Photoinducing a Mott Insulator in a Charge-Density-Wave System

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Abstract. A quasi-one-dimensional halogen-bridged Pd complex, of which the chemical formula is [Pd(chxn)2][Pd(chxn)2Br2]Br4, is explored theoretically to demonstrate its possibility for a ultrafast photoinduced phase transition (PIPT) from a charge-density-wave (CDW) state to a Mott-insulator (MI) state. We use a $dp$ model of which the parameter values are chosen to reproduce the absorption peak energies. First, we calculate adiabatic potential energy curves along possible relaxation channels from CDW to MI. The results show that there is no energy barrier in between. Exciton excitations in the former smoothly lead to a spin excitation plus a fractional charge pair excitation of $\pm 1/2e$ ($e = |e|$) in the latter. Second, assuming a high-energy photoexcitation, an extra electron or a hole is injected in the system. The result is that a PIPT can occur at least for a hole carrier case, again yielding a spin excitation and a fractional charge pair of $+1/2e$ and $+1/2e$.

1. Introduction
Quasi-one-dimensional halogen-bridged Pd complexes are known to have a charge-density-wave (CDW) ground state that is featured by a mixed-valency of the Pd ions and a halogen-sublattice dimerization. Compared with Pt systems, which also show CDW, the CDW gaps are much smaller, and it is thereby expected that the CDW state in the former systems is less stable than that in the latter systems. In fact, we can destroy such a CDW state by more than 50% of Ni inclusion [1, 2, 3]. This is interpreted as a formation of a Mott-insulator (MI) domain, because the Ni system prefers a MI state that is characterized by no halogen displacement and a mono-valency of the metal ions. It was therefore thought that this effect occurred as a kind of proximity effect. Very recently, however, a new experiment has been performed to suggest a hidden MI phase inherent in the Pd systems [4]. Actually, this MI state is realized by as small as 10% of Ni inclusion, and the phase character is theoretically reproduced assuming a metastable Mott-Hubbard state in a pure PdBr system.

Motivated by the above findings, we theoretically explore a new phenomenon, that is, a photoinduced phase transition (PIPT) from a CDW state to a MI in the pure Pd system [5]. Its schematic picture is illustrated in figure 1. The point of the theory is how to treat low-energy excitations typical to MI domains, namely, spin excitations. Since CDW is gapped for both charge and spin, the connection between the excited states of both the states is not trivial and needs careful treatment. We therefore resort to a density-matrix renormalization group (DMRG) method [6], to find not only the ground states but also the excited states as correctly as possible. Also, we make use of the spin symmetry to separate singlet and triplet states [7].
2. Model

We here use a one-dimensional $dp$ model that includes only the outermost $d_{z^2}$ and $p_z$ orbitals of Pd and Br, respectively:

$$
H = -\sum_{l\sigma} t(l) (C^\dagger_{l+1\sigma} C_{l\sigma} + \text{h.c.}) + \sum_l e(l) n_l + \sum_{l=\text{odd}} U_p n_l n_{l+1}
+ \sum_{l=\text{even}} U_d n_l n_{l+1} + \sum_l V(l) n_l n_{l+1} + \sum_{l=\text{odd}} V_{pp} n_l n_{l+2}
+ \sum_{l=\text{even}} V_{dd} n_l n_{l+2} + \sum_l \frac{K_l}{2} Q_l^2,
$$

where $C^\dagger_{l\sigma} (C_{l\sigma})$ is the creation (annihilation) operator of a hole with spin $\sigma$ at the $l$th site, and $Q_l$ is the chain-parallel displacement of the $l$th ion from the equidistant position. Here, the Pd and Br sites are alternate, and we put the Pd sites on the even-number sites. The number operators, $n_l^\uparrow$ and $n_l^\downarrow$, are for the holes at the $l$th site with spin up and down, respectively, and $n_l = n_l^\uparrow + n_l^\downarrow$. The inter-hole repulsions on the same site appear in the third and fourth terms, while the nearest- and next-nearest-neighbor repulsions are given in the fifth term and the sixth and seventh terms, respectively. The last term represents lattice elastic energy. The elastic constant $K_l$ takes a finite value $K$ for the Br sites, while it is assumed to be infinite for the Pd sites because the latter are strongly connected to the surrounding ligand molecules. The other site-dependent parameters are defined as

$$
t(l) = t_{dp} - \beta(Q_{l+1} - Q_l),
$$

$$
e(l) = \begin{cases} 
  e_p - 2\alpha(Q_{l+1} - Q_{l-1}) & \text{for odd } l \\
  e_d + \alpha(Q_{l+1} - Q_{l-1}) & \text{for even } l 
\end{cases},
$$

and

$$
V(l) = V_{dp} - \alpha(Q_{l+1} - Q_l).
$$

Except for the first one, some explanation will be needed. For a Br-Ni bond at the $l$th and $(l+1)$th sites, we write its intersite Coulombic energy as

$$
\frac{(-e)(1-n_l) \times (+e)(2+n_{l+1})}{a_0 + (Q_{l+1} - Q_l)},
$$

with $a_0$ as the original bond length. It should be here remarked that Ni$^{2+}$ and Br$^-$ are the vacuum states for the holes. The absolute value of this energy becomes smaller when Br receives...
a hole, because its valency approaches to zero. Expanding this and taking only the linear order of $Q_i$'s, we have various terms. Among them, the term that only includes $Q_i$'s vanishes in a periodic-boundary-condition (PBC) system within itself. In the case of a open boundary condition (OBC), on the other hand, two terms remain at the boundary, but it is not taken seriously because $Q_i$'s at the boundary are fixed in the following. As for the other terms, they appear in the hamiltonian, with the definition of $\alpha \equiv e^2/a^5_0$. The different signs and factors in odd and even $e(l)$'s are deduced naturally.

The parameter values are determined so as to reproduce experimental values for our target material $[\text{Pd(chxn)}_2][\text{Pd(chxn)}_2\text{Br}_2]\text{Br}_4$ (PdBr, hereafter), keeping in mind those for the Ni compounds, $[\text{Ni(chxn)}_2\text{Br}]\text{Br}_2$, because the two compounds are deeply related to each other. In particular, the absorption peak energies, which are about 0.72 eV and 0.6 eV in the CDW and MI phase, respectively, are correctly reproduced by $U_d = 2.75$ eV, $d_d = 0.0$ eV, $U_p = 2.3$ eV, $\epsilon_p = 2.2$ eV, $V_{dp} = 2.09$ eV, $V_{dd} = 0.8$ eV, $V_{pp} = 0.8$ eV, $t_{dp} = 1.5$ eV, and an appropriate combination of $\alpha^2/K$ and $\beta^2/K$. The reason why the values except for electron-lattice (e-l) interactions are definite is more information about them; some of them are common to the Ni compound because of the almost same structure, and the spin exchange energy [4] and the Br valency [8] are already known for the latter. Meanwhile, the e-l parameters are only determined by the CDW absorption peak energy. Since we have two remaining parameters for one constraint, the candidates make a curve that is drawn by a dotted line in figure 2. It is then found that the system is located very close to the phase boundary between the CDW state and the MI state, because the above curve and the phase boundary are very close to each other.

3. Results

3.1. Exciton excitation

Applying an adiabatic approximation for the lattice, we calculate the lowest excitation energies along possible paths of a domain formation, as

$$q_l = q_0(-1)abrac{\alpha - \mu}{2} \left(1 + \frac{1}{2}(\text{tanh}\left(\frac{l - l_2}{w}\right) - \text{tanh}\left(\frac{l - l_1}{w}\right))\right)$$

for odd $l$ (Br sites). The displacements at even $l$ (Pd sites) are fixed at zero, based on the above discussion. Here, the dimensionless displacements, $q_l \equiv Q_l K/\alpha$, is used, and $q_0$ is the CDW

![Figure 2. Phase Diagram with respect to effective electron-lattice strengths. The solid curve is the phase boundary, and the dotted one corresponds to the parameter sets that reproduce the absorption peak energy for PtBr in the CDW phase. It is emphasized that the two lines are very close to each other, even intersecting.](image-url)

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**Figure 2.** Phase Diagram with respect to effective electron-lattice strengths. The solid curve is the phase boundary, and the dotted one corresponds to the parameter sets that reproduce the absorption peak energy for PtBr in the CDW phase. It is emphasized that the two lines are very close to each other, even intersecting.
amplitude in this definition. The position variables, $l_1$ and $l_2$ ($l_2 > l_1$), are those of the two domain walls (DWs), and $w$ is the half width of each DW, as shown in figure 3.

In figure 4, we draw a result targeting PdBr, with the parameter set corresponding to point A in figure 2. Here, the system size $N=72$ (36 NiBr pairs), and the hole number is $N/2$. An OBC is used, and $w$ is set at its optimized value, that is, 5.0. From the figure, we easily see a monotonously decreasing energy of the singlet excited state. We have also calculated the lowest triplet excitations and obtained a similar tendency. Such tendencies are also confirmed at another candidate as point B, while the relaxation curve has an energy barrier if we depart from the boundary as is so at point C. The barrierless structure suggests a linear law for the conversion fraction as a function of light intensity, and is consistent with that observed by a recent experiment [11].

As another comment on this relaxation, we mention charges of the DW’s. The hole densities in the ground and first singlet excited states are drawn in figures 5 and 6, respectively. In both the figures, the MI domain is seen clearly with almost uniform hole densities at the Ni sites. Meanwhile, the charge structure at the DW is difficult to see. In fact, the differences between the two figures are very small and so do not give an explicit interpretation. Instead, we use a more phenomenological picture as shown in figure 7. We here focus on the Ni valencies and trace their changes in the course of domain formation. In particular, the change from the third line to the fourth line helps us to count the DW carriers. Namely, on the right (left) hand side, the DW moves $+2a$ (-$2a$) with $a$ as the nearest neighbor Ni-Ni distance. We then count the change in dipole moment, $\Delta \mu$, in two ways, namely, by the original electrons and by the DW’s [9], and equate them as

$$\Delta \mu = (-e) \times (-a) = Q \times (\pm 2a),$$

where $Q$ is the charge of a DW, and the plus (minus) signs are for the right (left) hand side. The resulting equation tells us the DW’s have fractional charges of $\pm 1/2e$ ($e = |e|$). A more mathematical method to count them is the phase hamiltonian and its counting formula [10], which give the same results. By the way, the above fact is not seen clearly in figures 5 and 6, because the inverted configurations are superimposed to make the two DW’s almost identical. In a situation with a large DW-DW distance, two configurations, $(+1/2e)+(-1/2e)$ and $(-1/2e)+(+1/2e)$, are almost degenerate because of negligible overlap. Moreover, the spin excitations in the MI domain approaches to zero representing its gapless feature. This tendency also is seen in figure 4.

### 3.2. High-energy excitation

We also investigate lattice relaxations after one extra electron or one hole is added. This situation simulates high energy excitations that yield free carriers. The system is chosen to be a ring of $N=60$. We here perform an optimization keeping the ground state with $N/2 \pm 1$ electrons. Since a seed is necessary for a simulation in the PBC, we prepare a 10% -reduction for the CDW displacements at the central two sites as the initial condition. We then find that at least a hole induces a MI domain, as shown in figure 8. The relaxation behavior in figure 9 is monotonous and hence suggests a quick phase conversion. Meanwhile, an excess electron seems to create a large polaron, although it is still ambiguous because of the limited system size. As for the charges of the DW’s, an argument similar to the previous one applies for this, too. In this case, we can say that they have $+1/2e$ in the hole case.

### 4. Conclusions

We have theoretically found that the photoexcitations of both low and high energies can induce a MI domain in this CDW insulator. Moreover, we predict the formation of CDW-MI domain
Figure 3. Lattice configuration with a DW-Domain-DW structure.

Figure 4. Adiabatic potential energy curves as a function of the MI domain size. The symbols “S” and “T” mean the spin singlet and triplet states, respectively.

Figure 5. Hole density in a DW-domain-DW structure of the ground state.

Figure 6. Hole density in a DW-domain-DW structure of the first singlet excited state.

Figure 7. Schematic picture explaining charge counting of domain walls. “2”, “0”, and “1” represent the hole numbers at the Ni sites, and the vertical arrows specify the DW positions.

walls of which the charges are ±1/2e. These new findings demonstrate the importance of this compound as a PIPT material, from both the viewpoints of ultrafast phase transformation and nonlinear excitations of fractional charges.
Figure 8. Hole densities and lattice displacements for (a) an extra electron case and (b) a hole case.

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