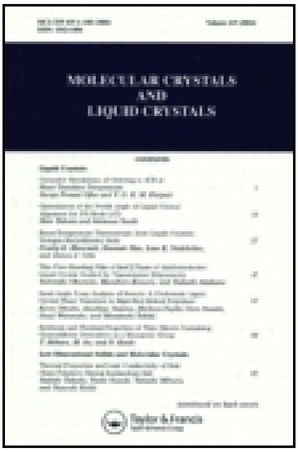

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Optical Excitations in XMMX Monomers and MMX Chains

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Optical Excitations in XMMX Monomers and MMX Chains

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We theoretically study optical excitations in $K_4[Pt_2(pop)_4X_2]$ monomers (X=Cl, Br, I), using an extended Hubbard model. We show that long-range transfer integrals and long-range Coulomb interactions are substantially large to reproduce the experimental results, and discuss effects of long-range Coulomb interactions on the electronic phases and the optical conductivity spectra of the MMX chains.

Keywords: MMX chain, optical conductivity, long-range transfer integral, long-range Coulomb interaction

INTRODUCTION

The halogen-bridged binuclear metal complexes (MMX chains) are quasi-one-dimensional materials consisting of dimer units of transition-metal (M) ions bridged by halogen (X) ions. They show a variety of charge ordering states accompanied with lattice modulations caused by strong electron-lattice coupling and electron-electron interaction; an averaged-valence (AV) state, a charge-density-wave (CDW) state, a charge-polarization (CP) state, and an alternate-charge-polarization (ACP) state [Fig.1(a)] [1, 2]. In $R_4[Pt_2(pop)_4X]$ (pop=$P_2O_5H_2$), the AV, CDW and CP states are realized by choosing the counter ions (R=K, $CH_3(CH_2)_7NH_2$, Na, Li) and the halogen ions (X=I, Br) [3-7]. In $Pt_2(dta)_4I$ (dta=CH_3CS_2), a metal-insulator transition has been found[2]. Above 300K it is a metallic AV state, and at least below 80K it is suggested to be the ACP

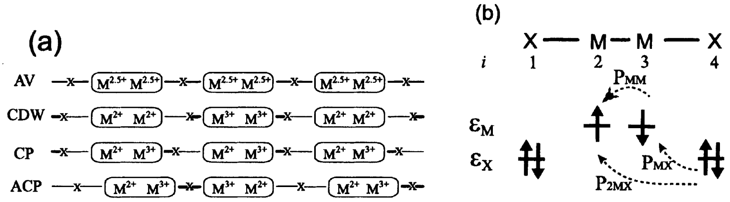

Figure 1: (a) Electronic states in the MMX chains, and (b) excitations in the XMMX monomer.

state. Theoretical studies for the origins of these ordering states have been performed with the extended Hückel calculation [8, 9], in the mean field approximation [10-12], and by the exact-diagonalization method[13, 14].

Recently, the optical conductivity of $K_4[Pt_2(pop)_4X_2]$ monomers (X=Cl, Br, I), which hereafter we call XMMX monomers, have been measured, and three peaks are found[15]. These peaks are ascribed to the excitation between the metal sites (P_{MM}) and the two excitations between the metal and halogen sites (P_{MX} and P_{2MX}), as schematically shown in Fig.1(b).

In this paper we study the optical conductivity of the XMMX monomers by using an extended Hubbard model. We determine the model parameters of the XMMX monomers to reproduce the experimental results, and discuss the electronic phases and the optical conductivity spectra of the MMX chains.

EXTENDED HUBBARD MODEL

We use a four-site system composed of two metal (M) sites ($i = 2, 3$) and two halogen (X) sites ($i = 1, 4$),

$$\begin{aligned} H &= -\sum_{i,\sigma} t_i [c^\dagger_{i,\sigma} c_{i+1,\sigma} + \text{h.c.}] - \sum_{i,\sigma} t'_i [c^\dagger_{i,\sigma} c_{i+2,\sigma} + \text{h.c.}] \\ &+ \sum_i \epsilon_i n_i + \sum_i U_i n_{i,\uparrow} n_{i,\downarrow} + \sum_i V_i n_i n_{i+1} + \sum_i V'_i n_i n_{i+2}, \quad (1) \end{aligned}$$

where $c^\dagger_{i,\sigma}$ creates an electron with spin σ at site i, $n_{i,\sigma} = c^\dagger_{i,\sigma} c_{i,\sigma}$ and $n_i = \sum_\sigma n_{i,\sigma}$. The transfer integral between the M sites is denoted by $t_2 = t_{\mathrm{MM}}$, that between the neighboring X and M sites $t_1 = t_3 = t_{\mathrm{MX}}$, and the next-nearest-neighbor transfer integral by $t'_1 = t'_2 = t_{2\mathrm{MX}}$.

The levels of the M d_{z^2}- and X p_z-orbitals are denoted by $\epsilon_2 = \epsilon_3 = \epsilon_{\mathrm{M}}$ and $\epsilon_1 = \epsilon_4 = \epsilon_{\mathrm{X}}$, respectively. The on-site repulsion strengths are $U_2 = U_3 = U_{\mathrm{M}}$ for M and $U_1 = U_4 = U_{\mathrm{X}}$ for X. The nearest-neighbor interaction between the M and X sites is denoted by $V_1 = V_3 = V_{\mathrm{MX}}$, and that between the M sites is $V_2 = V_{\mathrm{MM}}$. The parameter V_i' is for the next-nearest-neighbor interaction $V_1' = V_2' = V_{2\mathrm{MX}}$.

We exactly diagonalize the 4-site system. The real part of the optical conductivity is expressed, with the use of the current-current correlation function $\chi_{jj}(\omega)$, by

$$\sigma_1(\omega) = D\delta(\omega) + \frac{e^2}{\omega}\mathrm{Im}\chi_{jj}(\omega), \tag{2}$$

$$\chi_{jj}(\omega) = -\frac{1}{N}\langle\phi_0|j\frac{1}{E_0 - H + \omega + i\eta}j|\phi_0\rangle, \tag{3}$$

where $|\phi_0\rangle$ is the ground state, E_0 is its energy, j is the paramagnetic current-density operator, N is the number of sites, and η is a small positive number. The current-current correlation function was obtained as a continued fraction by using the Lanczos method[16].

RESULTS AND DISCUSSIONS

We consider a system with 6 electrons (2 holes) on the 4-site system. In the atomic limit ($t_{\mathrm{MM}} = t_{\mathrm{MX}} = t_{2\mathrm{MX}} = 0$), the energy of the ground state is $E_0 = -2\Delta_{\mathrm{h}} + V_{\mathrm{MM}}$ in the hole picture with $\Delta_{\mathrm{h}} \equiv \epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}} + U_{\mathrm{M}} - U_{\mathrm{X}} + 2V_{\mathrm{MM}}$ (i.e., by subtracting a constant term), that of the excited state P_{MM} in Fig.1 (b) is $E(\mathrm{P}_{\mathrm{MM}}) = -2\Delta_{\mathrm{h}} + U_{\mathrm{M}}$, that of P_{MX} is $E(\mathrm{P}_{\mathrm{MX}}) = -\Delta_{\mathrm{h}} + V_{2\mathrm{MX}}$, and that of $\mathrm{P}_{2\mathrm{MX}}$ is $E(\mathrm{P}_{2\mathrm{MX}}) = -\Delta_{\mathrm{h}} + V_{\mathrm{MX}}$. The intensities of the optical conductivity are proportional to $|\langle\phi_\nu|j|\phi_0\rangle|^2/(E_\nu - E_0)$, which are estimated by the lowest-order perturbation theory with respect to the transfer integrals,

$$\begin{aligned} I(\mathrm{P}_{\mathrm{MM}}) &= 4t_{\mathrm{MM}}^2/(U_{\mathrm{M}} - V_{\mathrm{MM}}), & (4)\\ I(\mathrm{P}_{\mathrm{MX}}) &= 2t_{\mathrm{MX}}^2/(V_{2\mathrm{MX}} - V_{\mathrm{MM}} + \Delta_{\mathrm{h}}), & (5)\\ I(\mathrm{P}_{2\mathrm{MX}}) &= 8t_{2\mathrm{MX}}^2/(V_{\mathrm{MX}} - V_{\mathrm{MM}} + \Delta_{\mathrm{h}}). & (6) \end{aligned}$$

According to the experimental results for $\mathrm{K_4[Pt_2(pop)_4X_2]}$ (X=Cl, Br, I) monomers, the relation $E(\mathrm{P}_{\mathrm{MX}}) < E(\mathrm{P}_{\mathrm{MM}}) < E(\mathrm{P}_{2\mathrm{MX}})$ is suggested[15]. Then, the relations $E(\mathrm{P}_{\mathrm{PtCl}}) > E(\mathrm{P}_{\mathrm{PtBr}}) > E(\mathrm{P}_{\mathrm{PtI}})$

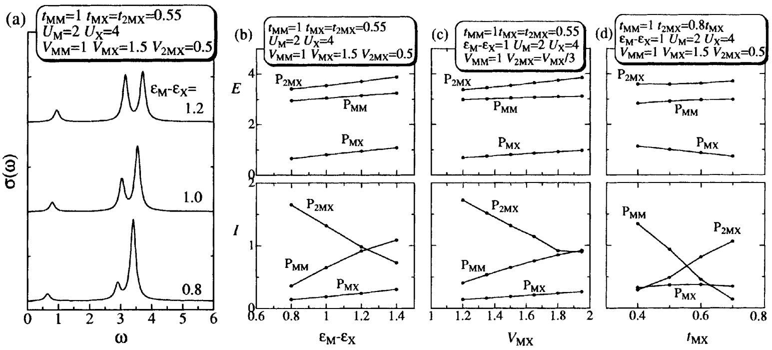

Figure 2: (a) Optical conductivity for $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}} = 0.8, 1.0$, and 1.2, and the peak positions and the intensities as a function of (b) $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}}$, (c) V_{MX}, and (d) t_{MX}.

and $E(\mathrm{P}_{2\mathrm{PtCl}}) > E(\mathrm{P}_{2\mathrm{PtBr}}) > E(\mathrm{P}_{2\mathrm{PtI}})$ are satisfied. The intensities of these peaks satisfy the relation $I(\mathrm{P}_{\mathrm{MX}}) < I(\mathrm{P}_{\mathrm{MM}}) < I(\mathrm{P}_{2\mathrm{MX}})$. The X dependence of the intensities is not simple: $I(\mathrm{P}_{\mathrm{PtCl}}) < I(\mathrm{P}_{\mathrm{PtBr}}) < I(\mathrm{P}_{\mathrm{PtI}})$; $I(\mathrm{P}_{2\mathrm{PtCl}}) < I(\mathrm{P}_{2\mathrm{PtBr}}) > I(\mathrm{P}_{2\mathrm{PtI}}) \sim I(\mathrm{P}_{2\mathrm{PtCl}})$. For P_{MM}, the peak position and the intensity do not depend so mach on X. From the relative peak positions for P_{MX}, P_{MM}, and $\mathrm{P}_{2\mathrm{MX}}$, we obtain the relation,

$$V_{2\mathrm{MX}} < -\Delta_{\mathrm{h}} + U_{\mathrm{M}} < V_{\mathrm{MX}}. \tag{7}$$

Note that the peak positions appear in the denominators of eqs.(4-6). The distance between the neighboring M and X sites d_{MX} has the relation, $d_{\mathrm{PtCl}} < d_{\mathrm{PtBr}} < d_{\mathrm{PtI}}$, while that between the neighboring M sites d_{MM} is almost a constant for all X. Therefore, it is reasonable to assume that V_{MX} and $V_{2\mathrm{MX}}$ decrease in order of Cl, Br and I. Furthermore, $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}}$ should also decrease in order of Cl, Br and I because of the relation, $\epsilon_{\mathrm{Cl}} < \epsilon_{\mathrm{Br}} < \epsilon_{\mathrm{I}}$. Thus $E(\mathrm{P}_{\mathrm{MX}})$ and $E(\mathrm{P}_{2\mathrm{MX}})$ would decrease in order of Cl, Br, I, while $E(\mathrm{P}_{\mathrm{MM}})$ would be almost independent of X, which is consistent with the experimental results[15].

In Fig.2 (a), the $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}}$ dependence of the optical conductivity is shown. The three peaks are shifted to lower energies as $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}}$ decreases. The peak positions and intensities are shown in Fig.2 as a function of (b) $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}}$, (c) V_{MX}, $V_{2\mathrm{MX}}$ and (d) t_{MX}, $t_{2\mathrm{MX}}$. The peak positions are found to be determined mainly by $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}}$, V_{MX} and $V_{2\mathrm{MX}}$. The t_{MX} or $t_{2\mathrm{MX}}$ dependence of the peak positions is relatively weak. Meanwhile the t_{MX} and $t_{2\mathrm{MX}}$ dependence of the intensities is substantially large, which is evident in eqs.(4-6). The intensity of $\mathrm{P}_{2\mathrm{MX}}$ decreases with decreasing $t_{2\mathrm{MX}}$. The transfer integrals t_{MX} and $t_{2\mathrm{MX}}$ for X=Br are expected to be smaller than those for X=Cl. In the experimental results, the intensity of $\mathrm{P}_{2\mathrm{MX}}$ is larger for X=Br than for X= Cl. Therefore, $t_{2\mathrm{MX}}$ for X=Br may be larger than for X=Cl, or it is due to the differences in $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}}$, V_{MX} and $V_{2\mathrm{MX}}$. It has been expected that t_{MX} for X=I is larger than those for Cl and Br[18]. It may be due to neglect of $t_{2\mathrm{MX}}$ in Ref.[18]. Since the t_{MX} and $t_{2\mathrm{MX}}$ dependence of the intensities is opposite to the $\epsilon_{\mathrm{M}} - \epsilon_{\mathrm{X}}$, V_{MX} and $V_{2\mathrm{MX}}$ dependence, we need care in searching for proper t_{MX} and $t_{2\mathrm{MX}}$.

The relation (7) indicates substantial importance of the long-range repulsion strengths, V_{MM}, V_{MX}, and $V_{2\mathrm{MX}}$. In our previous paper[17], we have studied the optical conductivity of the MMX chains and shown that two peaks appear in the CP state, where the intensities depend sensitively on the intradimer repulsion strength V_{MM} and the interdimer repulsion strength V_{MXM}. When V_{MXM} is substantially weaker than V_{MM}, only a single peak may be clearly observed because the oscillator strength of the interdimer charge transfer is much weaker. According to the present results, V_{MXM} is expected to be not so small. Then, two peaks may be observed in the CP state, especially for X=Cl (if the CP state is realized with X=Cl).

For the MMX chains, the energy for each state in the atomic limit is

$$\begin{aligned} E_{\mathrm{AV}} &= 2U_{\mathrm{M}} + 4V_{\mathrm{MM}} + 12V_{\mathrm{MX}} + 12V_{2\mathrm{MX}} + 6\epsilon_{\mathrm{M}} + 4\epsilon_{\mathrm{X}}, & (8)\\ E_{\mathrm{CDW}} &= 2U_{\mathrm{M}} + 5V_{\mathrm{MM}} + 12V_{\mathrm{MX}} + 12V_{2\mathrm{MX}} + 6\epsilon_{\mathrm{M}} - 2\delta + 4\epsilon_{\mathrm{X}}, & (9)\\ E_{\mathrm{CP}} &= 2U_{\mathrm{M}} + 4V_{\mathrm{MM}} + 12V_{\mathrm{MX}} + 12V_{2\mathrm{MX}} + 6\epsilon_{\mathrm{M}} - 2\delta + 4\epsilon_{\mathrm{X}}, & (10) \end{aligned}$$

per two MMX units, where δ is the deviation of the M d_{z^2} level from its position in the AV state due to site-diagonal electron-lattice coupling. Thus, the CP state is stable among the three states. For finite transfer integrals, the relative stability between the CDW and CP states can be estimated in the second-order perturbation theory with respect to the transfer integrals. In the CP state, the kinetic energy gain through the intradimer charge transfer is $t_{\mathrm{MM}}^2/(2\delta)$ per dimer unit, and the gain through the interdimer transfer is $t_{\mathrm{MXM}}^2/(2\delta + V_{\mathrm{MM}})$. In the CDW state, on the other hand, it is $t_{\mathrm{MM}}^2/[2(U_{\mathrm{M}} - V_{\mathrm{MM}})]$ for the intradimer transfer and $t_{\mathrm{MXM}}^2/(2\delta)$ for the interdimer transfer. Then, the CDW state becomes relatively stable for strong electron-lattice coupling (δ).

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