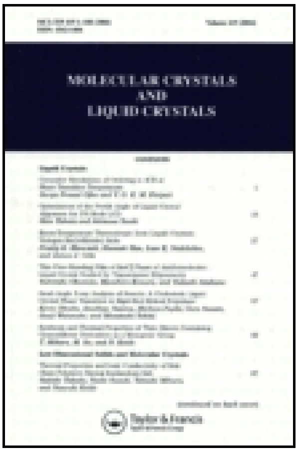

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Yosuke Eguchi [a] & Shoji Yamamoto [a]
[a] Department of Physics, Okayama University, Okayama, 700-8530, Japan

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# Halogen-Bridged Binuclear Metal Complexes Under Static Pressure

YOSUKE EGUCHI and SHOJI YAMAMOTO

*Department of Physics, Okayama University, Okayama 700-8530, Japan*

Two contrasting observations for halogen ($X$)-bridged binuclear platinum complexes $R_4[\mathrm{Pt}_2(\mathrm{P}_2\mathrm{O}_5\mathrm{H}_2)_4X]{\cdot}n\mathrm{H}_2\mathrm{O}$ are interpreted by finite-temperature Hartree-Fock calculations. Assuming pressure-induced simultaneous increases of the interdimer electron transfer and Coulomb repulsion, we reveal that an applied pressure turns the initial charge-polarization state into a charge-density-wave state at high temperatures, while the charge-density-wave state oppositely declines with increasing pressure at low temperatures. We predict pressure-induced phase transitions in another family of $MMX$ complexes, $\mathrm{Pt}_2(\mathrm{CH}_3\mathrm{CS}_2)_4\mathrm{I}$, as well.

*Keywords*: *MMX* chain; pressure-induced phase transition; Peierls-Hubbard model

Quasi-one-dimensional halogen ($X$)-bridged metal ($M$) complexes ($MX$ chains) have extensively been studied by both chemists and physicists due to their unique behavior featured by electron-electron correlations, electron-lattice interactions, low dimensionality and $d$-$p$ orbital hybridization [1]. Substituting the metals, bridging halogens, ligand molecules and counter ions, the electronic state can widely be tuned [2], which is a realization of the competition between the Peierls and Mott insulators. In recent years, a new class of these materials ($MMX$ chains) [3-5], which consists of binuclear metal units bridged by halogen ions, has been stimulating us to further explorations into one-dimensional unit-assembled spin-charge-lattice coupling systems. In comparison with $MX$ chains, $MMX$ chains indeed possess fascinating features. The formal oxidation state of the metal ions is 3+ in $MX$ chains, whereas it is 2.5+ in $MMX$ chains. Therefore, $MMX$ chains have an unpaired electron per metal dimer even in their trapped-valence states, contrasting with the valence-trapped state consisting of $M^{2+}$ and $M^{4+}$ in $MX$ chains. The $M(d_{z^2})$-$M(d_{z^2})$ direct overlap in $MMX$ chains effectively reduces the on-site Coulomb repulsion due to its $d_{\sigma^*}$ character and therefore enhances the electrical conductivity.

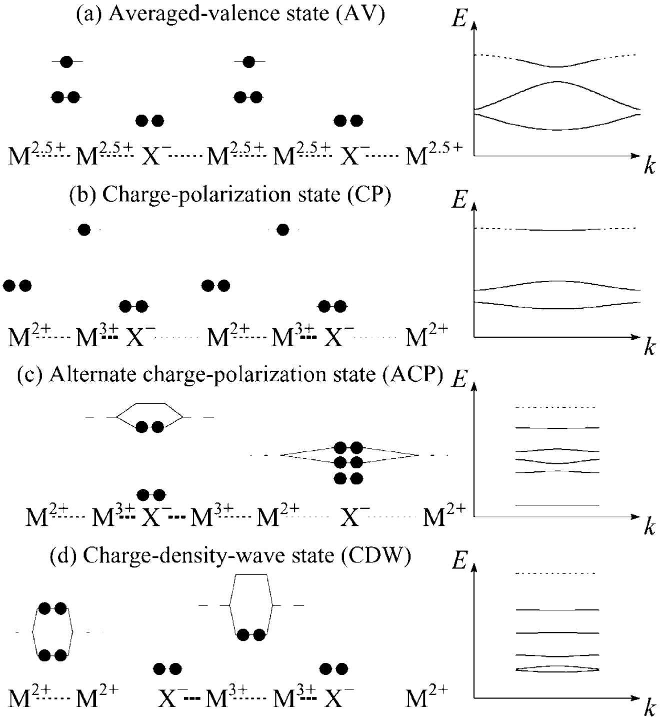

FIGURE 1. Electronic structures of the four charge-ordering modes and their typical band structures.

Four possible one-dimensional charge-ordering modes [6,7] have so far been observed in *MMX* chains, which are schematically shown in Figure 1. They are all successfully described in terms of the $\frac{5}{6}$-filled one-dimensional two-band three-orbital extended Peierls-Hubbard Hamiltonian [8-10]:

$$
\begin{aligned}
\mathcal{H} =& \sum_{m=1}^{N}\sum_{s=\uparrow,\downarrow}\sum_{j=1,2}\Big(\varepsilon_{\mathrm{M}}-\beta l_{j:n}\Big)n_{j:m,s}+\sum_{m=1}^{N}\sum_{s=\uparrow,\downarrow}\varepsilon_{\mathrm{X}}n_{3:m,s}+\sum_{m=1}^{N}\sum_{j=1,2}\frac{K}{2}l_{j:m}^{2}\\
&-\sum_{m=1}^{N}\sum_{s=\uparrow,\downarrow}\left[t_{\mathrm{MM}}\,a_{1:n,s}^{\dagger}a_{2:n-1,s}+\sum_{j=1,2}\Big(t_{\mathrm{MX}}-\alpha l_{j:n}\Big)a_{j:n,s}^{\dagger}a_{3:n,s}+\mathrm{H.c.}\right]\\
&+\sum_{m=1}^{N}\sum_{j=1,2}U_{\mathrm{M}}\,n_{j:m,+}n_{1:m,-}+\sum_{m=1}^{N}U_{\mathrm{X}}\,n_{3:n,+}n_{3:n,-}\\
&+\sum_{m=1}^{N}\sum_{s,s'=\uparrow,\downarrow}\sum_{j=1,2}\Big(V_{\mathrm{MX}}\,n_{j:m,s}n_{3:m,s'}+V_{\mathrm{MM}}\,n_{1:m,s}n_{2:m-1,s'}\Big)\,, \qquad (1)
\end{aligned}
$$

where $n_{j:m,s}=a_{j:m,s}^{\dagger}a_{j:m,s}$ with $a_{j:m,s}^{\dagger}$ being the creation operator of an electron with spin $s$ for the $M$ $d_{z^2}$ ($j=1,2$) or $X$ $p_z$ ($j=3$) orbital in the $m$th $MXM$ 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 $m$th $MXM$ unit from its equilibrium position. We always set $t_{\mathrm{MM}}$ and $K$ both equal to unity.

The $MMX$ family comprises $M_2(\mathrm{dta})_4\mathrm{I}$ ($M$ = Pt, Ni; dta = $\mathrm{CH_3CS_2^-}$) and $R_4[\mathrm{Pt_2(pop)_4}X]\cdot n\mathrm{H_2O}$ ($X$ = Cl, Br, I; $R$ = Li, K, $\cdots$; pop = $\mathrm{P_2O_5H_2^{2-}}$). The interchain hydrogen-bond network remains lying in the pop complexes, while the dta complexes possess neutral chain structures. $\mathrm{Pt_2(dta)_4I}$ exhibits metallic conduction around room temperature [11], which is the first observation in one-dimensional halogen-bridged metal complexes. With decreasing temperature, there occurs a metal-semiconductor transition, that is, a transition from the averaged-valence state Figure 1(a) to the trapped-valence state Figure 1(b), at 300 K, and further transition to the charge-ordering mode Figure 1(c) follows around 80 K. On the other hand, the pop complexes have charge-density-wave ground states of the conventional type [6,7], Figure 1(d). However, they have a large choice of bridging halogens, ligand molecules and counter ions and therefore exhibit a wide tunability of ground states [12]. An applied pressure also results in such a tuning of the electronic state and two contrasting observations [13,14] in this context are interpreted in this article.

Figure 1 shows that the orbital hybridization within every $M_2$ moiety originating from the electron transfer $t_{\mathrm{MM}}$ is essential to the stabilization of CDW, whereas ACP owes its stabilization to the interdimer electron transfer $t_{\mathrm{MX}}$. As the adjacent metals in the dimer are tightly locked to each other by the surrounding ligands, an applied pressure mainly reduces the $M$-$X$ distance. Therefore, from the viewpoint of the electron transfer, increasing pressure should transform CDW into ACP [see Figure 2(b)]. Swanson *et al.* [13] indeed demonstrated a *pressure-induced reverse Peierls instability* for a pop-family $MMX$ compound $\mathrm{K_4[Pt_2(pop)_4Br]\cdot 3H_2O}$ at 20 K. However, a recent experiment [14] has reported that an applied pressure oppositely stabilizes CDW. Matsuzaki *et al.* have systematically synthesized numerous pop-family iodo complexes substituting the counter ions and have found that as the $M$-$X$-$M$ distance increases, their valence structure is generally tuned from Figure 1(d) to Figure 1(b). They applied pressure to one of these samples, $\mathrm{[(C_2H_5)_2NH_2]_4[Pt_2(pop)_4I]}$, at room temperature and observed a phase transition from CP to CDW, that is, a *pressure-induced Peierls instability.* Increasing interdimer charge transfer and resultant charge proportionation look disadvantageous to both CP and CDW. Besides the electron transfer, the neighboring-site electron correlation and the on-site electron affinity may be influenced by an applied pressure. Thus we consider a combined pressure effect. We carry out finite-temperature Hartree-Fock calculations for the Hamiltonian (1) adiabatically determining lattice distortion so as to minimize the free energy at each temperature. Preliminary calculations at $N = 256$ and $N = 512$ resulted in almost the same estimates and thus we set $N$ to 256 in the following. The numerical accuracy of the phase boundary is between three and two digits.

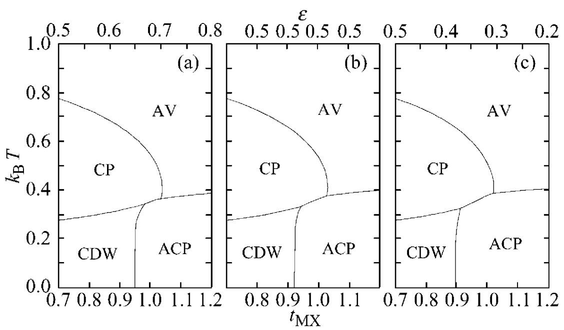

FIGURE 2. Thermal phase boundaries as functions of $t_{MX}$ and $\varepsilon = \varepsilon_M - \varepsilon_X$ varying under connections $\Delta\varepsilon = 0.6\Delta t_{MX}$ (a), $\Delta\varepsilon = 0$ (b) and $\Delta\varepsilon = -0.6\Delta t_{MX}$ (c). The parametrization, $\alpha = 0.7$, $\beta = 1.4$, $\varepsilon = 0.5$, $t_{MX} = 0.8$, $U_M = 1.5$, $U_X = 1.0$, $V_{MM} = 0.5$ and $V_{MX} = 0.5$, is common to all.

Figure 2 shows the thermal behavior as functions of the electron transfer and affinity simultaneously varying. On the one hand, increasing pressure enhances the overlap between the adjacent $M$ $d_{z^2}$ and $X$ $p_z$ orbitals, effectively reducing the difference between the two orbital energies, $\varepsilon_M - \varepsilon_X \equiv \varepsilon$. On the other hand, a reduction of the $M$-$X$ distance causes the Madelung potential on the metal sites to rise, enhancing $\varepsilon$. We have simulated both the cases [Figs. 2(a) and 2(c)] but they turn out not to be significantly different from the case of $t_{MX}$ singly varying [Figure 2(b)]. It is even likely that both the effects almost cancel out and increasing pressure ends up with no practical change of $\varepsilon$. Thus, $\varepsilon$ may be irrelevant to the pressure-induced phase transitions. It is true that CP may in principle be transformed into CDW with increasing $t_{MX}$, but such a transition is possible only in a narrow temperature range. Then we inquire into the effect of the electronic correlation.

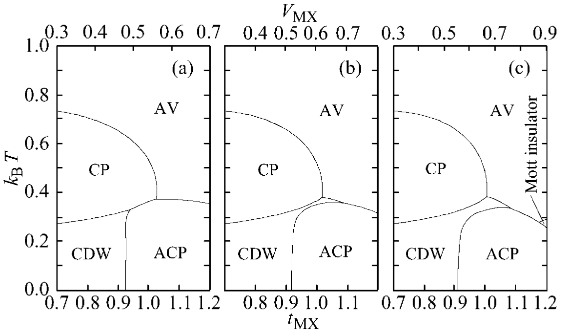

FIGURE 3. Thermal phase boundaries as functions of $t_{MX}$ and $V_{MX}$ varying under connections $\Delta V_{MX} = 0.8\Delta t_{MX}$ (a), $\Delta V_{MX} = 1.0\Delta t_{MX}$ (b) and $\Delta V_{MX} = 1.2\Delta t_{MX}$ (c), where the rest of the parameters are the same as those in Figure 2.

Figure 3 shows the thermal behavior under simultaneous increases of the electron transfer and the Coulomb repulsion. The low-temperature reverse Peierls instability with increasing pressure is steadfast under any parametrization. With increasing pressure, the energy gap decreases and then increases via the first-order transition from CDW to ACP, though the latter process has not yet been observed explicitly. On the other hand, the high-temperature behavior is much more sensitive to the parametrization. Assuming a predominant pressure effect on $t_{MX}$, there exists a little possibility of CP being transformed into CDW. With increasing pressure, CP is more likely to change directly into ACP at intermediate temperatures and into AV at sufficiently high temperatures. As we switch on the other pressure effect $\Delta V_{MX}$ in connection with $\Delta t_{MX}$, CP and ACP split with each other and CDW begins to grow between them. A careful observation of Figure 3 shows us that simultaneously increasing $t_{MX}$ and $V_{MX}$ more stabilize ACP than CDW in the quantum competition, while vice versa in the thermal competition.

Finally we discuss the dta complexes under pressure, where the intersite electron-phonon coupling $\alpha$ is much more relevant [8]. We show in Figure 4 the combined pressure effect under such parametrizations. Now the ground state is stabilized into ACP. The gapless CP state remains stable at higher temperatures. With a sufficiently large $\alpha$, the thermal behavior becomes insensitive to an applied pressure. Extensive pressure experiments may bring us a criterion for the material parameters.

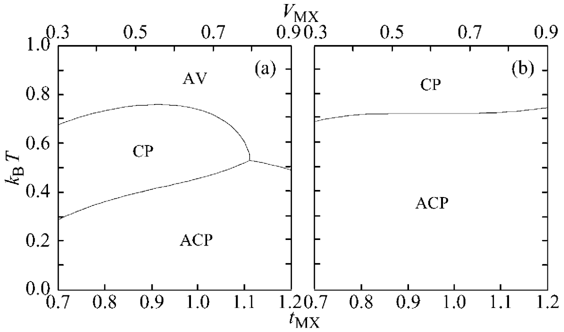

FIGURE 4. Thermal phase boundaries as functions of $t_{MX}$ and $V_{MX}$ varying under connections $\Delta V_{MX} = 1.2\Delta t_{MX}$, where the rest of the parameters are the same as those in Figure 2 except for $\alpha$ and $\beta$ being respectively set equal to 1.0 and 1.0 at (a) and to 1.4 and 0.7 at (b).

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