Nonlinear lattice relaxation of photogenerated charge-transfer excitation in halogen-bridged mixed-valence metal complexes. I. Soliton and self-trapped exciton

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

K. Nasu
Institute for Molecular Science, 38 Nishigonaka, Myodaiji, Okazaki 444, Japan

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The ground and excited states of a one-dimensional extended Peierls-Hubbard model with half-filled-band electrons are studied so as to clarify the lattice relaxation paths of photogenerated charge-transfer excitations in halogen-bridged mixed-valence metal complexes. The adiabatic potential-energy surfaces that describe the nonlinear relaxation from the Franck-Condon state to the solitonic states as well as to the self-trapped state of the exciton (STE) are calculated within the mean-field theory for electrons. It is shown that the lowest excited state is a pair of doubly charged solitons, and it gives a new absorption band with an energy of about a half of the gap. It is also shown that the STE is separated from this soliton pair by only a small barrier, in agreement with the experiments on the unusual short decay time of this state.

I. INTRODUCTION

Optical properties of halogen-bridged mixed-valence metal complexes (HMMC's) have been the object of very active researches in recent years, as one of typical materials with a quasi-one-dimensional charge-density-wave (CDW) state.[1-7] This material is composed of transition-metal ions M^{+3} ($=Pt^{+3}, Pd^{+3}, Ni^{+3}$) bridged by halogen ions X^- ($=Cl^-, Br^-, I^-$), as schematically shown in Fig. 1. M^{+3} has an unpaired electron in its d_{z^2} orbital ($\hat{z}$ is parallel to the chain), and this orbital makes an energy band through the supertransfer between neighboring two d_{z^2} orbitals. This supertransfer comes from the hybridyzation between the d_{z^2} orbital and the p_z orbital of X. Thus, this system is expected to be a metal with a half-filled energy band.

Because of the electron-phonon (e-ph) coupling, however, the charge transfer occurs between neighboring two M's so as to give the following mixed-valence state:

$$---X^-\_^{+(3+\delta)}\_X^-\_\_\_M^{+(3-\delta)}\_\_\_X^-\_\ , \qquad 0 \le \delta \le 1$$

wherein X^- has displaced towards $M^{+(3+\delta)}$ (where δ denotes the degree of charge transfer). This is nothing but the CDW state with twice the period of the original lattice. This state has a strong-light-absorption band in the visible region,[1-3] and it corresponds to the charge-transfer (CT) excitation from $(M^{+(3+\delta)}M^{+(3-\delta)})$ to $(M^{+3}M^{+3})$. Since this ground state is stabilized by the aforementioned charge transfer and the displacement of X^-, such a redistribution of the charge due to the excitation triggers a drastic motion of X^-, and after the relaxation, it results in nonlinear structural excited states such as the solitons and the polarons, as well as the self-trapped excitons.

In this connection, Kurita *et al.*[5] have found that new two light-absorption bands appear when the CT band is excited by an intense light. These photoinduced absorption bands are named A and B, and their energies are about 70% and 80% of the energy gap, respectively. These bands, being almost equal to the previously observed ones by the pressure effect,[4] are expected to come from the intrinsic nonlinear excited states created after the relaxation. The main purpose, in the present paper, is to clarify this relaxation process of the CT excitation.

To study the CDW in HMMC's is of great advantage, as compared with the polyacetylene, because we have many kinds of crystals with an almost same structure. Each crystal has its own electronic property which changes almost continuously as the combination of M and X changes. This continuous change makes it possible for us to get a deep insight into the common nature of the CDW. For example, the energy gap decreases as the atomic radius of M (r_M) decreases or as the radius of X (r_X) increases. The decrease of r_M makes the intraorbital Coulombic repulsion increase, and it reduces the energy gap,[8] while the increase of r_X makes the supertransfer increase, resulting in the reduction of the energy gap, provided the e-ph coupling remains unaltered. Judging from these results, Nasu[8] has proposed a new theory that the electronic state of HMMC is realized through a delicate balance between the three main factors: the supertransfer of an electron, the interelectron Coulombic repulsion, and the e-ph coupling. This theory was proved to be true by the discovery of a new HMMC composed of

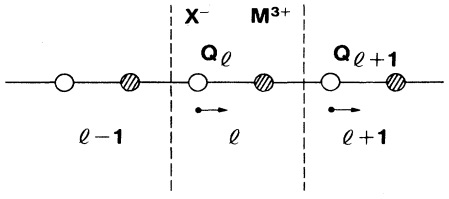

FIG. 1. Schematic structure of the halogen-bridged metal complex.

M=Ni and X=Br,[9] wherein the Peierls distortion is absent because of the large Coulombic repulsion of Ni. It is in the spin density wave state.

For these reasons, in the present paper, we calculate the ground and excited states of HMMC's, making use of the one-dimensional Peierls-Hubbard model, which takes the aforementioned three main factors into account with an almost equal weight of importance.

Very recently, Baeriswyl and Bishop[10] have described the exciton, the polaron, the bipolaron, and the solitonic defects of HMMC in the strong limit of the e-ph coupling, and discussed the effect of Coulombic interactions on the optical absorption from the defects. Onodera[11] also studied the soliton in the weak limit. However, for the reasons mentioned before, we will study, in the present paper, intermediate cases of the e-ph coupling.

II. EXTENDED PEIERLS-HUBBARD MODEL AND NUMERICAL RESULTS

To describe the ground and excited states of the CDW, we introduce the following one-dimensional extended Peierls-Hubbard model with half-filled-band electrons (setting $\hbar=1$):

$$H=-T\sum_{l,\sigma}(a_{l\sigma}^{\dagger}a_{l+1,\sigma}+\text{H.c.})+\omega\sum_{l}q_l^2/2 +\sqrt{S\omega}\sum_{l,\sigma}(q_l-q_{l+1})n_{l\sigma}+U\sum_{l}n_{l\alpha}n_{l\beta} +V\sum_{l,\sigma,\sigma'}n_{l\sigma}n_{l+1,\sigma'},\quad n_{l\sigma}\equiv a_{l\sigma}^{\dagger}a_{l\sigma}\ , \tag{2.1}$$

where $a_{l\sigma}^{\dagger}$ is the creation operator of the electron at site l ($-\infty\le l\le\infty$) with spin σ ($=\alpha,\beta$), and T is the energy of the supertransfer between neighboring two d_{z^2} orbitals. ω is the phonon energy of X^-, and q_l is its dimensionless coordinate. The kinetic energy of X^- is neglected according to the adiabatic approximation. S is the e-ph coupling energy, while U and V denote the intrasite and intersite Coulombic repulsions, respectively.

According to the Hückel theory,[12] T is about 1 eV. Combining this value with other experimental results such as the energies of the CT band and the luminescence, we assume the following relation holds in our system: $2S\approx T\ge U\gg V$. It corresponds to the intermediate coupling case. Transforming as $h\equiv H/T$, $s=S/T$, $u=U/T$, $v=V/T$, and $Q_l=q_l\sqrt{\omega/S}$, we get the following dimensionless Hamiltonian h:

$$h=-\sum_{l,\sigma}(a_{l\sigma}^{\dagger}a_{l+1,\sigma}+\text{H.c.})+s\sum_{l}Q_l^2/2 +s\sum_{l,\sigma}(Q_l-Q_{l+1})n_{l\sigma} +u\sum_{l}n_{l\alpha}n_{l\beta}+v\sum_{l,\sigma,\sigma'}n_{l\sigma}n_{l+1,\sigma'}\ . \tag{2.2}$$

Within the mean-field theory, we get a reduced Hamiltonian h_{HF}, wherein $n_{l\sigma}$ and $(a_{l+1,\sigma}^{\dagger}a_{l\sigma})$ in the fourth and fifth terms of h are replaced by their averages $\langle n_{l\sigma}\rangle$ and $m_{l\sigma}$

$$n_{l\sigma}\to\langle n_{l\sigma}\rangle,\quad (a_{l+1,\sigma}^{\dagger}a_{l\sigma})\to m_{l\sigma}\ ,$$
$$h\to h_{\text{HF}}=-\sum_{l,\sigma}[(1+vm_{l\sigma})a_{l\sigma}^{\dagger}a_{l+1,\sigma}+\text{H.c.}]+\sum_{l,\sigma}[s(Q_l-Q_{l+1})+u\langle n_{l,-\sigma}\rangle+v(\langle n_{l+1}\rangle+\langle n_{l-1}\rangle)]a_{l\sigma}^{\dagger}a_{l\sigma} +s\sum_{l}Q_l^2/2-u\sum_{l}\langle n_{l\alpha}\rangle\langle n_{l\beta}\rangle-v\sum_{l}\langle n_l\rangle\langle n_{l+1}\rangle+v\sum_{l,\sigma}m_{l\sigma}^{*}m_{l\sigma}\ . \tag{2.3}$$

Here $\langle n_{l\sigma}\rangle$ and $m_{l\sigma}$ are unknown parameters, and should be determined self-consistently. $\langle n_l\rangle$ is given as

$$\langle n_l\rangle\equiv\sum_{\sigma}\langle n_{l\sigma}\rangle\ . \tag{2.4}$$

Our main purpose of this section is to calculate the adiabatic potential-energy surfaces that describe the lattice relaxation paths of the photogenerated CT excitation. In the case of ordinary insulators, the CT exciton, just after the excitation, is in a plane-wave state extending over the crystal. This state is usually called the Franck-Condon state. After the lattice relaxation having been completed, however, the exciton is in a localized state, being trapped by a self-induced local lattice distortion.[13] This is called the self-trapped state of exciton (STE). In the case of CDW-type insulators, however, we have another relaxation channel. That is the nonlinear relaxation to the structural excited states such as the soliton pairs, wherein the phase of the Peierls distortion is locally inverted.

To cover all these possibilities of the relaxation, we introduce the following pattern for Q_l:

$$Q_l=(-1)^lQ\{1+\Delta Q[\tanh\theta(|l|-l_0/2)-1]\}\ , \tag{2.5}$$

where $(-1)^lQ$ denotes the Peierls distortion in the ground state of the CDW, and this Q should be determined beforehand. The second term in the curly brackets denotes the local lattice displacement from this ground state. ΔQ is its amplitude and [ ] denotes its pattern. θ denotes the spatial extension of the pattern, and l_0 denotes the intersoliton distance. When $l_0=0$, this pattern just corresponds to the STE-type local lattice distortion, and in this case θ corresponds to the reciprocal width of the STE. In the case of $l_0\gg1$, on the other hand, θ corresponds to the reciprocal width of a soliton. This can be easily seen when we put $\Delta Q=1$.

To determine the adiabatic potential energy surface, we solve the self-consistency equations for $\langle n_{l\sigma}\rangle$ and $m_{l\sigma}$ for given values of ΔQ and l_0, while θ is determined to minimize the total energy. Thus we can obtain the ener-

gies of the ground state E_G and of the excited states E'_{x_n} ($n=1,2,3,\ldots$), as well as their wave functions $|E_G\rangle$ and $|E_{x_n}\rangle$, which are numbered according to their energies from lower ones to upper ones. As for the excited states, we also take into account the difference between h and $h_{\rm HF}$ within the first-order perturbation theory,

$$\langle E_{x_n}|(h-h_{\rm HF})|E_{x_n}\rangle \ . \tag{2.6}$$

In the practical calculations, we at first numerically determine the following new operator $A^\dagger_{\lambda\sigma}$:

$$A^\dagger_{\lambda\sigma}=\sum_l f_{\lambda\sigma}(l)a^\dagger_{l\sigma} \ , \tag{2.7}$$

that can diagonalize $h_{\rm HF}$ as

$$h_{\rm HF}=\sum_\lambda e_{\lambda\sigma}A^\dagger_{\lambda\sigma}A_{\lambda\sigma}+\text{constant terms} \ . \tag{2.8}$$

Here $e_{\lambda\sigma}$ is the λth eigenvalue of $h_{\rm HF}$, and $f_{\lambda\sigma}(l)$ is its wave function. In the next, we rewrite h in terms of $A^\dagger_{\lambda\sigma}$ and $A_{\lambda\sigma}$. Expectation values of h rewritten in this form can be easily calculated numerically, and we can, thus, evaluate Eq. (2.6).

Adding this correction to the original energy E'_{x_n} coming from $h_{\rm HF}$, we can obtain the new energies of the excited states E_{x_n} ($n=1,2,\ldots$) as

$$E_{x_n}=E'_{x_n}+\langle E'_{x_n}|(h-h_{\rm HF})|E_{x_n}\rangle \ . \tag{2.9}$$

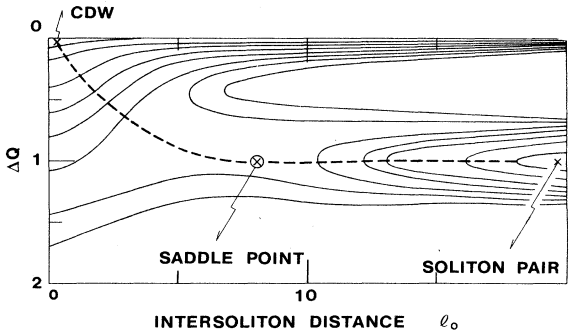

FIG. 2. Schematic nature of E_G as a function of ΔQ and l_0.

Figure 2 shows a very schematic nature of E_G common to the cases of intermediate coupling. The minimum at $\Delta Q=0$ and $l_0=0$ corresponds to the CDW ground state, while the local minimum at $\Delta Q=1$ and $l_0=\infty$ corresponds to the soliton-antisoliton pair. It is a pair of doubly charged solitons. There are other types of solitons, such as the spin soliton and the singly charged soliton. However, according to our calculation, other ones have higher energies than this.

This result can be intuitively understood in the following way. When the e-ph coupling is strong, $S/T\gg1$, δ becomes almost equal to unity, and the ground state of CDW, in this case, is just the alternate stack of M^{+4} and M^{+2}:

$$M^{+2}M^{+4}M^{+2}M^{+4}M^{+2}M^{+4}M^{+2}M^{+4}M^{+2}M^{+4}M^{+2}M^{+4} \ .$$

As one of structural excited states from this ground state, we can also think of the following state:

$$M^{+2}M^{+4}M^{+2}M^{+4}M^{+2}M^{+2}|M^{+4}M^{+4}M^{+2}M^{+4}M^{+2}M^{+4} \ ,$$

wherein $2e^-$ is transferred across the central line. We can see that the total excess charge in the left part of the chain is $2e^-$, while that in the right is $2e^+$. In our previous paper,[8] we have already shown that this state is a locally stable state in the adiabatic potential energy surface of the lattice, and its energy is almost same as that of the ground state, provided the e-ph coupling is strong. The appearance of such a new low-lying excited state is mainly due to the site-diagonal nature of e-ph coupling, where the lattice displacement modulates, not the transfer energy T, but the energy level of the d_{z^2} orbital. From these results, we can also easily infer that, when central two M's are separated by several units of ($M^{+4}M^{+2}$),

$$M^{+2}M^{+4}M^{+2}M^{+4}M^{+2}M^{+2}[M^{+4}M^{+2}M^{+4}M^{+2}]M^{+4}M^{+4}M^{+2}M^{+4}M^{+2}M^{+4} \ ,$$

a pair of doubly charged solitons appears. Figure 3 shows the charge-density profile of this type soliton calculated numerically. Its width is about 6 in the unit of the lattice constant, since the e-ph coupling of this case is not in the strong coupling, but in the intermediate region. The dashed line in Fig. 2 denotes the road that going over the saddle point from the ground state of CDW to this soliton pair, since these two minima are separated by a potential barrier.

Figure 4 shows a very schematic nature of the adiabatic potential surface of E_{x_1}, and the Franck-Condon state is at $\Delta Q=0$ and $l_0=0$. As ΔQ increases from zero along the line $l_0=0$, E_{x_1} reaches to a local minimum corresponding to the STE. In this state the electron and the hole are bound together not only by the local lattice distortion but also by the electron-hole attraction coming from V through the correction term Eq. (2.6). The local minimum at $\Delta Q=1$ and $l_0=\infty$ corresponds to a pair of another type solitons. It has a charge $\pm e$ and a spin $\pm\frac{1}{2}$, according to our calculation. The STE and this soliton pair are separated by only a small barrier, and the dashed line denotes the road that goes over the saddle point.

Figure 5 shows the numerical result for the potential surface as a function of ΔQ along the line $l_0=0$. In this

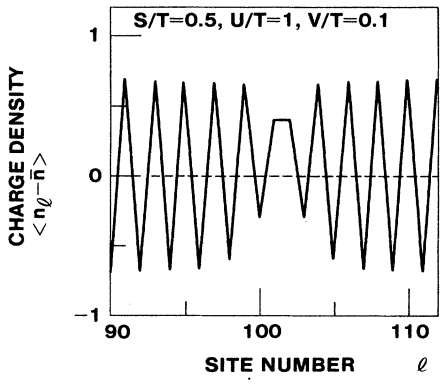

FIG. 3. Charge-density profile around the doubly charged soliton with $2e^-$. $\bar{n}=1$.

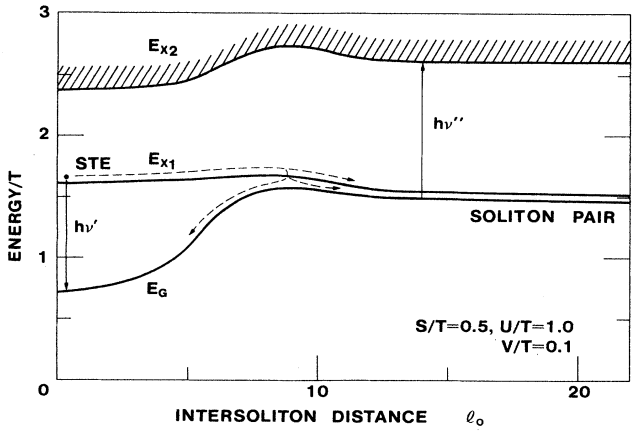

FIG. 6. Adiabatic potential energies as a function of l_0. All the energies are referenced from the ground state of CDW.

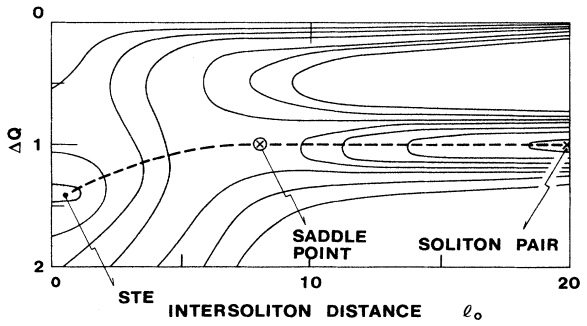

FIG. 4. Schematic nature of E_{x_1} as a function of ΔQ and l_0.

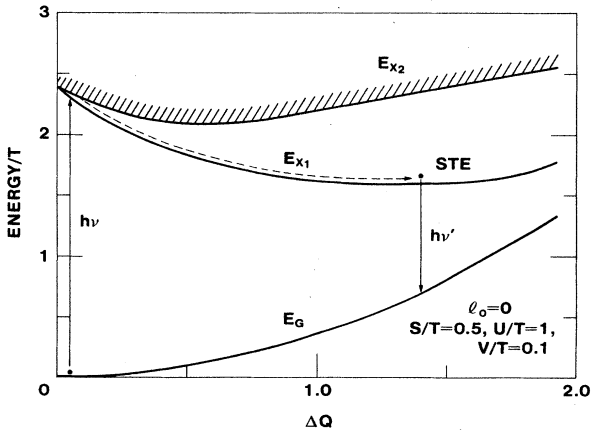

FIG. 5. Adiabatic potential energies as a function of ΔQ at $l_0=0$. All the energies are referenced from the ground state of CDW.

calculation θ is determined to minimize E_{x_1}. All the energies are referenced from the energy of the ground state of CDW, and this notation is used hereafter. This figure just corresponds to the self-trapping process of the CT excitation. As ΔQ increases from zero, the STE splits off from the electron-hole pair continuum, and at around the local minimum it emits a luminescence of an energy $h\nu'$, which is about a half of the exciting energy $h\nu$.

Figure 6 shows the adiabatic energies as a function of l_0 alone. ΔQ and θ are determined to minimize E_{x_1}. We can see that the lowest excited state is a pair of doubly charged solitons, mentioned before. Since there is only a small barrier between the STE and this pair, the transition between them is expected to occur easily through the tunneling or the thermal activation. It is also seen from Fig. 6 that the STE can decay into the ground state, too, nonradiatively through this barrier region. According to the very recent experiments by Wada *et al.*[6] and Tanino *et al.*[7] the lifetime of the STE is of the order of 100 psec, being exceptionally shorter than that of ordinary insulators such as alkali halides. Our result is consistent with this experiment.

When a pair of solitons is generated, we can expect to get a new absorption band due to the excitation from this state. As shown in Fig. 6, the energy $h\nu''$ of this excitation is about a half of the gap, which corresponds to the low-energy tail of the A band.

III. CONCLUSIONS

We have thus studied the ground and excited states of the CDW in HMMC's, using the one-dimensional extended Peierls-Hubbard model. The lowest nonlinear structural excited state is shown to be a pair of doubly

charged solitons, and it causes a new absorption band with an energy of about a half of the gap. The STE is also shown to be a locally stable state, separated from this soliton pair only by a small barrier, in agreement with recent experiments on the unusual short decay time of this state.

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