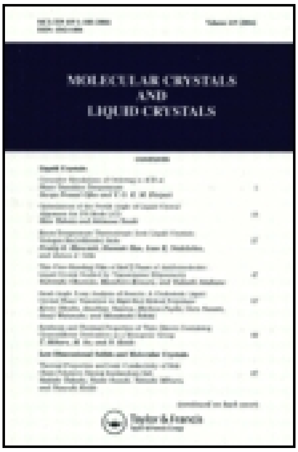

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Variation Mechanisms of Ground-State and Optical-Excitation Properties in Quasi-One-Dimensional Two-Band Electron Systems

Kenji Yonemitsu [a] [b] , Makoto Kuwabara [c] & Naoyuki Miyashita [b]
[a] Institute for Molecular Science, Okazaki, 444-8585, Japan
[b] Graduate University for Advanced Studies, Okazaki, 444-8585, Japan
[c] Molecular Photoscience Research Center, Kobe University, Nada, Kobe, 657-8501, Japan

Version of record first published: 18 Oct 2010

To cite this article: Kenji Yonemitsu, Makoto Kuwabara & Naoyuki Miyashita (2003): Variation Mechanisms of Ground-State and Optical-Excitation Properties in Quasi-One-Dimensional Two-Band Electron Systems, Molecular Crystals and Liquid Crystals, 379:1, 467-474

To link to this article: http://dx.doi.org/10.1080/713738642

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 467-474
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090903

Variation Mechanisms of Ground-State and Optical-Excitation Properties in Quasi-One-Dimensional Two-Band Electron Systems

KENJI YONEMITSU[a,b], MAKOTO KUWABARA[c]
and NAOYUKI MIYASHITA[b]

[a]*Institute for Molecular Science, Okazaki 444-8585, Japan,*
[b]*Graduate University for Advanced Studies, Okazaki 444-8585, Japan and*
[c]*Molecular Photoscience Research Center, Kobe University, Nada, Kobe 657-8501, Japan*

We study i) the ground-state and optical-excitation properties of halogen-bridged binuclear metal complexes, which are known as MMX chain compounds, by the strong-coupling expansion for a one-dimensional two-orbital extended Peierls-Hubbard model, and ii) the dynamics of domain walls between the neutral and ionic phases in mixed-stack charge-transfer complexes, by solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating energy levels. We find in i) that competition between electron-electron and electron-lattice interactions and competition between short- and long-range interactions are both important for the electronic phase variation, and in ii) that charge and lattice dynamics immediately after photoexcitations is complex and not explained simply within the domino picture.

Keywords: MMX chain; charge polarization; charge density wave; mixed-stack charge-transfer complex; neutral-ionic phase transition; photoinduced phase transition

INTRODUCTION

Assembled metal complexes in low electronic dimensions have a variety of broken symmetry states due to competing or collaborating electron-electron and electron-lattice interactions. Especially in low dimensions, the metallic phase with a partially filled band is unstable and consequently the ground state appears with a charge gap and/or a spin gap, which often originates from the broken symmetry and is accompanied with a long-range order. Because the long-range order is often produced by competing interactions and easily destroyed by large quantum fluctuations in low dimensions, the electronic phase is generally sensitive to a small change in the electronic environment, such as inter-molecular overlaps and inter-site repulsion strengths.

When different broken-symmetry states are nearly degenerate, the transition between them takes place often discontinuously. In some cases, the transition is induced not only by lowering the temperature or applying the physical or chemical pressure but also by irradiation of lights. The latter transition is a non-equilibrium process and nonlinearly depends on the photo-excitation energy and intensity, for example. Studying the dynamics of electrons and lattice displacements not only reveals the competing interactions but also leads to a possibility for dynamically controlling the nonlinear excitations with many external parameters.

Here we theoretically study i) the ground-state and optical-excitation properties of halogen-bridged binuclear metal complexes, which are known as MMX chain compounds, and ii) the dynamics of domain walls between the neutral and ionic phases in mixed-stack charge-transfer complexes, which are related to the MMX chain compounds.

ELECTRONIC PHASE VARIATION IN MMX CHAIN COMPOUNDS

In the MMX chain compounds with transition metal M=Pt, halogen X=I, ligand L=pop, where pop denotes $P_2O_5H_2^{2-}$, and different counter ions, various charge and lattice ordered phases are found[1]. With increasing the distance between the M atoms bridged by an X atom d_{MXM}, the electronic state is suggested change from the averaged-valence phase ($M^{2.5+}M^{2.5+}$-X-$M^{2.5+}M^{2.5+}$-X-; AV), the charge-density-wave phase ($M^{2+}M^{2+}$--X-$M^{3+}M^{3+}$-X--; CDW), to the charge-polarization phase ($M^{2+}M^{3+}$-X--$M^{2+}M^{3+}$-X--; CP)[2].

We use a one-dimensional two-orbital extended Peierls-Hubbard model for M d_{z2} and X p_z orbitals in the -M-M-X- unit. The transfer integral between the M sites within the unit is denoted by t_{MM}, while that between the M site and the nearest X site by $t_{MX} - \alpha y$, with y being the corresponding MX bond length relative to that in the regular lattice and α the site-off-diagonal electron-lattice coupling strength. The energy level of the X p_z orbital is denoted by ε_X, while that of the M d_{z2} orbital by $\varepsilon_M - \beta y$, with β being the site-diagonal electron-lattice coupling strength. The on-site repulsion strengths are denoted by U_M at M sites, and U_X at X sites. The inter-site repulsion strengths are denoted by V_{MM} for the nearest-neighbor M sites within the unit, V_{MX} for the nearest-neighbor M and X sites, V_{MXM} for the nearest-neighbor M sites bridged by an X site, V_{2MX} for an X site and the next-nearest M sites, and V_2 for the next-nearest-neighbor M sites. The M-M distance within the unit is regarded as rigid. The elastic constants are denoted by K_{MX} for the MX bond length, and K_{MXM} for the distance between the neighboring M-M units.

There are two classes of MMX chain compounds. In $Pt_2(RCS_2)_4I$ ($R=CH_3$, n-C_4H_9) containing neutral MMX chains, the electric resistivity is metallic at room temperature and the alternate-charge-polarization phase ($M^{2+}M^{3+}$-X-$M^{3+}M^{2+}$--X--; ACP) is suggested to be the ground state[3]. In this case, the MMX chains are not accompanied with counter ions; K_{MXM} is consequently small, so that the binuclear M-M unit can be alternately displaced to gain energy from the α term[4]. The other class, $R_4[Pt_2(pop)_4I]nH_2O$ [R=Na, K, NH_4, $(CH_3(CH_2)_7)_2NH_2$, *etc.*], has counter ions and water molecules, so that K_{MXM} is very large. As a consequence, the M-X-M distance d_{MXM} is not modulated, and the ACP phase is hardly achieved.

For small d_{MXM}, the transfer integrals would be large, which enhance the itinerant character of electrons, so that the realization of the AV phase is reasonable. For large d_{MXM}, on the other hand, electrons tend be localized. Then we consider the strong-coupling limit of $t_{MM}=t_{MX}=\alpha=0$. The energy difference between the CP and CDW phases per binuclear unit is given by $E_{CP}-E_{CDW}=V_2-V_{MM}/2$, on the assumption that the magnitudes of the lattice displacements are the same. The counter-ion-induced change in d_{MXM} would not so much affect V_{MM} but modify V_2, though V_2 itself is smaller than the other inter-site repulsion strengths. Then the increasing d_{MXM} reduces V_2 and thus $E_{CP}-E_{CDW}$, favoring the CP phase relative to the CDW phase. This is consistent with the experimental observation.

Next we consider small but finite transfer integrals. The present two-orbital model is reduced to the one-orbital model, where the effective transfer integral between the nearest-neighbor M sites bridged by an X site is given by $t_{MXM} \sim [(\Delta_h^2+8t_{MX}^2)^{1/2}-\Delta_h]/4$ for the CDW and

CP phases. Here Δ_h denotes the M d_{z2}-X p_z level difference in the hole picture, $\Delta_h = \varepsilon_M - \varepsilon_X + U_M - U_X + 2V_{MM} - 2V_{MX}$. The second-order perturbation theory with respect to t_{MM} and t_{MXM} gives more information on the electronic phase competition. In the CDW phase, the energy gain from the t_{MM} term is given by $2t_{MM}{}^2/(U_M - V_{MM})$, and that from the t_{MXM} term by $t_{MXM}{}^2/(2\beta|y| - V_{MM} + 2V_2)$. In the CP phase, the energy gain from the t_{MM} term is given by $t_{MM}{}^2/(2\beta|y| + V_{MXM} - 2V_2)$, and that from the t_{MXM} term by $t_{MXM}{}^2/(2\beta|y| + V_{MM} - 2V_2)$. This implies that the CDW phase is stabilized by the β term. The site-diagonal electron-lattice coupling β originates from the Coulomb repulsion, so that it would decrease and stabilizes the CP phase with increasing d_{MXM}. This is also consistent with the experimental observation.

The relative importance of the β and V_2 effects cannot be judged unless quantitative estimations are made. Usually the longer-range V_2 is assumed to be much weaker than β, but the screening effect would be very weak now. The optical conductivity spectra of the XMMX monomers support this idea[4]. Both effects would be important. The lowest-energy optical absorption appears at $2\beta|y| - V_{MM} + 2V_2$ in the CDW phase, and at $2\beta|y| + V_{MXM} - 2V_2$ in the CP phase, in the strong-coupling limit of the one-orbital model. Since $V_2 << V_{MM}$, $V_2 << V_{MXM}$ and $V_{MM} > V_{MXM}$, the CDW phase has lower-energy absorption than the CP phase with a similar magnitude of y. This is also consistent with the experimental observation[2]. The recently observed, pressure-induced phase transition[5] is also understood in the same manner as above for the variation with counter ions.

PHOTOINDUCED VARIATION IN CHARGE-TRANSFER COMPLEXES

Stability of almost degenerate, different-symmetry states is essential to photoinduced phase transitions[6]. Then we focus on the photoinduced dynamics in the mixed-stack charge-transfer complexes composed of alternating donor and acceptor molecules, which are described by a model simpler than but similar to the above. In the typical material, TTF-CA, the ground states are either neutral or ionic, and the ionic phase is accompanied with dimerization of a donor molecule and an acceptor molecule. Time-resolved spectroscopy measurements after photoexcitations have been extensively performed[7] and show threshold intensity of excitation[8]. More recently, ultrafast optical switching from the ionic to neutral states is observed to be accompanied with coherent motion of the macroscopic neutral-ionic domain boundary[9].

Since the theoretical studies so far have been limited to localized-electron systems coupled with lattice displacements[10] or to the adiabatic potential analysis of itinerant-electron-lattice systems[11], we fully solve the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating energy levels, not relying on the adiabatic approximation. The transfer integral is given by $t_0-\alpha y$, with y being the bond length relative to the regular case and α the linear coefficient. The on-site repulsion is denoted by U. The nearest-neighbor repulsion is given by $V(y)=V-\beta_1 y+\beta_2 y^2$, with two coefficients β_1 and β_2. The level difference between the acceptor and donor sites is $d-4V(y)$. The potential for y is $(k_1/2)y^2+(k_2/4)y^4$. We use the unrestricted Hartree-Fock approximation for the ionic ground state, change the occupancy of an equal number of the HOMOs and the LUMOs, and add random numbers to lattice displacements and velocities according to the Boltzmann distribution at finite temperature T. We use t_0=1, α=1, U=10, V=1, β_1=1, β_2=7, d=11.62, k_1=8, k_2=100, the optical phonon frequency ω=0.0576, T=0.0086, and 100 sites with periodic boundary condition. Figure 1 shows ionic domains (ρ_l>0.55) and neutral domains (ρ_l<0.55), as a function of site l time t (scaled by ω) after the photoexcitation. Here ρ_l denotes the locally averaged ionicity at site l, $\rho_l=(-1)^l(1/4)(2\langle n_l\rangle-\langle n_{l-1}\rangle-\langle n_{l+1}\rangle)+1$, with $\langle n_l\rangle$ being the electron density. One electron is excited in Figure 1(a), while eight electrons in Figure 1(b). The dynamics clearly shows the initial dependence on the intensity of excitation [the final state is ionic in (a), but neutral in (b)] and the oscillation of the neutral-ionic domain boundary [appearing at ωt >180 in (b)], which are reminiscent of the experiments[8,9].

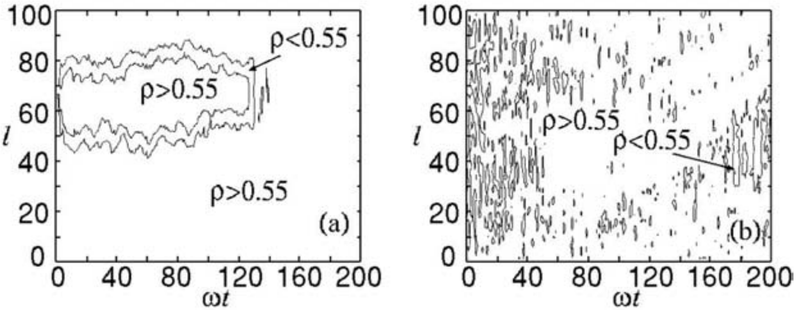

FIGURE 1 Contour lines for ρ=0.55, as a function of site l and time t (scaled by ω) after the photoexcitation. One electron is excited in (a), while eight electrons in (b). Parameters are explained in the text.

Acknowledgments

The authors are grateful to H. Kitagawa and H. Okamoto for showing the experimental data prior to publication and for enlightening discussions. This work was supported by the NEDO International Joint Research Grant Program, a Grant-in-Aid for Scientific Research (C) from Japan Society for the Promotion of Science, and a Grant-in-Aid for Scientific Research on Priority Area "Metal-Assembled Complexes" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1.] M. Yamashita, S. Miya, T. Kawashima, T. Manabe, T. Sonoyama, H. Kitagawa, T. Mitani, H. Okamoto, and R. Ikeda, *J. Am. Chem. Soc.*, **121**, 2321 (1999).
[2.] H. Matsuzaki, H. Kishida, H. Okamoto, T. Kawashima, K. Takizawa, T. Ishii, T. Ono, and M. Yamashita, *Meeting Abstracts of the Physical Society of Japan*, **55**, 744 (2000).
[3.] H. Kitagawa, N. Onodera, T. Sonoyama, M. Yamamoto, T. Fukawa, T. Mitani, M. Seto, and Y. Maeda, *J. Am. Chem. Soc.*, **121**, 10068 (1999).
[4.] M. Kuwabara and K. Yonemitsu, *J. Mater. Chem.*, **11**, 2163 (2001).
[5.] H. Matsuzaki, T. Matsuoka, H. Kishida, H. Okamoto, T. Kawashima, K. Takizawa, T. Ono, T. Ishii, and M. Yamashita, (unpublished).
[6.] K. Nasu (ed.), *Relaxation of Excited States and Photoinduced Structural Phase Transitions*, (Springer, Berlin, 1997).
[7.] S. Koshihara, Y. Takahashi, H. Sakai, Y. Tokura, and T. Luty, *J. Phys. Chem. B*, **103**, 2592 (1999).
[8.] T. Suzuki, T. Sakamaki, K. Tanimura, S. Koshihara, and Y. Tokura, *Phys. Rev. B*, **60**, 6191 (1999).
[9.] S. Iwai, S. Tanaka, K. Fujinuma, H. Kishida, H. Okamoto, and Y. Tokura, to appear in *Phase Transitions*.
[10.] K. Koshino and T. Ogawa, *J. Phys. Soc. Jpn.*, **67**, 2174 (1998).
[11.] P. Huai, H. Zheng, and K. Nasu, *J. Phys. Soc. Jpn.*, **69**, 1788 (2000).