

Perturbation theory for the formation energy of solitons and polarons in mixed-valence linear-chain complexes

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(Received 25 June 1991)

A perturbation calculation shows that the relative formation energies of solitons and polarons in halogen-bridged linear-chain complexes depend strongly on the transfer term and Coulomb interactions even if the electron-lattice coupling is dominant. As the values of the transfer term and Coulomb interactions increase, various soliton states tend to have energies close to one another. It is suggested that the neutral soliton of two-site type is the lowest-energy defect state in a certain range of the strengths of those perturbations. This situation is consistent with the results of the ultraviolet-induced EPR experiment in $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$ (with en =ethylenediamine). The present theory provides an explanation for a highly mobile character of the neutral soliton observed in this material.

I. INTRODUCTION

Halogen-bridged mixed-valence complexes of platinum and palladium consist of linear chains of the form of $-M^{2+}-X^{-}-M^{4+}-X^{-}-M^{2+}-X^{-}$, where M and X are metal and halogen atoms, respectively. The chains are sustained parallel to each other by a hydrogen bond network which links counterions with ligands of metal ions. The linearly periodic structure of the valence of metal ions is a charge-density-wave (CDW) state which results from electron transfer between neighboring metal sites in the original chain $-M^{3+}-X^{-}-M^{3+}-X^{-}-M^{3+}-X^{-}$. Most of the materials of this family exhibit order of the CDW state in one dimension only, indicating that the inter-chain interaction is very weak.^{1,2} In recent years, there has been a great deal of effort in characterizing the nature of the intrinsic defects excited in this quasi-one-dimensional CDW state. In particular, the complex $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$, where en denotes an ethylenediamine molecule, has attracted much attention because, in this material, a long-lived defect state bearing spin can be created by uv irradiation.^{3,4} The electron-paramagnetic-resonance (EPR) spectrum shows that this defect is formed by dimerization of a pair of Pt ions,⁵ and has solitonlike characters.⁴

Ichinose⁶ has described the excitation spectrum of the linear chain by introducing a nearly site-diagonal electron-lattice coupling which is in contrast to the site-off-diagonal coupling in *trans*-polyacetylene. According to his arguments, soliton excitations corresponding to propagating domain walls can take place if the electron-lattice coupling is strong compared to the transfer energy. Subsequently, Onodera⁷ has proven that the soliton excitations are possible even if the electron-lattice coupling is weak. To provide a guide for interpreting spectroscopic properties, Baeriswyl and Bishop⁸ have evaluated the electronic structures and formation energies of solitons, polarons, and bipolarons in the system where the transfer energy and Coulomb interactions are negligibly weak in comparison with the electron-lattice cou-

pling. More recently, Mishima and Nasu⁹ have studied an extended Peierls-Hubbard model to investigate the properties of these intrinsic defect states in an intermediate-coupling system. Upon choosing a set of the transfer energy and Coulomb interactions which are comparable in strength to the electron-lattice coupling, they have performed Hartree-Fock analyses of the adiabatic potential energies of solitons and polarons.

The purpose of the present paper is to calculate formation energies of intrinsic defects in the one-dimensional CDW system by extending Baeriswyl and Bishop's model. The small size of the solitonlike paramagnetic defect clarified by the EPR experiment^{4,5} verifies that $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$ is a strong electron-lattice coupling system. We, therefore, consider the cases where the transfer integral is smaller than that employed by Mishima and Nasu.⁹ We take account of the on-site and intersite Coulomb interactions, since these energies affect strongly the charge distributions in defects. Treating the effect of the transfer term by means of the perturbation theory, we investigate how the transfer term and Coulomb interactions influence the formation energies of intrinsic defects in the strong electron-lattice coupling system.

II. MODEL HAMILTONIAN AND GROUND STATE OF A REGULAR LATTICE

Since the interchain interaction is weak in the complexes we are concerned with, we consider a single and long chain which consists of Pt and Cl ions as shown in Fig. 1. It is assumed that each Pt^{3+} ion can supply or accept an electron to become Pt^{4+} or Pt^{2+} , respectively, and a strong electron-lattice coupling causes the mixed-valence state. The model Hamiltonian of this system is expressed as⁶⁻⁹

$$H = H_0 + H_1, \quad (1)$$

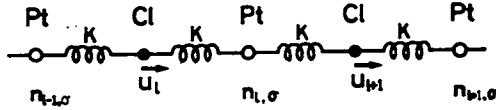


FIG. 1. A model structure of a chain. K is the spring constant of the bond connecting Pt and Cl ions, u_l is the displacement of the Cl^- ion at the l th site, and n_l is the number of electrons on the Pt ion at the l th site.

$$H_0 = \sum_l K u_l^2 + \sum_{l,\sigma} \xi (u_l - u_{l+1}) n_{l\sigma} + \frac{1}{2} \sum_{l,\sigma} U n_{l\sigma} n_{l,-\sigma} + \sum_{l,\sigma,\sigma'} V n_{l\sigma} n_{l+1,\sigma'}, \quad (2)$$

$$H_1 = - \sum_{l,\sigma} t (a_{l\sigma}^\dagger a_{l+1,\sigma} + a_{l+1,\sigma}^\dagger a_{l\sigma}), \quad (3)$$

where $a_{l\sigma}$ and $n_{l\sigma} (= a_{l\sigma}^\dagger a_{l\sigma})$ are, respectively, the annihilation and number operators of an electron with spin σ on Pt in the l th unit cell, u_l is the displacement of Cl^- along the chain direction, K is the spring constant of a Pt-Cl bond, ξ is the electron-lattice coupling constant, U is the on-site Coulomb interaction, V is the intersite Coulomb interaction, and t (>0) is the transfer integral between neighboring Pt sites via an intervening Cl^- ion.

Throughout the present theory, we employ an adiabatic approximation and regard u_l as a classical quantity which is determined by minimizing the energy of the system. Let $\langle n_{l\sigma} \rangle$ be the expectation number of electrons with spin σ on the l th site in the ground state determined by H . Then the equilibrium u_l can be expressed as follows:

$$u_l = \frac{\xi}{2K} (\langle n_{l-1} \rangle - \langle n_l \rangle), \quad (4)$$

$$\langle n_l \rangle = \sum_{\sigma} \langle n_{l\sigma} \rangle. \quad (5)$$

The unperturbed states are described in terms of H_0 . In spite of the absence of the transfer term in H_0 , we use the u_l 's given by Eq. (4) to generate the site potential of the unperturbed states. Those u_l 's are chosen so as to be consistent with the charge distribution which is realized in the presence of the transfer term. We introduce the electron numbers $\langle n_{l\sigma}^0 \rangle$'s to represent the starting eigenstates. The expectation number $\langle n_l \rangle$ can be a nonin-

teger, while $\langle n_l^0 \rangle (= \sum_{\sigma} \langle n_{l\sigma}^0 \rangle)$ should be only 0, 1, or 2 at any Pt site. Substituting Eq. (4) into Eq. (2) and replacing $n_{l\sigma}$ in Eq. (2) by $\langle n_{l\sigma}^0 \rangle$, we obtain the total energy of a state represented by given charge distribution $\langle n_{l\sigma}^0 \rangle$'s as

$$\mathcal{E}_0 = \sum_l \left[-\frac{\Delta}{8} \right] (\langle n_l \rangle - \langle n_{l-1} \rangle) [2(\langle n_l^0 \rangle - \langle n_{l-1}^0 \rangle) - (\langle n_l \rangle - \langle n_{l-1} \rangle)] + \frac{1}{2} \sum_l U \langle n_l^0 \rangle (\langle n_l^0 \rangle - 1) + \sum_l V \langle n_l^0 \rangle \langle n_{l+1}^0 \rangle, \quad (6)$$

with

$$\Delta = \frac{2\xi^2}{K}. \quad (7)$$

If t equals 0, the total energy of the regular lattice, that is, the state which supports no defect, can be calculated by further replacing $\langle n_l \rangle$ by $\langle n_l^0 \rangle$ in Eq. (6). A CDW state whose charge distribution is given by $\langle n_{2m}^0 \rangle = 2$ and $\langle n_{2m+1}^0 \rangle = 0$ for any integer m has its total energy

$$\mathcal{E}_0 = N(-\Delta + U), \quad (8)$$

where the number of Pt sites is assumed even ($2N$) and large enough for the end effects to be negligible.¹⁰ The state, on the other hand, whose charge distribution is given by $\langle n_l^0 \rangle = 1$ for any l has its total energy

$$\mathcal{E}_0 = 2NV. \quad (9)$$

It follows from Eqs. (8) and (9) that, if a relationship $U - 2V < \Delta$ holds because of the strong electron-lattice coupling, the CDW state becomes the ground state of the regular lattice.

Before proceeding to the calculation of the formation energies of defects, the perturbation correction to the total energy \mathcal{E}_0 of the regular CDW lattice is calculated here on the assumption that t/Δ is small enough to be an expansion parameter. We are interested in the intermediate states of the perturbation which are generated by transferring an electron while maintaining the displacements of Cl^- ions unchanged. Let $\mathcal{E}(m, +, \sigma)$ or $\mathcal{E}(m, -, \sigma)$ be the energy of the intermediate state resulting from the transfer of an electron with spin σ from the m th Pt site to the $(m+1)$ th or $(m-1)$ th site, respectively. After some algebraic manipulations we obtain

$$\begin{aligned} \mathcal{E}(m, +, \sigma) = \mathcal{E}_0 + \sum_l \left[-\frac{\Delta}{4} (2\langle n_l \rangle - \langle n_{l-1} \rangle - \langle n_{l+1} \rangle) + \frac{U}{2} [\langle n_l^0(m, +, \sigma) \rangle + \langle n_l^0 \rangle] \right. \\ \left. + \frac{V}{2} [\langle n_{l-1}^0(m, +, \sigma) \rangle + \langle n_{l-1}^0 \rangle + \langle n_{l+1}^0(m, +, \sigma) \rangle + \langle n_{l+1}^0 \rangle] \right] \\ \times [\langle n_l^0(m, +, \sigma) \rangle - \langle n_l^0 \rangle]. \end{aligned} \quad (10)$$

We may obtain $\mathcal{E}(m, -, \sigma)$ by replacing $+$ of $\langle n_l^0(m, +, \sigma) \rangle$ and $\mathcal{E}(m, +, \sigma)$ in Eq. (10) by $-$. The quantity $\langle n_l^0(m, +, \sigma) \rangle$ or $\langle n_l^0(m, -, \sigma) \rangle$ represents the electron number at the l th site in the intermediate state with the energy $\mathcal{E}(m, +, \sigma)$ or $\mathcal{E}(m, -, \sigma)$, respectively.

Thus $\langle n_l^0(m, +, \sigma) \rangle$ is identical with $\langle n_{l\sigma}^0 \rangle$ except for $l=m$ and $l=m+1$, while $\langle n_l^0(m, -, \sigma) \rangle$ is identical with $\langle n_{l\sigma}^0 \rangle$ except for $l=m$ and $l=m-1$.

The presence of the transfer term H_1 affects the equilibrium displacements of Cl^- ions. We choose $\langle n_l \rangle$'s

and thus u_l 's such that the deviations of u_l 's due to H_1 arise from the second- and/or higher-order terms of t/Δ . Then, as shown in the Appendix, the deviations of the u_l 's do not affect the total energy of the system as far as we are concerned with the energy within the accuracy up to $(t/\Delta)^2$. In the regular lattice, therefore, $\langle n_l \rangle$ in Eqs. (4) and (10) can be replaced by $\langle n_l^0 \rangle$, so that Eq. (10) gives

$$\left. \begin{aligned} \mathcal{E}(2m, +, \sigma) \\ \mathcal{E}(2m, -, \sigma) \end{aligned} \right\} = \mathcal{E}_0 + 2\Delta - U + 3V, \quad (11)$$

for any m . Applying the second-order perturbation theory to H_1 and using Eqs. (8) and (11), we obtain the energy of the regular CDW lattice $\mathcal{E}(R)$ as

$$\begin{aligned} \mathcal{E}(R) &= \mathcal{E}_0 + \sum_{m,\sigma} \frac{t^2}{\mathcal{E}_0 - \mathcal{E}(2m, +, \sigma)} + \sum_{m,\sigma} \frac{t^2}{\mathcal{E}_0 - \mathcal{E}(2m, -, \sigma)} \\ &= -N \left[\Delta - U + \frac{4t^2}{2\Delta - U + 3V} \right]. \end{aligned} \quad (12)$$

This expression has been also derived by Nasu on the basis of a mean-field theory.¹¹

III. CHARACTERIZATION OF DEFECT STATES

In this section, we summarize the characteristics of possible defect states. They are classified into two categories. One is the domain wall which intervenes between the ordinary charge order and its antiphased charge order. This category of defect is called soliton, which we specify by S in this paper. The other category is obtained by locally modifying charges and ion displacements without changing the phase of charge order. This state is called polaron, which we specify by P . There exist three cases of possible charge states. The positively and negatively charged defects are specified by the suffixes $+$ and $-$, respectively; the neutral state is specified by a suffix 0. In general, the energy and the size of a defect depend on its position. For simplicity, we deal with the following two types. One is the state which gains the maximum energy of the electron-lattice coupling at $t \rightarrow 0$.⁸ Its defect region is restricted mostly to a single site of Pt. We call this state type I. The other type, i.e., type II, is obtained by translating a defect which is originally of type I along the chain to the midpoint between the initial and next positions of the type-I defect. This state consists mainly of two Pt sites. We should also pay attention to the spin state. If a defect has an unpaired electron the defect forms a Kramers doublet, while if a defect contains two unpaired electrons, it forms the spin singlet and the spin triplet.

In this work, we calculate the formation energies of defects created on the initially perfect lattice in the CDW state. The total number of electrons and the total spin are conserved in forming defects. Besides, the phase of charge order at both ends of the lattice is assumed to be conserved, since we are interested in creating defects in the interior of a very long chain. Taking account of these conditions, we consider formations of pairs of mutually

"conjugate" forms. When a kind of defect D consists of conjugate forms \mathcal{D} and $\tilde{\mathcal{D}}$, this situation is written as

$$D = \{\mathcal{D}, \tilde{\mathcal{D}}\}. \quad (13)$$

Our classifications give the following kinds of defects:

$$\begin{aligned} S_0^I &= \{\mathcal{S}_0^I, \tilde{\mathcal{S}}_0^I\}, \quad S_0^{II} = \{\mathcal{S}_0^{II}, \tilde{\mathcal{S}}_0^{II}\}, \\ S_{\pm}^I &= \{\mathcal{S}_{\pm}^I, \tilde{\mathcal{S}}_{\pm}^I\}, \quad S_{\pm}^{II(T)} = \{\mathcal{S}_{\pm}^{II(T)}, \tilde{\mathcal{S}}_{\pm}^{II(T)}\}, \\ P_{\pm}^I &= \{\mathcal{P}_{\pm}^I, \tilde{\mathcal{P}}_{\pm}^I\}, \quad P_{\pm}^{II} = \{\mathcal{P}_{\pm}^{II}, \tilde{\mathcal{P}}_{\pm}^{II}\}, \end{aligned} \quad (14)$$

where the superscript T denotes spin triplet.

IV. FORMATION ENERGIES OF DEFECTS

In general, different kinds of defect which are defined in the preceding section are mixed with each other by the transfer term. However, if the electron-lattice coupling is sufficiently strong, $|u_l|$'s are so large that the overlap integrals between vibrational wave functions of different defects are sufficiently small. Consequently, the defect states in Eq. (14) are effectively orthogonal to each other even if t is nonvanishing.

Dividing the chain lattice consisting of $2N$ Pt sites into two portions, we introduce \mathcal{D} in one portion and $\tilde{\mathcal{D}}$ in the other portion as shown in Fig. 2. Let us denote the total energy of the portion containing \mathcal{D} as $\mathcal{E}(\mathcal{D})$. Then the formation energy of D is defined by

$$E(D) = \frac{1}{2} [\mathcal{E}(\mathcal{D}) + \mathcal{E}(\tilde{\mathcal{D}}) - \mathcal{E}(R)]. \quad (15)$$

Figures 3–9 show $\langle n_l \rangle$'s and/or $\langle n_l^0 \rangle$'s of all the defect states defined in Sec. III along with their electronic energy-level diagrams in the case of $U=V=0$ and $t \rightarrow 0$.

In this connection, we should remark upon the applicability of the adiabatic approximation in the present theory, which prepares two sites with equivalent potentials. The type-II defects can no longer be stable if the transfer energy is small compared to the phonon energy ϵ_p of the M - X stretching mode. Thus, as seen from the following arguments, the formation energies calculated for the type-II defects are meaningful in the region $t/\Delta > \epsilon_p/\Delta$ for solitons and $t/\Delta > \sqrt{\epsilon_p}/\Delta$ for polarons. The type-I defects, on the other hand, can be stable no matter how small the transfer energy.

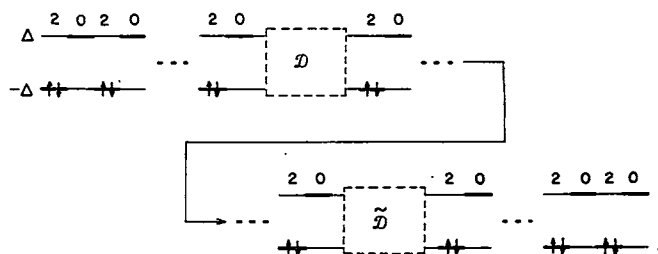


FIG. 2. General structure of the charge sequence of Pt ions in a chain supporting a defect \mathcal{D} and its "conjugate" $\tilde{\mathcal{D}}$. Both \mathcal{D} and $\tilde{\mathcal{D}}$ include odd and even numbers of Pt sites for solitons and polarons, respectively. Vertical arrows represent electrons with up and down spins. The horizontal lines represent the energy levels. Numbers represent $\langle n_l \rangle$'s of Pt sites.

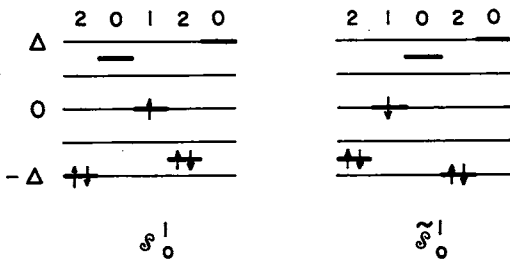


FIG. 3. Charge sequences and energy levels of the neutral solitons of type I, S_0^I and \tilde{S}_0^I . Numbers represent $\langle n_l^0 \rangle$'s of Pt ions. Vertical arrows represent electrons with up and down spins.

A. Neutral soliton of type I: S_0^I

The excited states given by Eq. (10) mix with the ground state through the transfer term. Since there exists no degeneracy in the ground state for $t=0$, $\langle n_l \rangle$ in Eq. (10) can be replaced by $\langle n_l^0 \rangle$ shown in Fig. 3. Substituting $\mathcal{E}(S_0^I)$ and $\mathcal{E}(\tilde{S}_0^I)$ obtained from second-order perturbation theory into Eq. (15), we arrive at

$$E(S_0^I) = E_0(S_0^I) + \frac{2t^2}{(-3\Delta/4)} + \frac{4t^2}{(-7\Delta/4) + U - 2V} - \frac{8t^2}{-2\Delta + U - 3V}. \quad (16)$$

Here, $E_0(D)$ represents $E(D)$ at $t \rightarrow 0$, given in Table I.

B. Neutral soliton of type II: S_0^{II}

The charge sequences $\langle n_l \rangle$ of S_0^{II} and \tilde{S}_0^{II} are shown in Fig. 4(a). Fractional $\langle n_l \rangle$'s $\dots, 0, 1.5, 1.5, 0, \dots$ of S_0^{II} , for instance, are realized by bonding of the two eigenstates $S_{0\alpha}^{II}$ and $S_{0\beta}^{II}$ whose $\langle n_l^0 \rangle$'s are $\dots, 0, 2, 1, 0, \dots$ and $\dots, 0, 1, 2, 0, \dots$, respectively, as shown in Fig. 4(b). Note that the energies $\mathcal{E}(S_{0\alpha}^{II})$ and $\mathcal{E}(S_{0\beta}^{II})$ are degenerate. We substitute $\langle n_l \rangle$'s and $\langle n_l^0 \rangle$'s into Eq. (10) and count the perturbation processes except the transfer between $S_{0\alpha}^{II}$ and $S_{0\beta}^{II}$ to obtain $\mathcal{E}(S_{0\alpha}^{II})$ and $\mathcal{E}(S_{0\beta}^{II})$. Then, Löwdin's perturbation theory¹² gives $\mathcal{E}(S_0^{II})$ as the lower eigenvalue of the matrix

$$\begin{bmatrix} \mathcal{E}(S_{0\alpha}^{II}) & -t \\ -t & \mathcal{E}(S_{0\beta}^{II}) \end{bmatrix}. \quad (17)$$

A parallel calculation is made to obtain $\mathcal{E}(\tilde{S}_0^{II})$. We finally

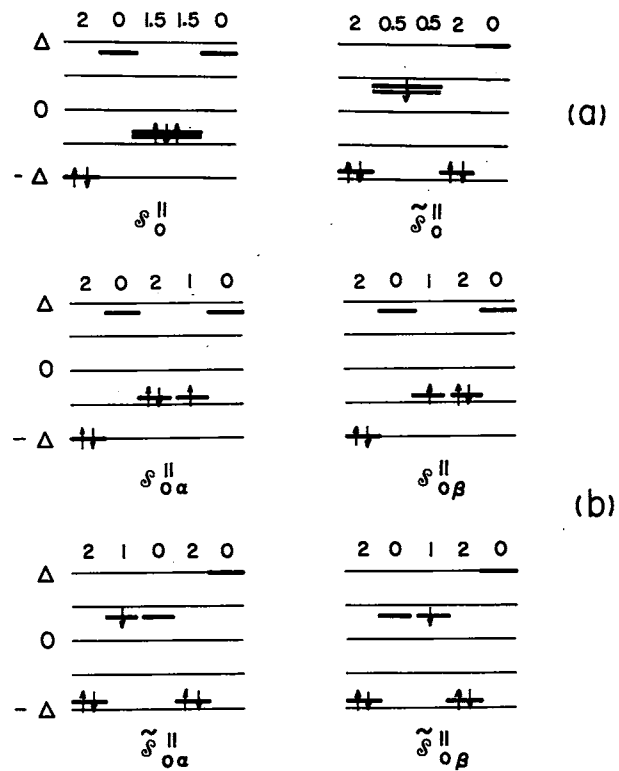


FIG. 4. (a) Charge sequences and energy levels of the neutral soliton of type II, S_0^{II} and \tilde{S}_0^{II} . Numbers represent $\langle n_l \rangle$'s of Pt ions. Vertical arrows represent electrons with up and down spins. (b) Starting eigenstates of S_0^{II} and \tilde{S}_0^{II} . Numbers represent $\langle n_l^0 \rangle$'s of Pt ions.

ly arrive at

$$E(S_0^{II}) = E_0(S_0^{II}) - t + \frac{2t^2}{(-5\Delta/4) + U - 2V} + \frac{2t^2}{(-15\Delta/8) + U - 3V} - \frac{10t^2}{-2\Delta + U - 3V} + \frac{t^2}{(-5\Delta/4)} + \frac{2t^2}{(-15\Delta/8) + U - 2V}. \quad (18)$$

Note that the bonding between the degenerate two states $S_{0\alpha}^{II}$ and $S_{0\beta}^{II}$ results in an energy gain of $-t$.

C. Charged soliton of type I: S_{\pm}^I

The charge sequences $\langle n_l^0 \rangle$'s are shown in Fig. 5. The same procedure as that described in Sec. IV A gives

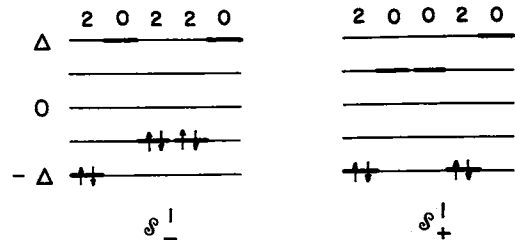


FIG. 5. Charge sequences and energy levels of the charged solitons of type I, S_{\pm}^I and \tilde{S}_{\pm}^I . Numbers represent $\langle n_l^0 \rangle$'s of Pt ions. Vertical arrows represent electrons with up and down spins.

TABLE I. Formation energies of various defects at $t/\Delta \rightarrow 0$.

Defects	$E_0(D)$
S_0^I	$0.75\Delta - 0.5U + 2V$
S_0^{II}	$(\frac{15}{16})\Delta - 0.5U + 2V$
S_{\pm}^I	$0.5\Delta + 2V$
S_{\pm}^{II}	$1.25\Delta - U + 3V$
P_{\pm}^I	$0.75\Delta - 0.5U + 2V$
P_{\pm}^{II}	$(\frac{7}{8})\Delta - 0.5U + 2V$

$$E(S_{\pm}^I) = E_0(S_{\pm}^I) + \frac{4t^2}{(-3\Delta/2) + U - V} - \frac{6t^2}{-2\Delta + U - 3V} \quad (19)$$

D. Charged soliton of type II: $S_{\pm}^{II(T)}$

Both the positively and negatively charged solitons of this type have two unpaired electrons, so that each is split into the spin singlet and the spin triplet.

First, we deal with the spin singlet S_{\pm}^{II} shown in Fig. 6(a). The transfer term mixes the three states $S_{+\alpha}^{II}$, $S_{+\beta}^{II}$, and $S_{+\gamma}^{II}$ shown in Fig. 6(b). The calculations analogous to the case described in Sec. IV B give $\mathcal{E}(S_{+\alpha}^{II})$, $\mathcal{E}(S_{+\beta}^{II})$, and $\mathcal{E}(S_{+\gamma}^{II})$. Clearly, $\mathcal{E}(S_{+\alpha}^{II})$ equals $\mathcal{E}(S_{+\beta}^{II})$. By the use of these results, $\mathcal{E}(S_{\pm}^{II})$ is given as the lowest-energy eigenvalue of the matrix

$$\begin{bmatrix} \mathcal{E}(S_{+\alpha}^{II}) & -\sqrt{2}t & 0 \\ -\sqrt{2}t & \mathcal{E}(S_{+\gamma}^{II}) & -\sqrt{2}t \\ 0 & -\sqrt{2}t & \mathcal{E}(S_{+\beta}^{II}) \end{bmatrix} \quad (20)$$

$\mathcal{E}(S_{\pm}^{II})$ can be obtained by making parallel calculations with respect to the states $S_{-\alpha}^{II}$, $S_{-\beta}^{II}$, and $S_{-\gamma}^{II}$ shown in Fig. 6(b). The formation energy of S_{\pm}^{II} is then given by

$$\begin{aligned} E(S_{\pm}^{II}) = E_0(S_{\pm}^{II}) + \frac{1}{2}(U - V) + & \left[\frac{t^2}{-\Delta - V} + \frac{2t^2}{(-7\Delta/4) + U - 2V} - \frac{10t^2}{-2\Delta + U - 3V} + \frac{t^2}{-\Delta + U - 3V} \right. \\ & \left. + \frac{t^2}{(-7\Delta/4) + U - 3V} + \frac{t^2}{(-7\Delta/4) + U - V} \right] \\ & - \frac{1}{2} \left[16t^2 + \left[U - V + \frac{2t^2}{-\Delta + U - 3V} + \frac{2t^2}{(-7\Delta/4) + U - 3V} + \frac{2t^2}{(-7\Delta/4) + U - V} \right. \right. \\ & \left. \left. - \frac{2t^2}{-\Delta - V} - \frac{4t^2}{(-7\Delta/4) + U - 2V} \right]^2 \right]^{1/2} \quad (21) \end{aligned}$$

For sufficiently large values of t in comparison with U and V , $E(S_{\pm}^{II})$ turns out to contain the term $-2t$. This energy gain originates from the fact that two electrons with different spins fall into a bonding state.

Next, we proceed to the spin triplet state S_{\pm}^{IIT} . The charge sequences $\langle n_i^0 \rangle$ of S_{-}^{IIT} and S_{+}^{IIT} are shown in Fig.

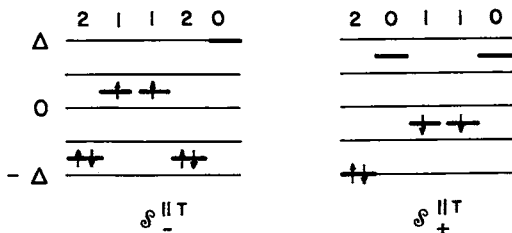


FIG. 7. Charge sequences and energy levels of the spin-triplet charged solitons of type II, S_{-}^{IIT} and S_{+}^{IIT} . Numbers represent $\langle n_i^0 \rangle$'s of Pt ions. Vertical arrows represent electrons with up and down spins.

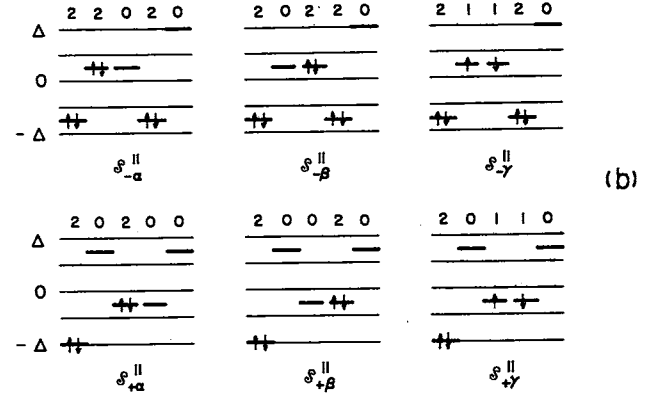
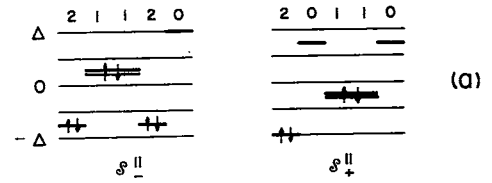


FIG. 6. (a) Charge sequences and energy levels of the spin-singlet charged solitons of type II, S_{-}^{II} and S_{+}^{II} . Numbers represent $\langle n_i \rangle$'s of Pt ions. Vertical arrows represent electrons with up and down spins. (b) Starting eigenstates of S_{-}^{II} and S_{+}^{II} . Numbers represent $\langle n_i^0 \rangle$'s of Pt ions.

7. Since both states have no orbital degeneracy, the calculation is straightforward, yielding

$$\begin{aligned} E(S_{\pm}^{IIT}) = E_0(S_{\pm}^{IIT}) + & \frac{2t^2}{-\Delta - V} \\ & + \frac{4t^2}{(-7\Delta/4) + U - 2V} - \frac{10t^2}{-2\Delta + U - 3V} \quad (22) \end{aligned}$$

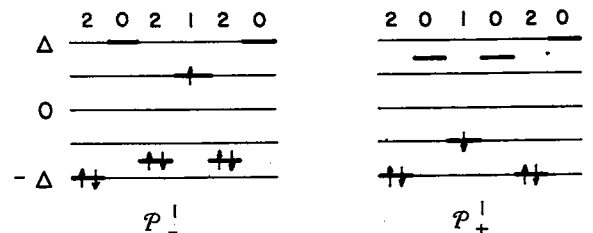


FIG. 8. Charge sequences and energy levels of the polarons of type I, P_{-}^I and P_{+}^I . Numbers represent $\langle n_i^0 \rangle$'s of Pt ions. Vertical arrows represent electrons with up and down spins.

E. Polaron of type I: P_{\pm}^I

In this case, there exists no degeneracy in the ground state for $t=0$, so that $\langle n_i \rangle$'s are replaced by $\langle n_i^0 \rangle$'s shown in Fig. 8. Then, we obtain

$$E(P_{\pm}^I) = E_0(P_{\pm}^I) + \frac{2t^2}{(-5\Delta/4) - 2V} + \frac{4t^2}{(-7\Delta/4) + U - 2V} - \frac{8t^2}{-2\Delta + U - 3V}. \quad (23)$$

F. Polaron of type II: P_{\pm}^{II}

The state P_{+}^{II} shown in Fig. 9(a) is constructed by mixing $P_{+\alpha}^{II}$, $P_{+\beta}^{II}$ and $P_{+\gamma}^{II}$ shown in Fig. 9(b). $\mathcal{E}(P_{+}^{II})$ is given by the lower eigenvalue of the matrix

$$\begin{pmatrix} \mathcal{E}(P_{+\alpha}^{II}) & \frac{t^2}{\mathcal{E}(P_{+\alpha}^{II}) - \mathcal{E}(P_{+\gamma}^{II})} \\ \frac{t^2}{\mathcal{E}(P_{+\alpha}^{II}) - \mathcal{E}(P_{+\gamma}^{II})} & \mathcal{E}(P_{+\gamma}^{II}) \end{pmatrix} \quad (24)$$

with $\mathcal{E}(P_{+\alpha}^{II}) = \mathcal{E}(P_{+\beta}^{II}) < \mathcal{E}(P_{+\gamma}^{II})$. Similar calculations with the use of $\langle n_i^0 \rangle$'s shown in Fig. 9(b) for $P_{-\alpha}^{II}$, $P_{-\beta}^{II}$, and $P_{-\gamma}^{II}$ give $\mathcal{E}(P_{-}^{II})$. The eigenvalues $\mathcal{E}(P_{+}^{II})$ and $\mathcal{E}(P_{-}^{II})$ yield

$$E(P_{\pm}^{II}) = E_0(P_{\pm}^{II}) + \frac{t^2}{(-3\Delta/2) - 2V} + \frac{t^2}{(-13\Delta/8) - 2V} + \frac{2t^2}{(-15\Delta/8) + U - 2V} + \frac{2t^2}{(-15\Delta/8) + U - 3V} + \frac{3t^2}{(-13\Delta/8) + U - 3V} + \frac{3t^2}{(-3\Delta/2) + U - 2V} - \frac{12t^2}{-2\Delta + U - 3V}. \quad (25)$$

V. NUMERICAL RESULTS AND DISCUSSION

Figure 10 shows the calculated formation energies of the defects as a function of t/Δ for $U=V=0$. For this case, Nishimura¹³ made a numerical calculation of the formation energies of solitons by using the tanh function as a trial function for the spatial variation of the ion displacements; the soliton size was chosen to be the variational parameter. In Fig. 10, his results are also plotted for comparison. The results of the two approaches agree well with each other, particularly for S_0^I and S_0^{II} , showing that our perturbation method gives satisfactory corrections as far as $t/\Delta \lesssim 0.4$. The disagreement seen for S_{\pm}^I and S_{\pm}^{II} suggests that, for the charged solitons, higher-order corrections become significant at comparatively

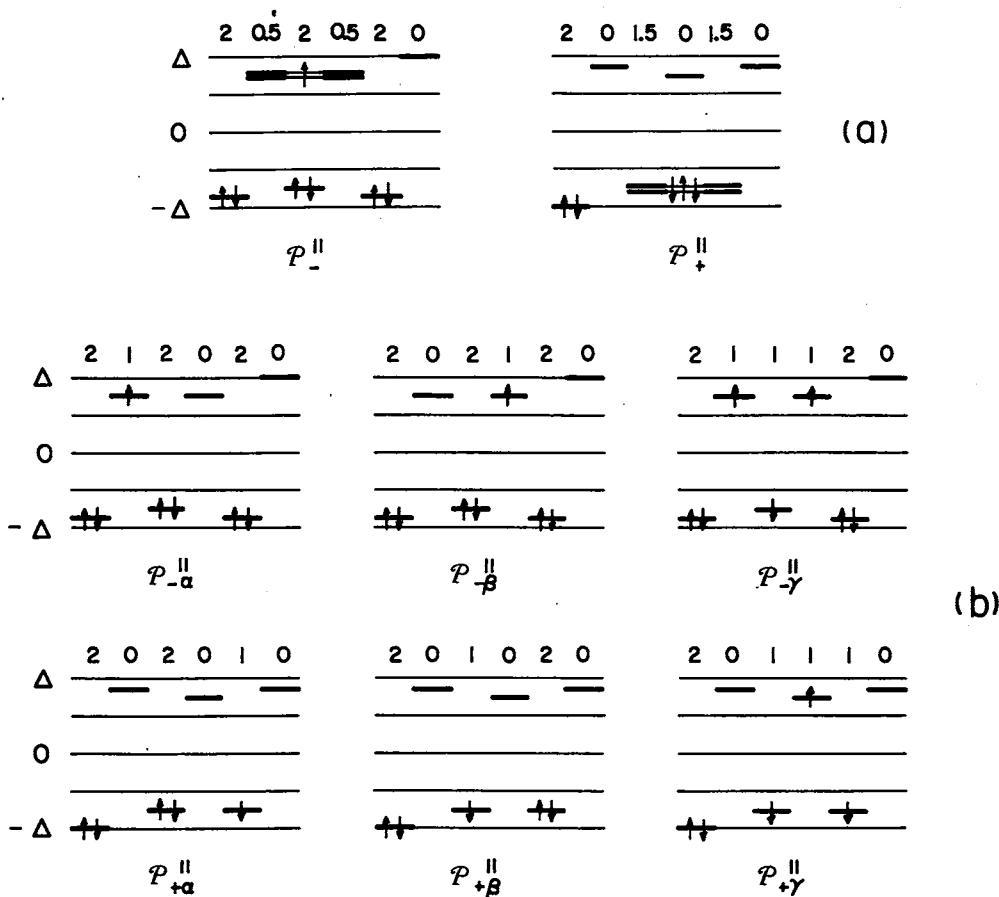


FIG. 9. (a) Charge sequences and energy levels of the polarons of type II, P_{\pm}^{II} and P_{\pm}^{II} . Numbers represent $\langle n_i \rangle$'s of Pt ions. Vertical arrows represent electrons with up and down spins. (b) Starting eigenstates of P_{\pm}^{II} and P_{\pm}^{II} . Numbers represent $\langle n_i^0 \rangle$'s of Pt ions.

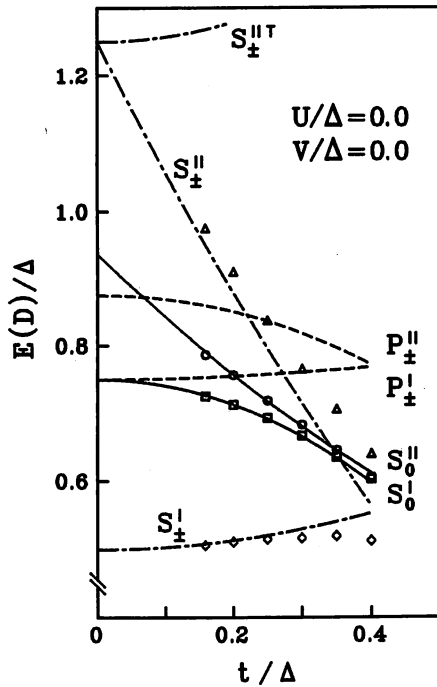


FIG. 10. Normalized formation energies $E(D)/\Delta$ of defects vs t/Δ for $U=V=0$. The values of $E(D)/\Delta$ calculated by Nishimura (Ref. 13) for S_{\pm}^I , S_0^I , S_{\pm}^{II} , and S_0^{II} are shown by diamonds, squares, triangles, and circles, respectively.

large values of t/Δ .

Figures 11 and 12 show the calculated formation energies as a function of t/Δ for $(U/\Delta, V/\Delta) = (0.25, 0.01)$ and $(0.5, 0.1)$, respectively. For small values of t/Δ , U/Δ , and V/Δ , the formation energy is dominated by the electron-lattice coupling, so that the type-II solitons have appreciably higher energies than the type-I solitons. (See also Table I.) As t/Δ increases, however, the energies of the type-II solitons except $S_{\pm}^{II T}$ are lowered almost linearly because the valence electrons in those type-II solitons occupy the bonding state rather than the states localized on Pt sites. The type-I solitons and $S_{\pm}^{II T}$ are unable to gain such a bonding energy. Consequently, the differences in energy between the type-I and type-II solitons (except $S_{\pm}^{II T}$) are reduced rapidly with increasing t/Δ ; $S_{\pm}^{II T}$ stays energetically far above other solitons.

As U increases, unpaired electron states become favorable. This means that U also affects significantly the energy-level scheme of the defects. Figures 13–15 show the U dependence of the formation energies for fixed values of t/Δ and V/Δ . We notice that there exist the following three cases concerning the defect with the lowest energy. (1) For small values of t/Δ and U/Δ , the lowest-energy state is S_{\pm}^I , which has no unpaired electron. (2) If U/Δ is significantly large, S_0^I may become the lowest-energy state. This is because unpaired electrons of S_0^I do not cost the on-site Coulomb energy, and localize at a Pt site to gain the electron-lattice coupling energy as much as possible. (3) If t/Δ is large compared to U/Δ , the S_0^{II} state becomes even lower than S_0^I as seen in Figs. 12 and 14. In this case, if the values of t/Δ and U/Δ exceed 0.3, all the solitons (except $S_{\pm}^{II T}$) have energies

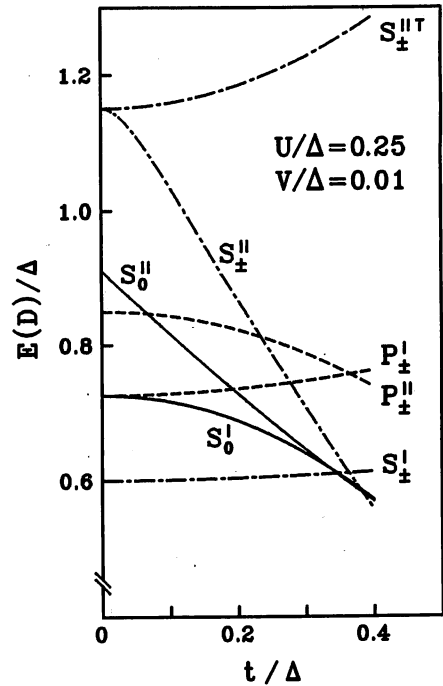


FIG. 11. Normalized formation energies $E(D)/\Delta$ of defects vs t/Δ for $U/\Delta=0.25$ and $V/\Delta=0.01$.

close to each other. Mishima and Nasu⁹ have treated the system with large t and U , i.e., $t/\Delta=U/\Delta=0.5$ and $V/\Delta=0.05$, in which the density of an unpaired electron of S_0^{II} spreads over about six Pt sites.

Although the polarons have unpaired electrons, they

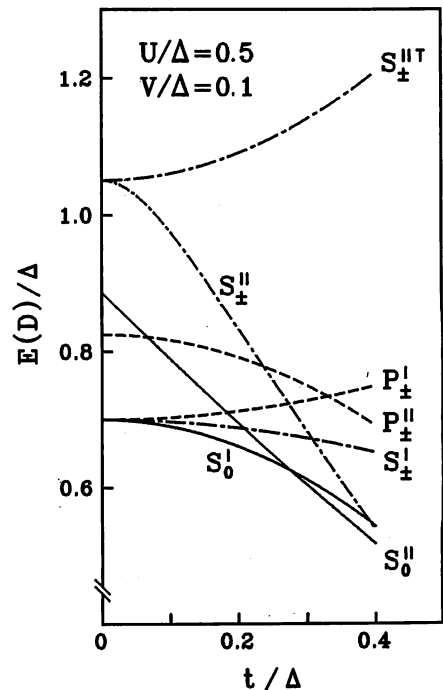


FIG. 12. Normalized formation energies $E(D)/\Delta$ of defects vs t/Δ for $U/\Delta=0.5$ and $V/\Delta=0.1$.

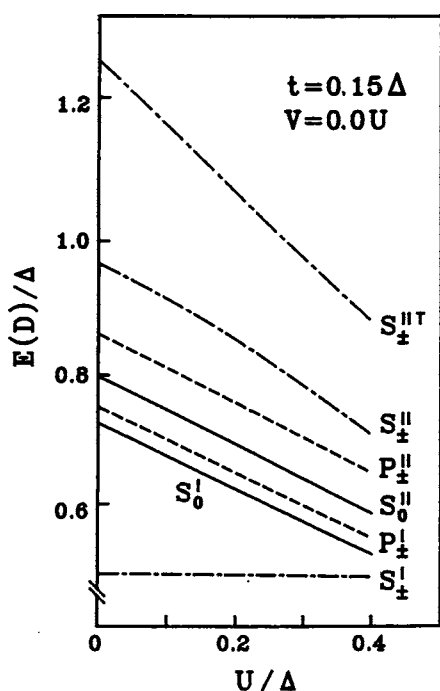


FIG. 13. Normalized formation energies $E(D)/\Delta$ of defects vs U/Δ for $t/\Delta=0.15$ and $V=0$.

cannot gain the transfer and electron-lattice coupling energies as much as the solitons can. Therefore, any set of the reasonable parameter values cannot make P_{\pm}^I and P_{\pm}^{II} lowest. One may also see from a comparison between Figs. 14 and 15 that the introduction of small V does not change the qualitative consequences obtained with $V=0$.

The energy parameters Δ and t reported to date^{14,15} for $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$ are summarized in Table II.

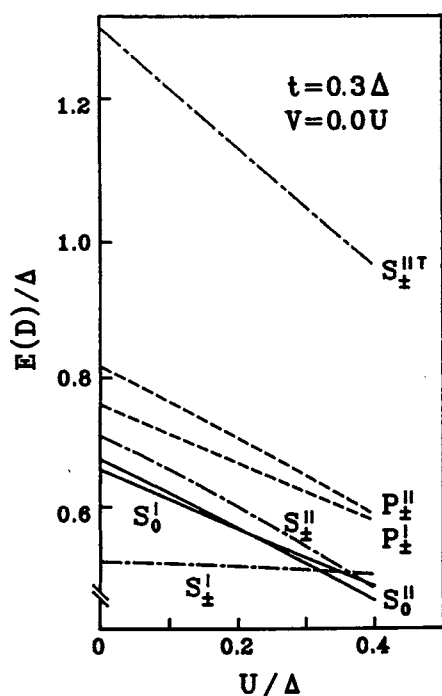


FIG. 14. Normalized formation energies $E(D)/\Delta$ of defects vs U/Δ for $t/\Delta=0.3$ and $V=0$.

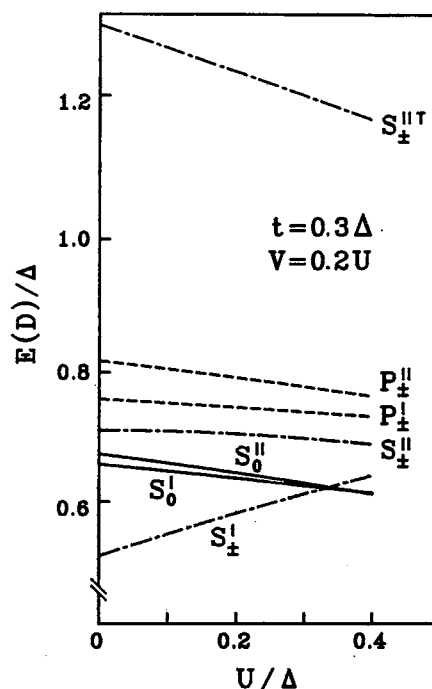


FIG. 15. Normalized formation energies $E(D)/\Delta$ of defects vs U/Δ for $t/\Delta=0.3$ and $V=0.2U$.

From optical measurements, Wada and Yamashita have deduced the exciton energy E_{CT} to be 2.74 eV.¹⁶ According to Nasu,¹⁷ the exciton energy is given by

$$E_{\text{CT}} = 2\Delta - U + 3V - \frac{2(2\Delta - U + 4V)t^2}{(2\Delta - U + 3V)^2}. \quad (26)$$

Substitution of $E_{\text{CT}}=2.74$ eV and the values of Δ and t listed in Table II into Eq. (26) enables us to estimate the value of $U-3V$. The results are also listed in Table II. The value of t/Δ ranges from 0.2 to 0.4, while the value of $(U-3V)/\Delta$ from 0.13 to 0.3. The energy \mathcal{E}_p of the $M-X$ stretching vibration is known to be 38 meV in this material.¹⁸ Then, we have $\mathcal{E}_p/\Delta \sim 0.02$ and $\sqrt{\mathcal{E}_p}/\Delta \sim 0.15$, both being smaller than t/Δ . This fact ensures that type-II defects are stable as well as type-I defects.

For the parameter values given in Table II, our calculation predicts that all the types of solitons except $S_{\pm}^{I T}$ are energetically close to each other. It appears from Figs. 11, 14, and 15 that the energy differences can be of

TABLE II. Values of gap parameter Δ , transfer integral t , and the Coulomb interaction parameter $U-3V$ in $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$.

Parameters	Ref. 14	Ref. 15
Δ (eV)	1.5	1.8
t (eV)	0.3	0.67
t/Δ	0.2	0.37
$U-3V$ (eV)	0.2 ^a	0.6 ^a
$(U-3V)/\Delta$	0.13	0.3

^aEstimated from Eq. (26) with the aid of the experimental value $E_{\text{CT}}=2.74$ eV (Ref. 16).

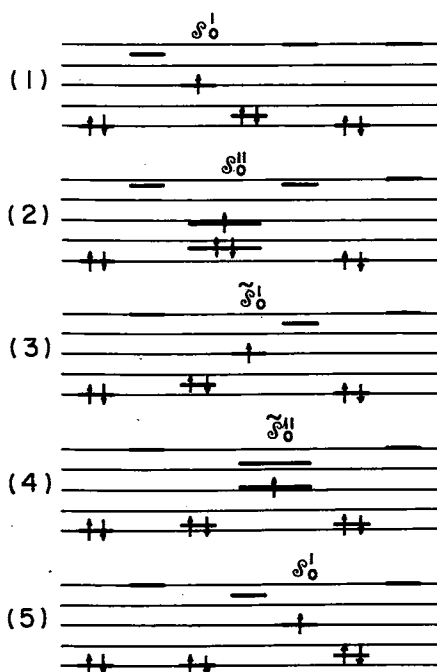


FIG. 16. Changes in the charge sequence and in energy levels of a neutral soliton during its translational motion. The flow from (1) to (5) corresponds to its movement from left to right by two lattice spacings.

order of 0.01Δ or less. This result gives us insight into the dynamical properties of solitons in $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$. The recent EPR experiment⁴ shows that S_0^{II} solitons are induced in this material by uv irradiation. Contrary to a previous conjecture,¹⁹ the induced solitons are quite mobile at moderate temperatures, since the thermal activation energy for their hopping motion is as low as 13 meV. Figure 16 illustrates the motion of a neutral soliton. It is seen from this figure that the S_0^{II} soliton moves from one site to the next via the S_0^{I} state. Nishimura¹³ has shown for $U=V=0$ that the formation energy takes its extremum values when the central position of a soliton accords with those of type I and type II. Based on an argument parallel to that given by Su, Schrieffer, and Heeger for polyacetylene,²⁰ we can expect that the energy difference between the S_0^{II} and S_0^{I} states corresponds to the activation energy for the hopping motion. Our calculated energy difference explains the observed activation energy of the order of 0.01Δ .

In CH polymers such as polyacetylene, if one takes $t/\Delta \sim 0.5$, the activation energy for the motion of a soliton amounts theoretically to about 0.1 eV,²¹ being much larger than that in the halogen-bridged linear-chain complexes treated in the present work. The soliton would be immobile in those polymers. Such a contrast between the two quasi-one-dimensional systems may originate from the difference in the scheme of the electron-lattice coupling.

Finally, we would like to point out that the calculated energy difference between charged and neutral solitons can be of the order of $0.01\Delta \sim 15$ meV, as well. This result suggests that once free solitons are created by any means, the charged solitons can also populate thermally at moderate temperatures.

VI. CONCLUSIONS

We have described a perturbation theory for the formation energies of intrinsic defects in the mixed-valence linear-chain complexes with a strong electron-lattice coupling. Particular attention is paid to the roles of the transfer integral and Coulomb interactions. The results provide the physical picture for the valence structures and the dynamical properties of the defects under the influences of these perturbations. The two-site-type neutral soliton S_0^{II} can have the lowest energy in a range of the strengths of the perturbations appropriate to the complex $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$. This result is consistent with the EPR experiment in this material.⁴ Our calculation gives also an explanation of the experimental observation that the S_0^{II} soliton is quite mobile along the chain axis.

ACKNOWLEDGMENTS

One of the authors (N.K.) is grateful to Professor Y. Onodera of Meiji University for informing us of Ref. 13. The authors would like to thank Dr. M. Sakai for helpful discussions during the course of this work. Comments from Professor A. Mishima of Kanazawa Institute of Technology are also acknowledged. This work was supported in part by a Grant-In-Aid for Scientific Research (Grant No. 63460025) from the Ministry of Education, Science and Culture of Japan.

APPENDIX

We show here that the perturbation corrections to the equilibrium Cl^- displacements give rise to terms of the order of t^4 in the total energy. For simplicity, we consider a nondegenerate ground state whose energy is given by

$$\mathcal{E}(\bar{u}_l) = K\bar{u}_l^2 + \xi\bar{u}_l(\langle n_l^0 \rangle - \langle n_{l-1}^0 \rangle) + f(\bar{u}_l)t^2(\langle n_l^0 \rangle + \langle n_{l-1}^0 \rangle), \quad (\text{A1})$$

where \bar{u}_l is the equilibrium displacement in the presence of the perturbation, the third term represents the second-order perturbation correction to the energy, and $f(\bar{u}_l)$ is a function of \bar{u}_l . Minimization of $\mathcal{E}(\bar{u}_l)$ with respect to \bar{u}_l gives

$$\bar{u}_l = u_l - \frac{1}{2K}(\langle n_l^0 \rangle + \langle n_{l-1}^0 \rangle) \frac{\partial f(\bar{u}_l)}{\partial \bar{u}_l} t^2, \quad (\text{A2})$$

where u_l is the equilibrium displacement in the absence of the perturbation corrections given by Eq. (4) with $\langle n_l^0 \rangle$ instead of $\langle n_l \rangle$. Substituting Eq. (A2) into Eq. (A1) and expanding $f(\bar{u}_l)$ in powers of t^2 , we obtain

$$\mathcal{E}(\bar{u}_l) = \mathcal{E}(u_l) - \frac{t^4}{4K} \left[(\langle n_l^0 \rangle + \langle n_{l-1}^0 \rangle) \frac{\partial f(u_l)}{\partial u_l} \right]^2. \quad (\text{A3})$$

It is evident from Eq. (A3) that the deviations of u_l due to the transfer term can be all neglected as far as we calculate the energy of the system within an accuracy up to $(t/\Delta)^2$. The above arguments can be easily extended to a system with degenerate ground states.

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