Broken-Symmetry Ground States of Halogen-Bridged Binuclear Metal Complexes

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Based on a symmetry argument, we study ground states of what we call MMX-chain compounds, which are the new class of halogen-bridged metal complexes. Commensurate density-wave solutions of a relevant multi-band Peierls-Hubbard model are systematically revealed within the Hartree-Fock approximation. We numerically draw ground-state phase diagrams, where various novel density-wave states appear.

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The competition between electron-electron (el-el) and electron-phonon (el-ph) interactions in one dimension is a fascinating subject to be studied. Halogen-bridged transition-metal linear-chain complexes (MX chains) are good target materials in this context and have a long history of both chemical and physical researches. The mixed-valence MX chains have been attracting extensive interest primarily due to their significant dichroism and unusual Raman spectra [1], while the discovery of the unusual Raman spectra [1] is also worth mentioning that the MX-chain system can be regarded as a one-dimensional analog of the CuO plane in high-\(T_c\) superconductors.

In an attempt to explore further into the family of these materials, new halogen-bridged metal complexes, which are abbreviated as MMX chains, have been synthesized, where binuclear metal units are bridged by halogen ions. \(K_4[Pt_2(P_2O_5H_2)_4X]\cdot nH_2O (X = Cl, Br, I) [7–10] and \(M_2(CH_3CS_2)_4\) (M = Pt, Ni) [10] have been attracting considerable attention in the chemical field, whereas they have less been studied in the physical field [8,9] so far. The MMX-chain system may exhibit a wider variety of electronic structures than the MX-chain system. In this letter, focusing on commensurate density-wave ground states, we present a systematic symmetry argument [21] and clarify what kinds of broken-symmetry solutions are possible and actually stabilized within the Hartree-Fock (HF) approximation.

In order to treat both M- and X-atom electronic orbitals explicitly, we employ the following one-dimensional model Hamiltonian

\[
\mathcal{H} = \sum_{n,s} \left[ (\varepsilon_M - \beta u_{3,n}) n_{1,n,s} + (\varepsilon_M + \beta u_{3,n}) n_{2,n,s} + \varepsilon_X n_{3,n,s} \right] + \sum_{n} Ku_{3,n}^2 \\
- \sum_{n,s} \left[ (t_{MX} - \alpha u_{3,n}) a_{1,n,s}^\dagger a_{3,n,s} + (t_{MX} + \alpha u_{3,n}) a_{2,n,s}^\dagger a_{3,n,s} + t_{MM} a_{1,n,s}^\dagger a_{2,n-1,s} + \text{H.c.} \right] \\
+ \sum_{n} (U_M n_{1,n,+} n_{1,n,-} + U_M n_{2,n,+} n_{2,n,-} + U_X n_{3,n,+} n_{3,n,-}) \\
+ \sum_{n,s,s'} (V_{MX} n_{1,n,s} n_{3,n,s'} + V_{MX} n_{2,n,s} n_{3,n,s'} + V_{MM} n_{1,n,s} n_{2,n-1,s'}). \tag{1}
\]

where \(n_{i,n,s} = a_{i,n,s}^\dagger a_{i,n,s}\) with \(a_{i,n,s}^\dagger\) and \(a_{i,n,s}\) being the creation operators of an electron with spin \(s = \pm\) (up and down) in the \(M_d_{32}\) and \(X_{p_2}\) orbitals at the \(n\)th MXM unit, respectively, and \(u_{3,n}\) the chain-direction displacement of the halogen ion from the midpoint between the metal ions at the \(n\)th MXM unit. Here we have assumed that the lattice distortion comes only from the halogen ions, which was the case with MX chains with ligand-locked metal ions. Although metal ions still look locked in the surrounding ligands in the present system, there seems to be an experiment [13] implying movable metal ions in certain MMX chains. However, the present model normally has plenty of parameters to be controlled and therefore we assume fixed metal ions in our first attempt. The momentum representation of the Hamiltonian is generally given by
\[ H = \sum_{i,j} \sum_{k,q} \sum_{s} \langle i : k + q | j : k \rangle a_{i;k+k,q,s}^\dagger a_{j;k,s} + K \sum_k u_{3;k} u_{3;k}^\dagger \]
\[ + \frac{1}{2} \sum_{i,j,m,n,k,k',q,s,t} \langle i : k + q | m : k' | j : k + q | n : k' + q | a_{i;k+k,q,s}^\dagger a_{m;k',t} a_{n;k'+q,s} a_{j;k+s} \],
\[ (2) \]

where the spin-free one-body and two-body interactions, \( \langle i : k + q | j : k \rangle \) and \( \langle i : k + q | m : k' | j : k' + q \rangle \), are straightforwardly obtained from the Hamiltonian [2].

Let us introduce the symmetry group of the system as
\[ G = P \times S \times T, \]
\[ (3) \]
where \( P = L_1 \wedge C_2 \) is the space group of a linear chain with the one-dimensional translation group \( L_1 \) whose basis vector is the unit-cell translation \( t_1 \), \( S \) the group of spin rotation, and \( T \) the group of time reversal. Here we have discarded the gauge group arriving at superconducting phases. Group actions on the electron operators are defined as follows [2]:
\[ l \in L_1 : \quad l \cdot a_{i;k,s}^\dagger = e^{-i kl} a_{i;k,s}^\dagger, \]
\[ (4) \]
\[ p \in C_2 : \quad p \cdot a_{i;k,s}^\dagger = a_{i;k,p,s}, \]
\[ (5) \]
\[ u(e, \theta) \in S : \quad u(e, \theta) \cdot a_{i;k,s}^\dagger = \sum_{s'} [u(e, \theta)]_{ss'} a_{i;k,s'}, \]
\[ (6) \]
\[ t \in T : \quad t \cdot (fa_{i;k,s}^\dagger) = -sf^* a_{i;-k,-s}, \]
\[ (7) \]
where \( f \) is an arbitrary complex number. The spin rotation of angle \( \theta \) around an axis \( e \), \( u(e, \theta) \), is explicitly represented as \( \sigma^\theta \cos(\theta/2) - (\sigma \cdot e) \sin(\theta/2) \) in terms of the \( 2 \times 2 \) unit matrix \( \sigma^\theta \) and a vector composed of the Pauli-matrices, \( \sigma = (\sigma^x, \sigma^y, \sigma^z) \).

Let \( \hat{G} \) denote the irreducible representations of \( G \) over the real number field, where their representation space is spanned by the Hermitian operators \( \{ a_{i;k,s}^\dagger a_{j;k,s}' \} \). There is a one-to-one correspondence between \( G \) and broken-symmetry phases of density-wave type. Any representation \( \hat{G} \) is obtained as a Kronecker product of the irreducible real representations of \( P, S, \) and \( T \):
\[ \hat{G} = P \otimes S \otimes T. \]
\[ (8) \]
\( \hat{P} \) is characterized by an ordering vector \( q \) in the Brillouin zone and an irreducible representation of its little group \( P(q) \), and is therefore labeled \( q \hat{P}(q) \). The relevant representations of \( S \) and \( T \) are, respectively, given by
\[ \hat{S}^0(u(e, \theta)) = 1, \quad \hat{T}^1(u(e, \theta)) = O(u(e, \theta)), \]
\[ (9) \quad \hat{T}^0(t) = 1, \quad \hat{T}^1(t) = -1, \]
\[ (10) \]
where \( O(u(e, \theta)) \) is the \( 3 \times 3 \) orthogonal matrix satisfying \( u(e, \theta) \sigma^\lambda u(e, \theta)^* = \sum_{\mu=x,y,z} [O(u(e, \theta))]_{\mu\lambda} \sigma^\mu \quad (\lambda = x, y, z) \). The representations \( \hat{P} \otimes \hat{S}^0 \otimes \hat{T}^0, \hat{P} \otimes \hat{S}^1 \otimes \hat{T}^1, \hat{P} \otimes \hat{S}^0 \otimes \hat{T}^0, \) and \( \hat{P} \otimes \hat{S}^1 \otimes \hat{T}^0 \) correspond to charge-density-wave, spin-density-wave, charge-current-wave, and spin-current-wave states, respectively. We leave out current-wave states, because in one dimension all of them but one-way uniform-current states break the charge- or spin-conservation law. We consider two ordering vectors \( q = 0 \) and \( q = \pi \), which are labeled \( \Gamma \) and \( X \), respectively. Thus the instabilities labeled \( K \hat{P}(K) \otimes \hat{S}^0 \otimes \hat{T}^0 \quad (K = \Gamma, X; \quad i = 0, 1) \) are of our interest. Since \( P(\Gamma) = P(X) = C_2, \) \( \hat{P}(\Gamma) \) and \( \hat{P}(X) \) are either \( A \) (\( C_2 \)-symmetric) or \( B \) (\( C_2 \)-antisymmetric) representation of \( C_2 \).

In the HF approximation the Hamiltonian [2] is replaced by
\[ \mathcal{H}_{HF} = \sum_{i,j} \sum_{k,s,s'} \sum_{\lambda=0,\pi} \left[ x_{ij}^\lambda \langle \Gamma ; k | a_{i;k,s,s'}^\dagger a_{j;k,s'} + x_{ij}^\lambda \langle X ; k | a_{i;k,s,s'}^\dagger a_{j;k,s'} \right] \sigma^\lambda_{ss'} . \]
\[ (11) \]

The present model arrives at no helical-spin \( (\lambda = x, y) \) solution. The self-consistent field \( x_{ij}^\lambda (K; k) \) is expressed as
\[ x_{ij}^\lambda (\Gamma; k) = \langle i : k | j : k \rangle + \sum_{m,n} \rho_{nm}(\Gamma; k') \]
\[ \times \left( 2 \langle i : k | m : k' | j : k + \pi \rangle - \langle i : k + \pi | m : k' \rangle \right), \]
\[ (12) \]
\[ x_{ij}^\lambda (X; k) = \langle i : k + \pi | j : k \rangle + \sum_{m,n} \rho_{nm}(X; k' + \pi) \]
\[ \times \left( 2 \langle i : k + \pi | m : k' | j : k + \pi \rangle - \langle i : k + \pi | m : k' + \pi | j : k \rangle \right), \]
\[ (13) \]
\[ x_{ij}^\lambda (\Gamma; k) = - \sum_{m,n} \rho_{nm}(\Gamma; k') \langle i : k | m : k' | j : k \rangle, \]
\[ (14) \]
\[ x_{ij}^\lambda (X; k) = - \sum_{m,n} \rho_{nm}(X; k' + \pi) \langle i : k + \pi | m : k' | j : k \rangle, \]
\[ (15) \]
\[
\rho_{ij}^{\lambda}(\Gamma; k) = \frac{1}{2} \sum_{s,s'} \langle a_{i;k,s}^\dagger a_{i;k,s'} \rangle_{HF} \sigma_{ss'}^{\lambda},
\]
\[
\rho_{ij}^{\lambda}(X; k) = \frac{1}{2} \sum_{s,s'} \langle a_{j;k+s,s}^\dagger a_{j;k,s'} \rangle_{HF} \sigma_{ss'}^{\lambda},
\]
where \( \langle \cdots \rangle_{HF} \) means the quantum average in a HF eigenstate. The HF Hamiltonian \([13]\) is decomposed as \([23]\)
\[
\mathcal{H}_{HF} = \sum_{D=A,B} \sum_{K=A,X} \sum_{\lambda=0,z} h^\lambda(K; D),
\]
where the irreducible components \( h^\lambda(K; D) \) are given by
\[
h^\lambda(K; D) = \frac{1}{2} \sum_{p \in C_2} \chi^{(D)}(p) p \cdot x^\lambda_\nu(K; k) a_{i;k,s}^\dagger a_{j;k,s'} \sigma_{ss'}^{\lambda},
\]
with \( \chi^{(D)}(p) \) being the irreducible character of the \( D \) representation for the group element \( p \). Now we obtain the relevant broken-symmetry Hamiltonian for the representation \( KD \otimes S^i \otimes T^i \) as \( h^0(\Gamma; A) + h^\lambda(K; D) \), where \( \lambda = 0 \) for \( i = 0 \) and \( \lambda = z \) for \( i = 1 \).

The charge and spin densities on site \( i \) at the \( n \)th MXM unit are, respectively, expressed as
\[
d_{i;n} = \sum_s \langle a_{i;n,s}^\dagger a_{i;n,s} \rangle_{HF},
\]
\[
s_{i;n}^z = \frac{1}{2} \sum_{s,s'} \langle a_{i;n,s}^\dagger a_{i;n,s'} \rangle_{HF} \sigma_{ss'}^z,
\]
while the bond and spin bond orders between site \( i \) at the \( n \)th MXM unit and site \( j \) at the \( m \)th MXM unit are, respectively, defined as
\[
p_{i;n;j;m} = \sum_s \langle a_{i;n,s}^\dagger a_{j;m,s} \rangle_{HF},
\]
\[
p^z_{i;n;j;m} = \frac{1}{2} \sum_{s,s'} \langle a_{i;n,s}^\dagger a_{j;m,s'} \rangle_{HF} \sigma_{ss'}^z.
\]
The halogen-ion displacements \( u_n \) are self-consistently determined so as to minimize the HF energy \( E_{HF} = \langle \mathcal{H} \rangle_{HF} \). All the order parameters \([17],[22]\), as well as \( E_{HF} \), are expressed in terms of the density matrices whose symmetry properties are definitely determined by the corresponding invariance group (Table \([1]\)). Here we simply describe all the phases obtained and schematically show them in Fig. \([1]\).

(a) \( \Gamma A \otimes \hat{S}^0 \otimes \hat{T}^0 \)

The paramagnetic state with the full symmetry \([3]\), abbreviated as PM.

(b) \( \Gamma B \otimes \hat{S}^0 \otimes \hat{T}^0 \)

Electron-lattice-coupled bond order wave accompanied by alternating metal charge densities, abbreviated as BOW.

(c) \( XA \otimes \hat{S}^0 \otimes \hat{T}^0 \)

Charge density wave on halogen sites accompanied by alternating metal charge densities, abbreviated as X-CDW.

(d) \( XB \otimes \hat{S}^0 \otimes \hat{T}^0 \)

Electron-lattice-coupled charge density wave on metal sites, abbreviated as M-CDW.

(e) \( \Gamma A \otimes \hat{S}^1 \otimes \hat{T}^1 \)

Ferromagnetism with uniform spin bond orders, abbreviated as FM.

(f) \( \Gamma B \otimes \hat{S}^1 \otimes \hat{T}^1 \)

Spin bond order wave accompanied by alternating metal spin densities, abbreviated as SBOB.

(g) \( XA \otimes \hat{S}^1 \otimes \hat{T}^1 \)

Spin density wave on halogen sites accompanied by alternating spin bond orders and metal spin densities, abbreviated as X-SDW.

(h) \( XB \otimes \hat{S}^1 \otimes \hat{T}^1 \)

Spin density wave on metal sites accompanied by alternating spin bond orders, abbreviated as M-SDW.

Magnetic instabilities are generally not coupled with phonons. The reason X-CDW is a purely electronic state is just because we have restricted the lattice distortion to halogen ions. X-CDW is not stabilized within our assumption but may be by metal-ion displacements.
Let us observe a few pieces of numerical investigation. We show in Fig. 2 typical ground-state phase diagrams obtained by computing \( E_{\text{HF}} \). As-grown MMX-chain compounds have the \( \frac{5}{6} \)-filled band structure, where \( q = \pi \) instabilities are dominant unless both \( U_M \) and \( U_X \) are large enough. Once we go beyond the mean-field theory, the ferromagnetic region should more or less shrink due to multiscattering effects [24]. As holes are doped into the system, \( q = \pi \) instabilities are generally replaced by \( q = 0 \) ones. Further hole doping beyond the \( \frac{4}{6} \) band filling again stabilizes \( q = \pi \) phases. However, in the heavily hole-doped region where the closed-shell electronic structure of halogen ions is broken, M-SDW with no spin density on halogen sites seems to be much less stabilized.

Energy calculations suggest that all the transitions between broken-symmetry phases are of first order. Further numerical investigations, including microscopic information on the electronic structure, will be presented elsewhere. It seems that physical research on MMX-chain compounds is still in its early stage. We hope the present calculation will motivate and accelerate further synthesis and measurements of these fascinating materials.

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### TABLE I. Invariance groups characteristic of each irreducible representation.

| Representation | Invariance group |
|----------------|------------------|
| $\Gamma A \otimes S^0 \otimes T^0$ | $L_1C_2ST$ |
| $\Gamma B \otimes S^0 \otimes T^0$ | $L_1ST$ |
| $XA \otimes S^0 \otimes T^0$ | $L_2C_2ST$ |
| $XB \otimes S^0 \otimes T^0$ | $(1 + l_1C_2)L_2ST$ |
| $\Gamma A \otimes S^1 \otimes T^1$ | $L_1C_2A(e_z)M(e_\parallel)$ |
| $\Gamma B \otimes S^1 \otimes T^1$ | $(1 + C_2u(e_\parallel, \pi))L_1A(e_z)M(e_\parallel)$ |
| $XA \otimes S^1 \otimes T^1$ | $(1 + l_1u(e_\parallel, \pi))L_2C_2A(e_z)M(e_\parallel)$ |
| $XB \otimes S^1 \otimes T^1$ | $(1 + l_1C_2)(1 + l_1u(e_\parallel, \pi))L_2A(e_z)M(e_\parallel)$ |

$L_2 = \{E, l_1^{n}\mid n \in \mathbb{N}\}$.

$A(e_z) = \{u(e_z, \theta)\mid 0 \leq \theta \leq 4\pi, e_z\parallel \text{(the z direction)}\}$.

$M(e_\parallel) = \{E, tu(e_\parallel, \pi)\mid e_\parallel\parallel \text{(the chain direction)}\}.$