Quantum and Thermal Phase Transitions of Halogen-Bridged Binuclear Transition-Metal Complexes

Shoji Yamamoto
Department of Physics, Okayama University, Tsushima, Okayama 700-8530, Japan
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Aiming to settle the controversial observations for halogen-bridged binuclear transition-metal (MMX) complexes, finite-temperature Hartree-Fock calculations are performed for a relevant two-band Peierls-Hubbard model. Thermal, as well as quantum, phase transitions are investigated with particular emphasis on the competition between electron itinerancy, electron-phonon interaction and electron-electron correlation. Recently observed distinct thermal behaviors of two typical MMX compounds Pt2(CH3CS2)2I and (NH4)4[Pt2(P2O5H2)4I]·2H2O are supported and further tuning of their electronic states is predicted.

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There is a class of quasi-one-dimensional materials containing chains of transition-metal (M) complexes bridged by halogens (X). Their representatives such as Wolf fram’s red (M = Pt, X = Cl) and Reihlen’s green (M = Pt, X = Br) salts \[\text{[Pt}_2\text{(pop)}\text{Cl}_2\text{]}\] are composed of mononuclear metal complexes and are thus referred to as MX chain compounds. These PtX chains generally exhibit a mixed-valence ground state with strong dimerization of the X sublattice. When Pt is replaced by Ni, a mono-valence regular-chain structure is instead stabilized, which is nothing but a tuning from the Peierls to Mott insulator. The electronic state of the MX chain system can such widely be tuned that the optical energy gap changes from 0 to 3.3 eV by varying the transition metal and may therefore enhance the electrical conductivity. In the dta complexes with no counter ion, the on-site Coulomb repulsion due to its \[\frac{z}{6}\text{filled one-dimensional two-band three-orbital extended Peierls-Hubbard Hamiltonian:}\]

\[
\mathcal{H} = \sum_{m,s} \sum_{j=1,2} (\varepsilon_M - \beta j_m) a^\dagger_{j,m,s} a_{j,m,s} + \sum_{m,s} \varepsilon_X n_{3,m,s}
- \sum_{m,s} \sum_{j=1,2} (t_{MX} - \alpha j_n) (a^\dagger_{j,m,s} a_{3,n,s} + a^\dagger_{3,n,s} a_{j,m,s})
- \sum_{m,s} t_{MM} (a^\dagger_{1,n,s} a_{2,n-1,s} + a^\dagger_{2,n-1,s} a_{1,n,s})
+ \sum_{m} \sum_{j=1,2} U_M n_{j,m,+} n_{j,m,-} + \sum_{m} U_X n_{3,m,+} n_{3,m,-}
+ \sum_{m,s,s'} \sum_{j=1,2} V_{MX} n_{j,m,s} n_{3,m,s'}
+ \sum_{m,s,s'} V_{MM} n_{1,m,s} n_{2,m-1,s'} + \sum_{m=1,2} K \sum_{j=1,2} t_{j,m},
\]

where \(n_{j,m,s} = a^\dagger_{j,m,s} a_{j,m,s}\) with \(a^\dagger_{j,m,s}\) being the creation operator of an electron with spin \(s = \pm (\uparrow \text{and } \downarrow)\) for the M \(d_{z^2}\) \((j = 1, 2)\) or X \(p_z\) \((j = 3)\) orbital in the nth MMX unit, and \(l_{j,m} = (-1)^j (u_{j,m} - u_{3,m})\) with \(u_{j,m}\) being the chain-direction displacement of the metal \((j = 1, 2)\) or halogen \((j = 3)\) in the nth MMX unit from its equilibrium position. \(\alpha\) and \(\beta\) are, respectively, the intersite and intrasite electron-lattice coupling constants, while \(K\) is the metal-halogen spring constant. We assume, based on the thus-far reported experimental observations, that every \(M_2\) moiety is not deformed, namely, \(u_{1,n} = u_{2,n-1}\), \(\varepsilon_M\), and \(\varepsilon_X\) are the on-site energies of isolated metal and halogen atoms, respectively. The electron hoppings between these levels are modeled by \(t_{MM}\) and \(t_{MX}\), whereas the electron-electron Coulomb interactions by \(U_M\), \(U_X\), \(V_{MM}\) and \(V_{MX}\). Though different-site Coulomb interactions may in principle be coupled with lattice displacements in a two-band description, any
alternation of them is usually neglected renormalizing $\beta$ under the mean-field treatment of $\sum_i n_{i,n,m,s}$. We always set $t_{MX}$ and $K$ both equal to unity.

Current empirical arguments on the electronic structures of MMX compounds are aiming to distinguish between four types of one-dimensional charge ordering mode [12], which are illustrated as (a) to (d) in Fig. 1, assuming that the X $p_z$ orbitals are stably filled and irrelevant. Quite recently, potential magnetic phases have also been pointed out ((e) to (h) in Fig. 1) and a systematic study of broken-symmetry solutions in the two-band scheme has been presented [13]. The two-band description of all the phases is also given in Fig. 1. We learn that (c) and (g) should be characterized by charge and spin modulation on the X sublattice, respectively, rather than by any density wave on the M$_2$ sublattice. The relevance of the X $p_z$ orbitals in these states has indeed been visualized numerically [14].

Most of the ground states of the pop-family MMX compounds have now been assigned to (d) [15–18], though early structural analyses [7,8] were rather controversial. However, due to the relatively small Peierls gaps in comparison with those of MX compounds, they can be tuned from the strongly valence-trapped state toward the paramagnetic or antiferromagnetic valence-delocalized state by replacing halogen and/or counter ions [15,19]. Since the halogen character increases in the halogen character increases in the $d_{xy}$ Pt-Pt wave functions in the order Cl $<$ Br $<$ I, even further charge fluctuation toward (c) [20] may be observed in the iodo complexes. Such a reverse Peierls instability can be reinforced under external pressure [21,22]. In general, the complete valence localization breaks down with increasing temperature [13–17]. (NH$_4$)$_4$[Pt$_2$(pop)$_4$I]·2H$_2$O clearly exhibits a thermal phase transition from (d) to (a) [23].

There has also been a controversy over the electronic structures of the dta-family compounds. Early investigations [10] reported similar semiconducting behaviors for both Pt and Ni complexes. However, later magnetic-susceptibility [24] and proton-spin relaxation-time [24] measurements claimed to distinguish Ni$_2$(dta)$_4$I from Pt$_2$(dta)$_4$I elucidating the distinct antiferromagnetic spin structure with strong exchange coupling for the former. Furthermore, recent extensive physical measurements [25] on Pt$_2$(dta)$_4$I have revealed its metallic conduction above room temperature as well as a totally different scenario for its valence structure: With decreasing temperature, there occurs a metal-semiconductor transition at room temperature, which can be regarded as the transition from the valence-delocalized state (a) to the trapped-valence state (b), and further transition to the Peierls-insulating charge-ordering mode (c) follows around 80 K.

**FIG. 1.** Schematic representation of possible density-wave states within the single-band approximation and in terms of the two-band description. In the left half, the circles and arrows denote electron total (when closed) or half (when shaded) occupancy with unpolarized and polarized spins, respectively, where the valence numbers denote formal oxidation states, namely, $2^+$ and $3^+$ should generally be regarded as $(2 + \delta)^+$ and $(3 - \delta)^+$ ($0 \leq \delta \leq 0.5$), respectively. In the right half, the various circles and segments qualitatively denote the variation of local electron densities and bond orders, respectively, whereas the signs ± in circles and strips denote the alternation of local spin densities and spin bond orders, respectively, where 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 $p_{i,n;j,m} = \sum_s c_{i,n,s}^\dagger a_{j,m,s}$ and $t_{i,n;j,m} = \frac{1}{2} \sum_s s c_{i,n,s}^\dagger a_{j,m,s}$. Symbols shifted from the regular position qualitatively represent lattice distortion.
bands, which is visualized in Fig. 3. Since an energy gap is essential in the strongly valence-trapped M-CDW state, while it is the overlap of the $d_{x^2}$ orbitals on neighboring M$_2$ moieties that stabilizes the relatively valence-delocalized X-CDW state. Therefore, M-CDW is more stabilized with increasing $t_{MM}$. Based on semiempirical quantum-chemical band calculations, Borschch et al. [20] pointed out a possibility of twisting of the dta ligand reducing the electronic communication by $\pi$ delocalization between adjacent metal sites and ending in X-CDW with charge disproportionation in the M$_2$ moiety. The transition from PM to BOW can also be understood as charge disproportionation within every M$_2$ moiety with decreasing $t_{MM}$. However, the contrast between the pop crossing over the Fermi level is disadvantageous in gaining entropy via thermal excitations, PM and BOW may compete with X-CDW and M-CDW at finite temperatures. Figure 3 suggests that the conduction band for X-CDW is transformed into PM via BOW, whereas M-CDW directly into PM, each of which coincides with the thermal behaviors of the dta and pop complexes, respectively. The thermal stabilization of PM and BOW is convincing when we consider their electronic structures. In comparison with X-CDW and M-CDW with cell doubling, PM and BOW maintain the original lattice symmetry and therefore possess effectively half-filled conduction bands, which is visualized in Fig. 3. Since an energy gap

FIG. 2. Thermal phase boundaries as functions of the transfer integral (a: $\alpha = 0.6$, $\beta = 1.5$, $U_M = 2.0$, $U_X = 1.0$, $V_{MM} = V_{MX} = 0.5$), the electron-lattice coupling (b: $t_{MM} = 1.2$, $\beta = 1.5$, $U_M = 2.0$, $U_X = 1.0$, $V_{MM} = V_{MX} = 0.5$), the M-site Coulomb repulsion (c: $t_{MM} = 1.2$, $\alpha = 0.8$, $\beta = 1.5$, $U_M = 1.0$, $V_{MM} = V_{MX} = 0.5$) and the X-site Coulomb repulsion (d: $t_{MM} = 1.2$, $\alpha = 0.6$, $\beta = 1.5$, $U_M = 2.0$, $V_{MM} = V_{MX} = 0.5$) at various values of $\Delta \varepsilon \equiv \varepsilon_M - \varepsilon_X$.

FIG. 3. Band dispersions of PM (a), BOW (b), X-CDW (c) and M-CDW (d) at $t_{MM} = 1.2$, $\alpha = 0.8$, $\beta = 1.5$, $\Delta \varepsilon = 0.5$, $U_M = 2.0$, $U_X = 1.0$ and $V_{MM} = V_{MX} = 0.5$.
and dta complexes may not be attributable mainly to their transfer integrals. Early x-ray structural investigations \cite{5} reported the Pt-Pt distance in the dimer to be 2.813 Å and 2.677 Å for K₄[Pt₂(pop)₄Cl]·3H₂O and Pt₂(dta)₄I, respectively. Even if we assume the general tendency \( \ell_{\text{Pt-Pt}} < \ell_{\text{Pt-Br}} < \ell_{\text{Pt-I}} \), it is rather hard to conclude that \( \ell_{\text{MXM}}/\ell_{\text{MX}} \) for the dta complex is generally smaller than those for the pop complexes. The idea of larger \( M(d_{z^2})-M(d_{z^2}) \) overlap of the dta complex can further be justified by its higher conductivity (13 Ω⁻¹ cm⁻¹) compared with those of the pop-family iodo complexes (\( \sim 10^{-2} - 10^{-4} \Omega^{-1} \text{ cm}^{-1} \)).

Then, what is the leading factor of such a striking contrast between the pop and dta complexes? We seek it in their electron-lattice interactions. Figure 2(b) shows that M-CDW is stabilized with increasing \( \beta \), whereas X-CDW with increasing \( \alpha \). The orbital hybridization mainly stays within every \( M_2 \) moiety for M-CDW, while it essentially extends over neighboring \( M_2 \) moieties for X-CDW. Therefore, X-CDW is quite sensitive to \( \alpha \) effectively describing the alternation of the MXM interdimer transfer. In comparison with \( \beta \) which is a measure for the mobility of the X sublattice, \( \alpha \) relatively describes the mobility of the \( M_2 \) sublattice. The halogen ions are rather free in both pop and dta complexes and therefore \( \beta \) may not characterize these materials well. On the other hand, \( \alpha \) must distinguish Pt₂(dta)₄I from the pop-family compounds. The \( M_2 \) moieties are tightly locked together in the pop complexes due to the hydrogen bonds between the ligands and the counter cations, whereas they are rather movable in the dta complex owing to its neutral chain structure. Thus, explicitly considering interdimer elastic constants as well, a significantly larger \( \alpha \) is expected for Pt₂(dta)₄I. Now Fig. 2(b) allows us to attribute the distinct thermal behaviors of the pop and dta complexes mainly to their electron-phonon interactions. We never exclude out the effect of their transfer integrals as an underlying driving force. Phase transitions from this point of view may definitely be observed under external pressure \cite{20,21}. As the adjacent metals in the dimer are tightly locked to each other by the surrounding ligands, an applied pressure enhances \( \ell_{\text{MX}} \) rather than \( \ell_{\text{MM}} \).

In relation to replacing the metals and the halogens, it is also interesting to observe the phase competition as a function of the Coulomb interactions. Such a tuning of the electronic state is visualized in Figs. 2(c) and 2(d). Pt can be replaced by Ni in the dta complexes. Considering that the orbital energies of Ni and I are so close as to be possibly reversed (\( \varepsilon_M - \varepsilon_i \equiv \Delta \varepsilon < 0 \)) in the crystal and the on-site d-d Coulomb repulsion is considerably strong for Ni \( \equiv \beta \), Fig. 2(c) well supports the observations \cite{25} for Ni₂(dta)₄I—no Peierls distortion and the Mott-insulating behavior exhibiting an antiferromagnetic spin susceptibility. On the other hand, as \( \Delta \varepsilon \) increases, M-CDW begins to compete with X-CDW. This is quite convincing from the point of view of orbital hybridization. We have already learnt in Fig. 2 that X-CDW should be characterized by the charge density wave on the X sublattice. When we add up the charge densities on the adjacent metal sites in every \( M_2 \) moiety, they shall no more modulate for X-CDW but still oscillate for M-CDW. Furthermore Fig. 2(b) shows that the largest gap opens between the two highest-lying bands primarily of \( d_{\sigma^*} \) character for M-CDW, whereas between the two lowest-lying ones for X-CDW implying an essential hybridization of the \( d_{z^2} \) and \( p_z \) orbitals. We are thus convinced that M-CDW and X-CDW are stabilized and destabilized, respectively, with the increase of \( \Delta \varepsilon \). Figure 2(c) is then an interpretation of the close Pt \( d_{z^2} \) and I \( p_z \) orbital energies. Finally we take a look at Fig. 2(d) raising a possibility of the novel antiferromagnetic state X-SDW appearing by the replacement of the halogens. \( U_X \) increase in close cooperation with the increase of \( \Delta \varepsilon \) and therefore its stabilization is not so trivial in practice. A somewhat tricky situation \( V_{\text{MM}} < V_{\text{MX}} \) advantageously acts on X-SDW \cite{4}. Otherwise we wonder whether a Pd chain chloride could be synthesized.

We hope that the present calculations will settle the controversial observations especially for Pt₂(dta)₄I \cite{8,9} and contribute to a semiquantitative estimation of the essential parameters. In such circumstances that even the hopping amplitudes are not yet revealed, a close collaboration between experimental and theoretical investigations is really expected.

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\begin{thebibliography}{9}
\bibitem{1} R. J. H. Clark: in \textit{Advances in Infrared and Raman Spectroscopy}, edited by R. J. H. Clark and R. E. Hester (Wiley, New York, 1984) Vol. II, p. 95.
\bibitem{2} H. Töftlund and O. Simonsen: Inorg. Chem. \textbf{23} (1984) 4261.
\bibitem{3} K. Toriumi, Y. Wada, T. Mitani, S. Bandow, M. Yamashita and Y. Fujii: J. Am. Chem. Soc. \textbf{111} (1989) 2341.
\bibitem{4} H. Okamoto, T. Mitani, K. Toriumi and M. Yamashita: Mater. Sci. Eng. B \textbf{13} (1992) L9.
\bibitem{5} P. Stein, M. K. Dickson and D. M. Roundhill: J. Am. Chem. Soc. \textbf{105} (1983) 3489.
\bibitem{6} C. M. Che, F. H. Herbst, W. P. Schaefer, R. E. Marsh and H. B. Gray: J. Am. Chem. Soc. \textbf{105} (1983) 4606.
\bibitem{7} M. Kurmoo and R. J. H. Clark: Inorg. Chem. \textbf{24} (1985) 4420.
\bibitem{8} R. J. H. Clark, M. Kurmoo, H. M. Dawes and M. B.
Hursthouse: Inorg. Chem. 25 (1986) 409.
[9] C. Bellitto, A. Flamini, L. Gastaldi and L. Scaramuzza: Inorg. Chem. 22 (1983) 444.
[10] C. Bellitto, G. Desy and V. Fares: Inorg. Chem. 24 (1985) 2815.
[11] K. Sakai, Y. Tanaka, Y. Tsuchiya, K. Hirata, T. Tsubomura, S. Iijima and A. Bhattacharjee: J. Am. Chem. Soc. 120 (1998) 8366.
[12] M. Kuwabara and K. Yonemitsu: J. Phys. Chem. Solids. 62 (2001) 435.
[13] S. Yamamoto: Phys. Lett. A 258 (1999) 183.
[14] S. Yamamoto: Phys. Rev. B 63, 15 March (2001).
[15] L. G. Butler, M. H. Zietlow, C.-M. Che, W. P. Schaefer, S. Sridhar, P. J. Grunthaner, B. I. Swanson, R. J. H. Clark and H. B. Gray: J. Am. Chem. Soc. 110 (1988) 1155.
[16] S. Jim, T. Ito, K. Toriumi and M. Yamashita: Acta Cryst. C 45 (1989) 1415.
[17] N. Kimura, H. Ohki, R. Ikeda and M. Yamashita: Chem. Phys. Lett. 220 (1994) 40.
[18] Y. Wada, T. Furuta, M. Yamashita and K. Toriumi: Synth. Met. 70 (1995) 1195.
[19] M. Yamashita, S. Miya, T. Kawashima, T. Manabe, T. Sonoyama, H. Kitagawa, T. Mitani, H. Okamoto and R. Ikeda: J. Am. Chem. Soc. 121 (1999) 2321.
[20] S. D. Conradson, M. A. Stroud, M. H. Zietlow, B. I. Swanson, D. Baeriswyl and A. R. Bishop: Solid State Commun. 65 (1988) 723.
[21] B. I. Swanson, M. A. Stroud, S. D. Conradson and M. H. Zietlow: Solid State Commun. 65 (1988) 1405.
[22] M. A. Stroud, H. G. Drickamer, M. H. Zietlow, H. B. Gray and B. I. Swanson: J. Am. Chem. Soc. 111 (1989) 66.
[23] M. Yamashita, Y. Wada, K. Toriumi and T. Mitani: Mol. Cryst. Liq. Cryst. 216 (1992) 207.
[24] R. Ikeda, N. Kimura, H. Ohki, T. Furuta and M. Yamashita: Synth. Met. 71 (1995) 1907.
[25] H. Kitagawa, N. Onodera, T. Sonoyama, M. Yamamoto, T. Fukawa, T. Mitani, M. Seto and Y. Maeda: J. Am. Chem. Soc. 121 (1999) 10068.
[26] S. A. Borshtch, K. Prassides, V. Robert, and A. O. Solomon: J. Chem. Phys. 109 (1998) 4562.
[27] H. Okamoto, Y. Shimada, Y. Oka, A. Chainani, T. Takahashi, H. Kitagawa, T. Mitani, K. Toriumi, K. Inoue, T. Manabe, M. Yamashita: Phys. Rev. B 54 (1996) 8438.