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Formation process of a bipolaron and light-absorption bands in halogen-bridged mixed-valence metal complexes

A. Mishima
Kanazawa Institute of Technology, Nonoichi, Ishikawa, 921, Japan

K. Nasu
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan
and Institute for Science Interchange, Villa Gualino, Viale Settimio Severo, 65-10133, Torino, Italy
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A formation process of a singlet bipolaron from two doped polarons in halogen-bridged mixed-valence metal complexes is studied by using a one-dimensional extended Peierls-Hubbard model with N ($\gg 1$) lattice sites and $N+2$ electrons. The ground and the excited states of this system are calculated within the unrestricted Hartree-Fock theory and by the adiabatic approximation. Two doped polarons are shown to make a singlet bound state as the result of competition between the Coulombic repulsion and the phonon-mediated attraction, and its interpolaron distance becomes a few times the lattice constant. A new light-absorption band due to this bound state is also shown to appear at an energy of about 50% of the intrinsic gap. These theoretical results agree well with recent optical and electron-spin-resonance experiments. A pair of solitons is also studied, and is shown to have no bound state.

I. INTRODUCTION

Nonlinear excitations such as solitons and polarons in quasi-one-dimensional charge-density-wave (CDW) states have been the subject of considerable interest in recent years. At present, we have two kinds of typical quasi-one-dimensional materials: polyacetylene[1,2] and the halogen-bridged mixed-valence metal complex (HMMC),[3] which have stable CDW states in their electronic ground states. The HMMC's are a group of materials whose crystals structure are the same with each other, while their electronic properties change almost continuously, as we change the constituent halogen atoms and transition-metal atoms. By analyzing this continuous change, we derive deep insight into the nature of a many-electron system coupling strongly with phonons in these materials.

Applying a high pressure on this material, Kuroda *et al.*[4] have recently found that a new light-absorption band appears in the energy-gap region of the CDW state. They assigned this band to the soliton. On the other hand, Kurita *et al.*[5] have found that two new absorption bands, called A and B bands, appear when the HMMC is excited by an intense light with an energy greater than the gap. The peak energies of these A and B bands are 70% and 80% of the gap, respectively, and Kurita *et al.* assigned them to the polaron created by the light. In connection with these photoinduced absorption phenomena, Baeriswyl and Bishop[6] have theoretically studied the kink, polarons, and bipolarons of HMMC's, assuming that the electron-phonon (e-ph) coupling of this material is in the strong limit. Nasu *et al.*[3] and Mishima *et al.*[7,8] have clarified the nonlinear relaxation processes of an exciton, using the one-dimensional extended Peierls-Hubbard model with an intermediate strength of e-ph coupling. They have shown that the A and B bands originate from a distant pair of the electron polaron and the hole polaron. Bishop *et al.*[9] have also studied the same problem, using a two-band model composed of the halogen band and the metallic band. They obtained almost the same conclusions for the origin of the photoinduced absorptions. Thus, the nature of the photoinduced absorption phenomena has been well clarified.

All these studies are concerned with only undoped HMMC's, which have a very low electric conductivity of the order of $10^{-7}\ \Omega^{-1}\,\mathrm{cm}^{-1}$. Very recently, however, Haruki *et al.*[10,11] succeeded in obtaining highly doped HMMC's using extra iodine and chlorine atoms as dopants, and the conductivity has increased up to the order of $10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$. Since the light-absorption spectra of these doped HMMC's show the structures due to the aforementioned A and B bands, the polarons are expected to exist in this material in a high density, and contribute to the electronic conductivity. Haruki *et al.* have also found that a new light-absorption band appears at an energy of about 65% of the gap, and it is confirmed to come from the high doping effect. In addition to this, they found that the intensity of ESR signal decreases as this new band develops. These experimental facts suggest that the doped polarons make a singlet bound state resulting in a new absorption band. This singlet bound state is expected to be a bipolaron or a pair of solitons.

For these reasons, in the present paper, we study a formation process of a singlet bipolaron from a distant pair of doped polarons, as well as the formation process of the soliton pair, so that we can clarify the origin of the new absorption band.

II. EXTENDED PEIERLS-HUBBARD MODEL

The HMMC is a quasi-one-dimensional crystal composed of transition-metal ions M^{3+} (M^{3+} is Pt^{3+}, Pd^{3+}, or Ni^{3+}) bridged by halogen ions X^- (X^- is Cl^-, Br^-, or I^-). M^{3+} has an unpaired electron in its d_{z^2} orbital (z is parallel to the chain), and this d_{z^2} orbital makes a one-dimensional energy band through the hybridization with the p_z orbitals of X^-. Since this energy band is half-filled, this material is expected to be a Pauli paramagnetic metal. As is well known, however, the one-dimensional metallic state is always unstable against the e-ph coupling. In the case of the HMMC, the alternate displacement of X^- along the z direction causes the charge transfer between two neighboring M^{3+}'s, resulting in the following CDW state,

$$\cdots X^- \text{-} M^{3+\delta} \text{-} X^- \cdots M^{3-\delta} \cdots X^- \text{-} M^{3+\delta} \text{-} X^- \cdots .$$

where δ ($0<\delta\leq 1$) denotes the degree of the charge transfer.

Electronic properties of these HMMC's are already well studied from various points of view, and at present we have a systematic knowledge of their natures. According to the theory by Nasu *et al.*,[3] the electronic state of this material is brought about through a delicate balance between three main natures of the electron: its itineracy, the e-ph coupling, and the interelectron Coulombic repulsion. None of these three can be neglected in order to describe electrons in this material. For this reason, we use the following extended Peierels-Hubbard model, which takes these three features into account with an equal amount of importance:

$$\begin{aligned} H=&-T\sum_{l,\sigma}(a_{l\sigma}^{\dagger}a_{l+1,\sigma}+\text{H.c.}) \\ &+\omega\sum_{l}q_l^2/2+(s\omega)^{1/2}\sum_{l,\sigma}(q_l-q_{l+1})n_{l\sigma} \\ &+U\sum_{l}n_{l\alpha}n_{l\beta}+V\sum_{l,\sigma,\sigma'}n_{l\sigma}n_{l+1,\sigma'} , \\ n_{l\sigma}\equiv&\, a_{l\sigma}^{\dagger}a_{l\sigma} , \end{aligned} \tag{1}$$

where $a_{l\sigma}^{\dagger}$ ($a_{l\sigma}$) denotes the creation (annihilation) operator of an electron with spin σ ($=\alpha,\beta$) at a site l ($-\infty<l<+\infty$). Since we are going to study a singlet pair of the polarons and the solitons, we assume that there are two more electrons than the total number of lattice sites in the chain. T, in Eq. (1), is the transfer energy between two neighboring d_{z^2} orbitals, ω, is the phonon energy of X^-, and q_l is its dimensionless coordinate. S is the e-ph coupling energy, and U (V) denotes the intrasite (intersite) Coulombic repulsion. We should note that the e-ph coupling of the HMMC is site-diagonal, in contrast to the case of polyacetylene, wherein it is site-off-diagonal.[1,2] The kinetic energy of X^- is neglected according to the adiabatic approximation. For later convenience, we introduce the following dimensionless forms, $h\equiv H/T$, $s\equiv S/T$, $u\equiv U/T$, $v\equiv V/T$, and $Q_l\equiv(\omega/S)^{1/2}q_l$, and we also apply the mean-field theory to h. Thus, we get an approximated Hamiltonian ($\equiv h_{\text{HF}}$), which is given as

$$\begin{aligned} h_{\text{HF}}=&-\sum_{l,\sigma}[(1+vm_{l\sigma})a_{l,\sigma}^{\dagger}a_{l+1,\sigma}+\text{H.c.}]+\sum_{l,\sigma}[s(Q_l-Q_{l+1})+u\langle n_{l,-\sigma}\rangle+v(\langle n_{l+1}\rangle+\langle n_{l-1}\rangle)]a_{l\sigma}^{\dagger}a_{l\sigma} \\ &+s\sum_{l}Q_l^2/2-u\sum_{l}\langle n_{l\alpha}\rangle\langle n_{l\beta}\rangle-v\sum_{l}\langle n_l\rangle\langle n_{l+1}\rangle+v\sum_{l,\sigma}m_{l\sigma}^{*}m_{l\sigma} , \\ \langle n_l\rangle\equiv&\sum_{\sigma}\langle n_{l\sigma}\rangle , \end{aligned} \tag{2}$$

where $\langle n_{l\sigma}\rangle$ and $m_{l\sigma}$ are averages of $n_{l\sigma}$ and $a_{l+1,\sigma}^{\dagger}a_{l\sigma}$, respectively, and they should be determined self-consistently.

As we have already demonstrated in our previous papers,[3,7,8] the itineracy of electron T in the HMMC is of the same order as that of the e-ph coupling S, and even the Coulombic repulsion U is expected to be only a little smaller than T. In order to calculate the ground and the excited states of a system in such a delicate balance, we consider the following intermediate case: $T\simeq 2S\geq U\gg V$, where T is about 1 eV.

III. A PAIR OF SOLITONS AND POLARONS

Let us now calculate the ground and excited states of a system in which a pair of polarons or solitons exists. We ar mainly interested in whether a singlet bound state can be formed when two polarons or two solitons approach from two opposite sides of a chain. In order to describe this binding process, we use the following Q_l for polarons:

$$Q_l=(-1)^l Q\{1+\Delta Q[\tanh\theta(||l|-l_0/2|)-1]\} , \tag{3}$$

and for solitons as

$$Q_l=(-1)^l Q\{1+\Delta Q[\tanh\theta(|l|-l_0/2)-1]\} . \tag{4}$$

Here, $(-1)^l Q$ denotes the original Peierls distortion, and its amplitude Q should be determined beforehand within the mean-field theory for the ground state of the CDW. The second terms in the curly braces of Eqs. (3) and (4) denote the local displacements from this original Peierls distortion. ΔQ is the amplitude of this local displacement centered both in the right half ($l>0$) and the left half ($l<0$) of the chain. Its center is at $l=\pm l_0/2$, and θ denotes the reciprocal width of this displacement. l_0 is nothing but the interpolaron or the intersoliton distance in the unit of the lattice constant. In the practical calcu-

lations, ΔQ and θ are determined so as to minimize the total energy for given l_0.

Results of calculations are shown in Fig. 1. The energy of the ground state of the polaron pair for given l_0 is denoted by E_G, and is shown by the low-lying solid line, while that of the soliton pair denoted by E_G', is written by the low-lying dashed line. We can see a local minimum of a polaron pair at $l_0=2$, but no local minimum of a soliton pair, except at $l_0=\infty$. Thus, we can conclude that the two polarons can make a bound state, which is usually called a bipolaron. Incidentally, all the energies in Fig. 1 are referenced from the total energy of the system with $l_0=0$, which is common to the polaron pair and the soliton pair.

Figure 2 shows charge and spin densities of the bipolaron with $l_0=2$. However, the spin is zero at all sites, and it means that this bipolaron is a singlet one. We should note that the numbering for the sites, in Figs. 2 and 3, is inconsistent with that in Eq. (3) since the center of the chain is placed at $l=102$ in these figures. In Fig. 3, we have shown charge and spin densities at $l_0=8$, and we can see that the positive and the negative spins appear. They correspond to the two polarons. The spatial extension of each polaron is about six in the units of the lattice constant.

When the HMMC is doped, the electron polarons will be created randomly in the chain, with an interpolaron

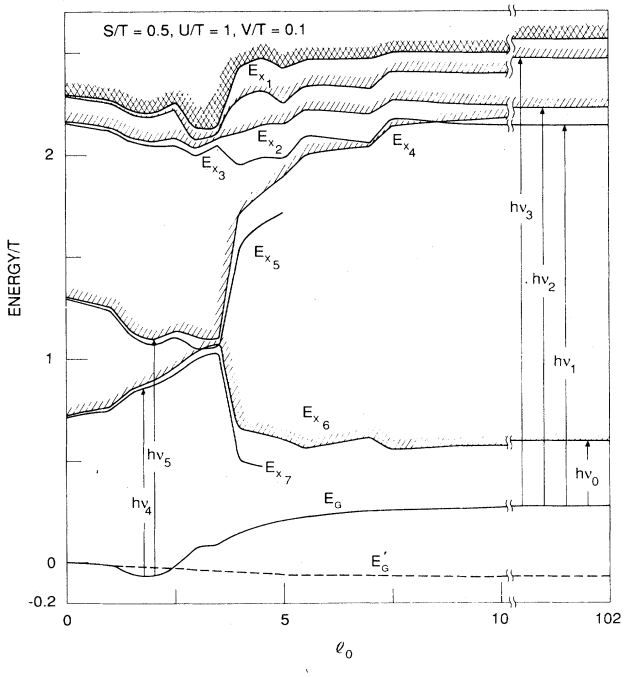

FIG. 1. The adiabatic potential energies as a function of l_0. E_G and E_G' denote the energies of the ground states for a polaron pair and a soliton pair, respectively. All the energies are referenced from the total energy of the system with $l_0=0$, which is common to the polaron pair and the soliton pair. E_{x_i} ($i=1,\ldots,7$) denote the energies of the excited states for a polaron pair. The oblique lines denote the electron and the hole continua. $h\nu_0,\ldots,h\nu_5$ are the exciting energies.

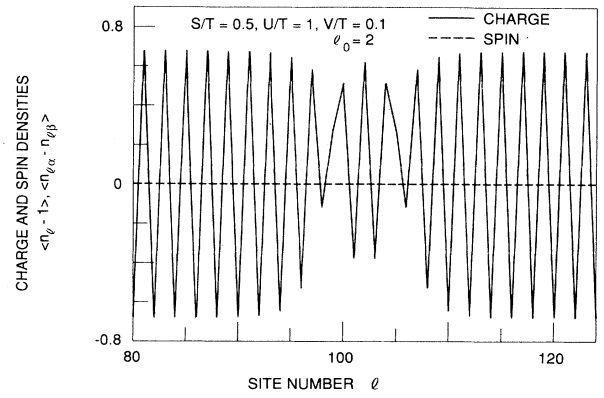

FIG. 2. The charge- and spin-density profiles of a bipolaron with $l_0=2$. The numbering for the sites is inconsistent with that of Eq. (3). $l=0$ in Eq. (3) corresponds to $l=102$ in this figure.

distance much longer than the lattice constant. Between these polarons, an attraction acts through the overlap of their lattice distortion clouds. Because of this attraction, two polarons with opposite spins come together along the potential surface E_G as shown in Fig. 1. When they are too close together, however, the Coulombic repulsion begins to act. As the result of these competing two effects, we get a bound state at around $l_0=2$. Once such a singlet bipolaron is formed, the ESR signal is easily seen to decrease, while the electric conductivity will not be changed as much since the bipolaron itself can move through hopping from site to site. These results are quite consistent with recent experiments.[10,11]

In the case of the soliton and antisoliton pair, on the other hand, the interaction is always repulsive because of the following frustration in the choice of the phase of Peierls distortion. In the region outside the pair [$l > l_0/2$ in Eq. (4), for example], the soliton centered at $l=l_0/2$ wants to make the phase of the Peierls distortion positive, while the antisoliton centered at $l=-l_0/2$ wants to

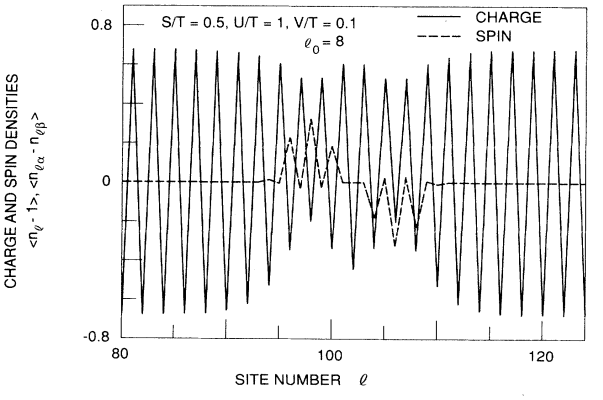

FIG. 3. The charge- and spin-density profiles of a polaron pair with $l_0=8$. The numbering for the sites is inconsistent with that of Eq. (3). $l=0$ in Eq. (3) corresponds to $l=102$ in this figure.

make it negative. Thus, the frustration occurs, and consequently, the most stable state of a pair appears only at $l_0=\infty$, as seen from Fig. 1.

Let us consider the nature of a soliton pair obtained from the bipolaron. As mentioned in our previous papers,[3,7,8] the ground state in the strong limit of e-ph coupling is an alternating stack of M^2 and M^4:

$$M^4M^2M^4M^2M^4M^2M^4M^2|M^4M^2M^4M^2M^4M^2M^4M^2 .$$

If we assume that the ligand molecule coordinated to each M has a charge $-2e$, the total charge of a chain including X^{-1}, which is not written explicitly, is easily seen to be zero. Through the transfer of charges $-e$ or $-2e$ from the left half to the right half of this chain across the central line, we get the following two excited states:

$$\cdots M^4M^2M^4M^3|M^3M^2M^4M^2\cdots ,$$

$$\cdots M^4M^2M^4M^4|M^2M^2M^4M^2\cdots .$$

Comparing these states with the ground state, we can call the first one a self-trapped exciton (STE) and the second one two STE's. Both of them have already been confirmed to be locally stable states.[12] When these excited states are separated by several units of a neutral pair (M^2M^4), we get four solitons, A, A', B, and B':

$$A'=M^4M^2M^4M^2M^4M^3M^2M^4M^2M^4 ,$$

$$A=M^2M^4M^2M^4M^3M^2M^4M^2M^4M^2 ,$$

$$B'=M^4M^2M^4M^2M^4M^4M^2M^4M^2M^4 ,$$

$$B=M^2M^4M^2M^4M^2M^2M^4M^2M^4M^2 .$$

The charges of B and B' are $-2e$ and $+2e$, while those of A and A' are $-e$ and $+e$. A and A' also have their spins $\pm 1/2$. In the case of a bipolaron, it can be written as

$$\cdots M^4M^2M^3M^2M^3M^2M^4M^2\cdots ,$$

and according to the results of our calculations, the soliton pair, appearing at $l_0=\infty$ in Fig. 1, is a pair of B and (M^4BM^4). The former is charged and the latter is neutral, while both of them have no spin. Thus, the spin of each polaron disappears when they make a singlet bipolaron and it never recovers, even though the bipolaron is converted into a pair of solitons.

Incidentally, let us consider the effective charge which is carried through the motion of B. In order to clarify this problem, we hypothetically set a counter at a certain site of the chain, and count the total number of charges that pass this site as B passes it from left to right. The value of the total charge will change as follows, as a function of time,

$$-1\ 0\ -1\ 0\ -1\ -2\ -1\ -2\ -1\ -2 ,$$

where the first -1 corresponds to M^2 in the right end of B, and the last -2 corresponds to M^2 in the left end of B. Thus, the average change of the counter between before and after the passage of B is $-e$. Consequently, the effective charge carried by B is $-e$. Using the same procedure, we can find that the effective charge carried by A is zero. This difference between the effective charge and the total charge is mainly due to the site-diagonal nature of the e-ph coupling of this system. In the case of polyacetylene, all the carbon atoms in the ground state are equally neutral, and hence such a difference does not appear.

IV. DOPING-INDUCED ABSORPTIONS

Let us now study the new light-absorption bands induced by the doping. When two polarons with opposite spins are in the right half and the left half of the chain, with a long interpolaron distance $l_0 \gg 1$, we get four localized levels $|P^{\pm}_{R,L}\rangle$ in the gap as shown in Fig. 4. Here, the superscripts plus and minus signs denote the hole polaron and the electron polaron, respectively, while R and L denote the right and the left. Since we have two excess electrons, the states $|P^+_L\rangle$ and $|P^+_R\rangle$ are doubly occupied, while the states $|P^-_L\rangle$ and $|P^-_R\rangle$ are singly occupied.

As the l_0 decreases, these four states are mixed up together, resulting in new four states $|P^{\pm}_{A,B}\rangle$, where A and B denote the antibonding and bonding states as shown in Fig. 4. In this case, only the state $|P^-_A\rangle$ is vacant. Low-lying optical excitations from this ground state are the following three transitions: from $|P^-_B\rangle$ to $|P^-_A\rangle$, from $|P^-_B\rangle$ to the electron continuum, and from $|P^+_B\rangle$ to the electron continuum. The energies of the first two transitions are almost the same and are denoted only by $h\nu_4$ in Fig. 1. Their l_0 dependencies are also shown by the lines labeled E_{x_7} and E_{x_6}. The energy of the third transition is denoted by $h\nu_5$, and its l_0 dependency is shown by the line labeled E_{x_4}. The transition energy from $|P^+_B\rangle$ to $|P^-_A\rangle$ is denoted by E_{x_5}, but this transition is forbidden by the parity. We also have other transitions with much higher energies, which are denoted by E_{x_1}, E_{x_2}, and E_{x_3}.

Haruki *et al.*[10,11] have recently observed a new absorption band with an energy of about 65% of the gap in the highly doped HMMC, as mentioned before. According to

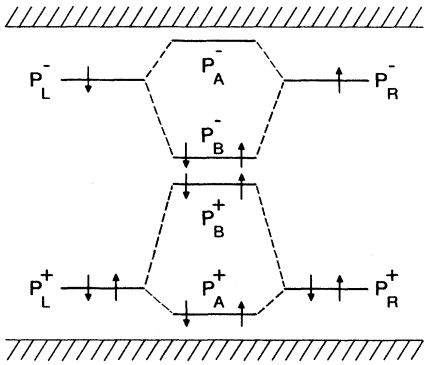

FIG. 4. The schematic energy levels of the ground states of a polaron pair. ↑ and ↓ denote the electrons with up and down spins, respectively. The oblique lines denote the electron and hole continua. Superscripts $-$ and $+$ of P correspond to the electron and the hole. L and R correspond to the left and the right, when $l_0=\infty$. B and A correspond to the bonding and the antibonding states, when $l_0\approx 2$.

our theory $h\nu_5$ is about 50% of the gap, in agreement with this experiment. Theoretical results obtained by Bishop *et al.*[9] based on the two-band model are almost consistent with our results. However, the Coulombic repulsion is not included in their calculations for the transition energies.

Let us now return to a somewhat old problem of light-absorption bands due to the presence of the electron polaron alone. As mentioned in Sec. I, the A and B bands come from this polaron. Our calculations, given in Refs. 3,7, and 8, for these transition energies are somewhat insufficient because, in that case, the self-consistency equation for $\langle n_{l\sigma} \rangle$ is solved only for the ground state of the system which consists of N lattice sites and N electrons. The transition energies are calculated using this ground state as a base. In the present paper, however, we have solved the self-consistency equation for $\langle n_{l\sigma} \rangle$ in the system with N sites and $N+2$ electrons. Hence, it can give more refined transition energies than the previous ones. The results are shown in Fig. 1 (at $l_0=\infty$). Within the mean-field theory, we have the following four transition energies: $h\nu_0$, $h\nu_1$, $h\nu_2$, and $h\nu_3$. $h\nu_0$ corresponds to the transition from $|P_R^-\rangle$ to the electron continuum in Fig. 4. $h\nu_1$ denotes the transition from $|P_R^+\rangle$ to $|P_R^-\rangle$, and it corresponds to the A band mentioned before. $h\nu_2$ corresponds to the transition from the doubly occupied $|P_R^+\rangle$ to the electron continuum, while $h\nu_3$ corresponds to the transition from the hole continuum to the singly occupied $|P_R^-\rangle$. In our previous calculation, $h\nu_2$ and $h\nu_3$ were equal, since the single occupancy of $|P_R^-\rangle$ is not fully taken into account even within the mean-field theory, and these two transitions are all assigned to the B band. Our refined result tells us that they are not equal, because of the difference of occupancy of the two levels $|P_R^-\rangle$ and $|P_R^+\rangle$. Very recently, Matsushita *et al.*[13] have found a new absorption band in the region higher in energy than the B band. This band is expected to correspond to $h\nu_3$.

V. CONCLUSIONS

We have thus calculated the ground and excited states of a polaron pair using an extended Peierls-Hubbard model. In the case of intermediate strength of e-ph coupling, the singlet bipolaron is shown to be formed from a distant pair of doped polarons. The theoretical prediction for the new light-absorption band due to this bipolaron, as well as its spinless nature, agree well with the recent experiments. In contrast to the bipolaron, a pair of solitons is shown to have no bound state. We have been concerned with only the single isolated chain. The effects of interchain couplings will be studied in the future.

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