice coupling. As a rule for $(0+-) -$ $-CDW$, holes are doped into a single chain and the rest two remain half filled until the metallic chain is emptied. In $(+++) -$ $-CDW$, on the other hand, the highest-lying filled band is made from a couple of Peierls-distorted chains in phase [Fig. 3(b)] and therefore, doped holes immediately eat into the two $-CDW$ chains. The two Peierls-distorted chains in $(0+-) -$ $-CDW$ are free from doped holes and thus remain stable, while two of the Peierls-distorted chains in $(+++) +$ $-CDW$ suffer from hole doping and are thus destabilized. Once the conduction electrons are removed out, $(0+-) -$ $-CDW$ is no more free from holes invading divalent platinum ions and suffers a rapid collapse. Thus ans thus, there may be a re-entrant transition between $(+++) +$ $-CDW$ and $(0+-) -$ $-CDW$. Figure 6 illustrates hole injection into $(+++) +$ $-CDW$ and $(0+-) -$ $-CDW$ under strong valence localization. Their $d$-electron energies are evaluated as

$$E_{(++) +} -CDW = 3(1 - \delta)\varepsilon_{\text{M}} + \frac{2 + (2 - 3\delta)^2}{4} U_\text{M} + \frac{(2 - 3\delta)^2}{2} V_{\text{MM}}^\perp + 4(2 - 3\delta)V_{\text{MM}}^\|,$$

$$-\frac{2 + (2 - 3\delta)^2 \beta_\text{M}^2}{2 K_{\text{MM}}^\perp} \left( 0 \leq \delta \leq \frac{2}{3} \right),$$  \(3.5\)

$$E_{(0+-) -} -CDW = 3(1 - \delta)\varepsilon_{\text{M}} + 4(1 - 3\delta)^2 U_\text{M} + \frac{(1 - 3\delta)^2 V_{\text{MM}}^\perp + 2(1 - 3\delta)V_{\text{MM}}^\|}{4} + 4(2 - 3\delta)V_{\text{MM}}^\|,$$

$$-\frac{2(3 - \delta)^2 \beta_\text{M}^2}{K_{\text{MM}}^\perp} \left( 0 \leq \delta \leq \frac{1}{3} \right),$$  \(3.6\)

$$E_{(0+-) +} -CDW = 3(1 - \delta)\varepsilon_{\text{M}} + \frac{9(1 - \delta)^2}{4} U_\text{M} + 9(1 - \delta)\varepsilon_{\text{M}}$$

$$- \frac{9(1 - \delta)^2 \beta_\text{M}^2}{2 K_{\text{MM}}^\perp} \left( \frac{1}{3} \leq \delta \leq \frac{2}{3} \right),$$  \(3.7\)

and are plotted in Fig. 6. In $(0+-) -$ $-CDW$ doped holes are distributed differently according as their density, defined as $3 - 4\nu \equiv \delta$, exceeds one third or not. That is why $(0+-) -$ $-CDW$ once replaces $(+++) -$ $-CDW$ but soon disappears with decreasing electron occupancy. The naivest estimates $(3.5) - (3.7)$ succeed in predicting such a re-entrant transition, though they over-stabilize $(0+-) -$ $-CDW$ against $(+++) +$ $-CDW$. The preceding transition point is well explained, but the succeeding one is harder to understand. It is likely that linear corrections of hopping energy to both $E_{(++) +} -CDW$ and $E_{(0+-) -} -CDW$ should make their competition under doping much less intuitive.

IV. SUMMARY AND DISCUSSION

Platinum-halide triangular prisms are thus identified as frustrated Peierls-Hubbard nanotubes and are pro-
FIG. 5: (Color online) The single-particle energy dispersion relation $\epsilon_k$ and the local (total) density of states $\rho_n(lA)$ [$\rho(\epsilon) \equiv \sum_{n,l,A} \rho_n(lA)$] for $(+++)\text{-}M$-CDW (a), $(--+)\text{-}M$-CDW (b) and $(0+-)\text{-}M$-CDW (c). We focus on the highest-lying six bands mainly of Pt character, where solid and dotted lines consist of occupied and vacant states, while thin and thick lines denote singly and doubly degenerate bands, respectively. $\epsilon_F$ indicates the Fermi level.

FIG. 6: (Color online) Electron occupancy of the Pt $d_{z^2}$ orbitals as a function of the density of doped holes under strong valence localization on the assumption that the $X_p$ orbitals remain fully filled and inactive. Energy estimates (3.5)-(3.7) are plotted as functions of $\delta \equiv 3 - 4\nu$, where $\epsilon_M$ is set equal to zero.
FIG. 7: (Color online) Metastable CDW states of $Q \neq \pi$ against the ground states, with $Q = \pi$, at various values of $\nu$, where the local electron densities $d_{n_M}$ are measured in comparison with the average occupancy of the relevant chain labeled $l$. Seventeen metal triangles are clipped out of the prism of $N = 300$.

Pt $d_{z^2}$ orbitals are effectively 2/5- and 3/5-filled, where subharmonic, namely, cell-quintupled, $M$-CDW states are found. Trimerized CDW solutions are available at $0.646 \lesssim \nu \lesssim 0.694$ and $0.805 \lesssim \nu \lesssim 0.847$, whereas pentamerized ones are detectable at $0.691 \lesssim \nu \lesssim 0.733$ and $0.783 \lesssim \nu \lesssim 0.833$, but they are never stabilized into the ground state under the standard parametrization. With increasing $\beta$, however, they closely compete in energy with dimerized CDW solutions and finally become preferable in general. In the cases of $\nu = 2/3$ and 5/6, the transition points are estimated at $\beta/\sqrt{t_{MX}^\parallel K_{MX}^\parallel} \simeq 0.705$ and 0.814, respectively, while in the cases of $\nu = 7/10$ and 4/5, they turn out $\beta/\sqrt{t_{MX}^\parallel K_{MX}^\parallel} \simeq 0.765$ and 0.855, respectively, all of which may be too large to be realized in available platinum halides. It was predicted for a single $MX$ chain that incommensurate ground states should appear even at 3/4 filling provided the site-diagonal electron-lattice coupling is sufficiently strong,\textsuperscript{10} but they are not yet observed experimentally.

There is an attempt at fabricating a platinum-bromide triple-chain compound.\textsuperscript{51} Substitution of platinum ions with nickel ions should lead to stronger correlations between $d$ electrons and might result in novel spin arrangements. We hope our calculations will stimulate further chemical explorations of tubed $MX$ compounds.

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