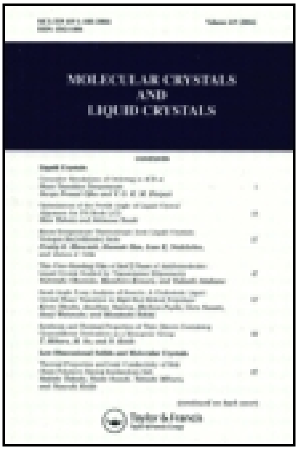

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Strong commensurability effect on metal-insulator transition in (DCNQI) 2 Cu

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STRONG COMMENSURABILITY EFFECT ON METAL-INSULATOR TRANSITION IN (DCNQI)$_2$Cu

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Stability of three-fold lattice distortion in the insulating state of (DCNQI)$_2$Cu is studied by exactly diagonalizing a two-band Peierls Hubbard model on the 6×2 lattice. Self-doping is essentially important and caused by strong commensurability pinning, which are a consequence of moderate coupling of DCNQI π electrons with lattice and strong correlation of Cu d electrons.

Keywords: two-band Peierls-Hubbard model; π-d electron-system; metal-insulator transition; commensurability pinning

INTRODUCTION

(DCNQI)$_2$Cu salts, which are one-dimensional π-d electron systems, have been of great interest due to their unique physical properties associated with hybridization between π bands of DCNQI molecules and d orbitals of Cu[1]. A first-order metal-insulator transition takes place at a low temperature under high pressure [2–7]. In the metallic state, the valence of Cu is near 4/3 on average [8]. In the insulating state, three-fold lattice distortion has been found accompanied with a periodic array of local spins surviving on Cu sites: Cu^{+}–Cu^{+}–Cu$^{2+}\cdots$ [9–11]. The metal-insulator transition is regarded as a cooperative phenomenon due to the Peierls

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*Corresponding author. E-mail: mkuwa@ims.ac.jp instability in the 1/3-filled π band and the Mott instability in the d orbitals, 5/6 of which are occupied [12–14].

The purpose of this paper is to reveal that strong electron-electron interaction among d electrons reinforces the structure with three-fold periodicity by charge transfer between π and d orbitals (self-doping) even in the case where the hypothetical band fillings are not optimal without interactions.

TWO-BAND PEIERLS-HUBBARD MODEL

We consider a two-band Peierls-Hubbard model in which DCNQI π electrons are coupled with Cu d electrons,

$$\begin{aligned} H = &-\sum_{i,\sigma}^{N}(t_\pi - \alpha_\pi y_{\pi,i})[c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.}] - \sum_{i,\sigma}^{N} t_d[d_{i,\sigma}^\dagger d_{i+1,\sigma} + \text{h.c.}] \\ &- \sum_{i,\sigma}^{N} t_{\pi d}[c_{i,\sigma}^\dagger d_{i,\sigma} + \text{h.c.}] + \sum_{i}^{N} \epsilon_\pi n_{\pi,i} + \sum_{i}^{N}(\epsilon_d - \beta_d v_{d,i}) n_{d,i} \\ &+ U_\pi \sum_{i}^{N} n_{\pi,i,\uparrow} n_{\pi,i\downarrow} + U_d \sum_{i}^{N} n_{d,i,\uparrow} n_{d,i,\downarrow} + \frac{K}{2}\sum_{i}^{N}(y_{\pi,i}^2 + v_{d,i}^2) \end{aligned}$$

where $c_{i,\sigma}^\dagger (d_{i,\sigma}^\dagger$ creates a π (d) electron with spin σ on the ith site, $n_{\pi,i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$ and $n_{d,i,\sigma} = d_{i,\sigma}^\dagger d_{i,\sigma}$ are the number operators for π and d electrons, $n_{\pi,i} = \sum_\sigma n_{\pi,i,\sigma}$, $n_{d,i} = \sum_\sigma n_{d,i,\sigma}$. The intrachain transfer integrals are t_π for π electrons and t_d for d electrons. The lattice displacement parallel to the chain is introduced for the DCNQI chain ($y_{\pi,i}$), which modulates the intrachain transfer integral with coupling constant α_π. The interchain transfer integral is denoted by $t_{\pi d}$. The parameters ϵ_π and ϵ_d are the π and d level. The d level is modified by another displacement $v_{d,i}$ with coupling constant β_d. The on-site Coulomb interactions on DCNQI and Cu sites are denoted by U_π and U_d, respectively. The elastic constant for the lattice displacements y_π and v_d are both set to be K by a scale transformation if necessary.

We exactly diagonalize a 6×2 lattice system with the periodic boundary condition in the chain direction. The electronic ground state is determined in the self-consistent manner with the static lattice displacements.

RESULTS AND DISCUSSIONS

We consider a system with 14 electrons on the 6×2 lattice, in which distribution of 4 electrons in π orbitals and 10 electrons in d orbitals corresponds to the experimentally observed insulating state. Depending on the level difference between π and d electrons $\Delta \equiv \epsilon_\pi - \epsilon_d$, we found three electronic configurations. (I) When the d level is much deeper than the π level, the d orbitals are almost completely occupied and the filling of the π band is about 1/6 ($2\pi + 12d$ electrons). (II) When the d level is relatively close to the π level, the π band becomes nearly half-filled and 2/3 of d orbitals are occupied ($6\pi + 8d$). (III) The d level is located in-between so as for nearly 1/3 of π orbitals and 5/6 of d orbitals to be occupied ($4\pi + 10d$). Figure 1 shows the total energies of these three states for (a) week and (b) strong U_d as a function of Δ. For small U_d, the state (III) is not realized as a stable phase. For large U_d, the state (III) is found in a wide Δ region. This demonstrates the importance of strong correlation among d electrons to stabilize the three-fold state composed of Cu^{+}, Cu^{+}, and Cu^{2+} in a wide pressure range. In the adiabatic approximation for the lattice displacements, twice the Δ derivative of the total energy E_{tot} is given by $\sum_i \langle n_{\pi,i} - n_{d,i} \rangle$. If both the electron-lattice coupling and electron-electron interaction are absent, E_{tot} is a smooth function of Δ because of charge transfer between π and d orbitals. In Figure 1, the line (II) is almost straight because of strong pinning of bipolarons on Cu sites, Cu^{+}, Cu^{+}, and Cu^{3+}. Without electron-lattice coupling or for small U_d, the state (III) is not stabilized. In other words, both interactions cooperatively work to stabilize the state (III). The slope of the line (III) is about -3 reflecting 4 electrons in π orbitals and 10 electrons in d orbitals.

In Figure 2, physical quantities in the state (II) of Figure 1(a) are shown on the left panels, and those in the state (III) of Figure 1(b) on the right panels, as a function of Δ. The charge density is shown in the upper four panels of Figure 2: (a,d) $\rho_{\pi,i} \equiv \langle n_{\pi,i} \rangle$ for DCNQI sites and (b,e) $\rho_{d,i} \equiv \langle n_{d,i} \rangle$ for Cu sites. Because of three-fold periodicity, it is shown for three sites $i = 1$, 2, 3. In the state (II) for small U_d, the charge density at DCNQI sites is almost constant, $\rho_{\pi,1} \sim \rho_{\pi,2} \sim \rho_{\pi,3} \sim 1$, while that at Cu sites is disproportionated, $\rho_{d,1} = \rho_{d,3} \sim 2$ and $\rho_{d,2} \sim 0$

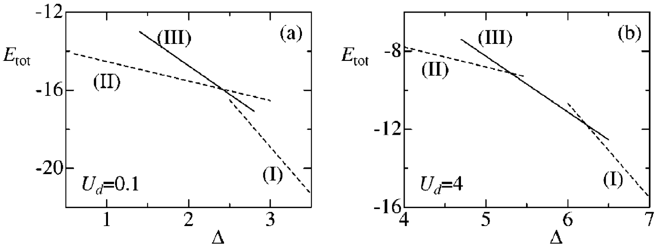

FIGURE 1 Dependence of the total energies E_{tot} of the three states explained in the text on the level difference Δ for (a) $U_d = 0.1$ and (b) $U_d = 4$. The other parameters are $t_\pi = 1$, $t_d = 0.1$, $t_{\pi d} = 0.4$, $\epsilon_\pi = 0$, $\alpha_\pi = 3$, $\beta_d = 3$, $U_\pi = 0.1$, $U_d = 4$, and $K = 6$.

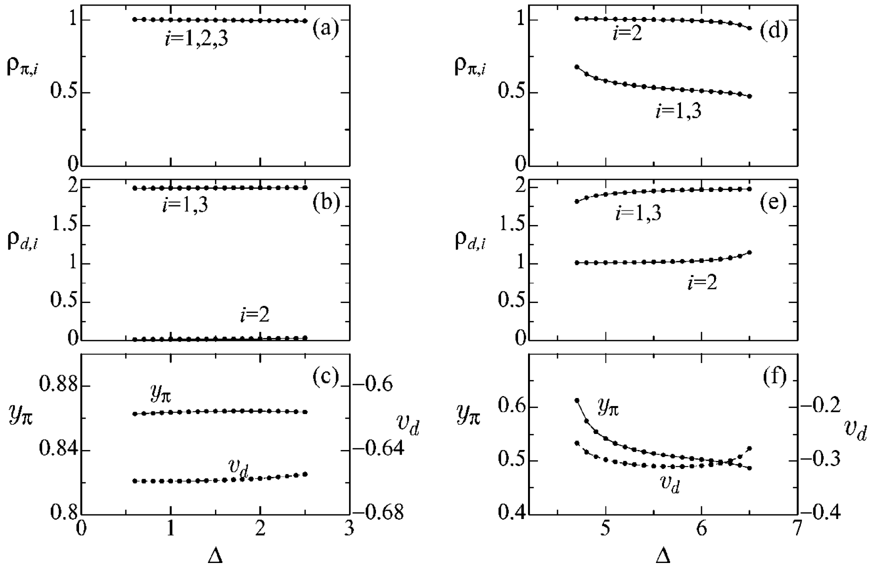

FIGURE 2 Dependence on the level difference Δ of (a,d) the charge density on DCNQI sites, (b,e) that on Cu sites, and (c,f) the lattice displacements y_π and v_d, for (a,b,c) $U_d = 0.1$ [state (II)] and (d,e,f) $U_d = 4$ [state (III)]. The other parameters are the same as in Figure 1.

corresponding to Cu^+–Cu^{3+}–Cu^+–$\cdots$. The lattice displacements are $y_{\pi,2} = y_{\pi,2} = -\frac{1}{2}y_\pi$, $y_{\pi,3} = y_\pi$, and $v_{d,1} = v_{d,3} = -\frac{1}{2}v_d$, $v_{d,2} = v_d$ with y_π and v_d shown in the lower two panels of Figure 2. In the state (III) for large U_d, the charge density at Cu sites shows $\rho_{d,1} = \rho_{d,3} \sim 2$ and $\rho_{d,2} = 1$ reflecting the ordering of Cu^+–Cu^{2+}–Cu^+–$\cdots$. The charge density at Cu sites and that at DCNQI sites are almost unchanged in a wide Δ range. Without electron-lattice coupling, the charge transfer from DCNQI sites to Cu sites takes place more rapidly when Δ increases (unless the occupation of *d* orbitals becomes nearly half and U_d is large).

In this paper, we have studied the commensurate state with three-fold lattice distortion. It is obvious from Figure 1(b) that the Δ derivative of E_{tot} is almost a three-stage step function of Δ. Near the edges of the middle stage (i.e. near the phase boundaries), the commensurate state would be destabilized, when a much larger system is studied, to form an incommensurate state with (3+δ) periodicity. Competition between the commensurate and incommensurate states will be studied by the density matrix renormalization group method in a forthcoming paper.

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