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Dimerization transition versus neutral-ionic transition in organic mixed-stack compounds

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The neutral-ionic transition in organic mixed-stack compounds is studied by using the finite-size extrapolation procedure. It is shown that when neglecting the electron-phonon interaction, the low-ionicity phase has a nondegenerate ground state and all excitations have a finite gap, while the high-ionicity phase has a highly degenerate ground state and both the charge-transfer and spin-flip excitations are gapless. The transition is of first or second-order depending on the strength of the overlap integral. When electron-phonon coupling is taken into account, these excitations acquire a gap even in the ionic phase and the order parameter is then the dimerization. The phase boundaries are shifted considerably.

I. INTRODUCTION

The discovery of "neutral-to-ionic" (N-I) phase transitions in a variety of mixed-stack charge-transfer compounds[1,2] has led to extensive studies on the nature of this transition.

A mixed-stack compound consists of donor (D) and acceptor (A) molecules which stack alternately on top of each other.[3] A single stack of molecules has the form $D^{+\rho}A^{-\rho}D^{+\rho}A^{-\rho}\ldots$ where ρ is the average charge transfer. As the name neutral-to-ionic suggests, the charge transfer ρ is of central importance. The difference $I-A>0$ of the donor ionization energy I and the acceptor affinity A favors a neutral lattice $\rho=0$ while the intersite Coulomb energies V favor an ionic lattice $\rho=1$. By changing these parameters a first-order transition from $\rho=0$ to $\rho=1$ occurs.[1]

This simple description must be considerably modified when the transfer integral t between D and A orbitals is included. Note first that since this transfer integral is appreciable only along the stack a one-dimensional model is appropriate. Secondly, $t\neq 0$ implies that $\rho=0$ or $\rho=1$ cannot be exact values and therefore the role of the charge transfer ρ as an order parameter for this transition is not obvious.

Experimentally the transitions are induced by pressure and in some cases by temperature. In most of the studied compounds the transition is accompanied by a shift of the absorption in the (3–5)-eV range,[2] similar to the shift between D°,A° and D^{+},A^{-} molecules in solution. Also, values of phonon frequencies[4] are consistent with a significant change of ρ. Thus ρ is an important feature of the transition, but it cannot be an actual order parameter due to the following reasons: (a) In some compounds the transition is continuous[5–7], and in others the order of the transitions is controversial.[2] For a continuous transition a change in symmetry is required and just a change in ρ does not amount to a symmetry change. (b) Some compounds show a similar transition as seen from ESR and phonon spectroscopy, but yet are classified as "ionic" (i.e., $\rho>\frac{1}{2}$) on both sides of the transition. This is the case for tetrathiafulvalene-bromanil (TTF-BA),[5] 5,10-dihydro-5,10 dimethylphenazine-7,7,8,8 tetracyanoquinodimethane (M_2P-TCNQ),[6] and probably also for tetramethyl-p-phenylene-diamine chloranil (TMPD-CA).[7,8]

The first model which includes a finite transfer integral was studied by Soos and Mazumdar.[9] Neglecting intersite Coulomb interaction they found a continuous transition at $\rho=\rho_c\simeq 0.68$ and that the gap for spin excitations vanishes for $\rho>\rho_c$. Thus on the ionic side, $\rho>\rho_c$, the susceptibility for spin-density-wave ordering diverges. The onset of a spin-density wave would break the translation symmetry of the spin degrees of freedom and is a valid order parameter.

An intersite Coulomb interaction was included in a model which, however, neglected the spin of the electrons.[10] The N-I transition was found to be of first order below come critical transfer integral t_c. Above t_c a line of singularities was found and claimed to represent a continuous transition. This line, however, does not represent a usual phase transition, since on both sides of this line the excitation gaps are finite and no symmetry is changed. This feature is drastically modified when the electron spin is included,[9] as also found below.

More recently it was suggested that the proper order parameter in these systems is the dimerization;[11] the lattice then distorts so that the D-A distances alternate in their magnitude. The inversion symmetry at the center of either a D or an A molecule is broken in the dimerized phase. The model[11] included the electron-phonon coupling but neglected all Coulomb interactions.

The broken inversion symmetry accounted for the appearance of some phonon normal modes in both Raman- and infrared-absorption experiments.[4,8,12] The prediction of the onset of dimerization was also directly confirmed by x-ray studies[13] in tetrathiafulvalene-chloranil (TTF-CA); the transition was found to be weakly first order near $\simeq 82$ K.[13,14]

The unusual nature of the ionic phase is manifested by its spin and charge excitations. In TTF-CA the activation energy from conductivity data[13] is much smaller than the optical gap while the spin susceptibility shows[14] a Curie behavior indicating localized spins. In contrast, TMPD-CA shows that the spin susceptibility is thermally activated,[7] with activation energies of $\simeq 0.1$ eV above 250 K and of $\simeq 0.01$ eV below 250 K. Both of these energies are much smaller than the optical gap of $\simeq 1$ eV. From phonon spectroscopy it seems that the lattice also dimerizes at a nearby temperature.[8] A recent study of TTF-CA under pressure[15] has shown the onset of dimerization at $\simeq 9$ kbar and an additional first-order transition at $\simeq 11$ kbar. Thus it is possible that in some cases there are two transitions.

Very recent theoretical works[16–20] have extended the previous models to include intersite Coulomb interactions, electron-phonon interactions by allowing for dimerization and the possibility of soliton excitations. The methods used range from the valence-bond technique for finite rings[16,19] to real-space renormalization-group methods[20] or to Monte Carlo simulations.[17,18]

These papers, however, do not give a comprehensive picture of the phase transition, especially when dimerization is taken into account, which is a very important feature. In the present paper we will use a finite-size extrapolation technique to study the ground-state and low-lying excitations of a mixed-stack chain, and from that we will infer the phase diagram. The model will be introduced in Sec. II. Neglecting first the electron-phonon interaction, the phase diagram of the model is determined in Sec. III. It is shown that the charge transfer is usually not a good quantity to distinguish the two phases, rather the excitation energy for charge-transfer and spin-flip excitations is finite or zero in the two phases. The effect of electron-phonon interaction is considered in Sec. IV. It is found that dimerization is the relevant order parameter. In some cases the dimerization is accompanied by a sudden jump in the ionicity, it may happen, however, that the ionicity changes smoothly across the dimerization transition. Finally, a summary of the results will be given in Sec. V.

II. THE MODEL

The mixed-stack chain consists of alternating donor and acceptor molecules on the even and odd sites, respectively, of the chain. In its neutral state (D°) the donor molecule has its highest-lying occupied orbital filled with two electrons of opposite spins. The ionization energy to remove an electron from this orbital is I. The second ionization energy, to remove the other electron and create a doubly ionized donor D^{2+}, will be assumed to much larger than I, it will be denoted by $I_2 = 2I + U_D$, with $U_D \gg I$.

The acceptor molecules in their neutral states (A°) have their lowest unoccupied orbital empty. The electron affinity to ionize the acceptor by one electron is $-A$, while creating a doubly ionized acceptor A^{2-} costs a high energy $-2A + U_A$ with $U_A \gg A$. Measuring the energies with respect to the neutral configuration, the ionization energies of the donor and acceptor molecules can be written as

$$H_{DA} = I \sum_{\substack{\text{even}\\ \text{sites}}} (2-n_i) + U_D \sum_{\substack{\text{even}\\ \text{sites}}} (1-n_{i\uparrow})(1-n_{i\downarrow}) - A \sum_{\substack{\text{odd}\\ \text{sites}}} n_i + U_A \sum_{\substack{\text{odd}\\ \text{sites}}} n_{i\uparrow} n_{i\downarrow} \,, \tag{2.1}$$

where $n_{i\uparrow}$ ($n_{i\downarrow}$) is the occupation number at site i with spin $\uparrow$ ($\downarrow$) and $n_i = n_{i\uparrow} + n_{i\downarrow}$. It is important to notice that due to charge conservation $2\sum_{\text{odd}} n_i = 2\sum_{\text{even}} (2-n_i)$.

When the molecules are ionized, the Coulomb coupling between them should be taken into account. Taking, as an approximation, first-neighbor interaction only, the Coulomb energy is

$$H_C = -V \sum_{\substack{\text{even}\\ \text{sites}}} (2-n_i) n_{i+1} - V \sum_{\substack{\text{odd}\\ \text{sites}}} n_i (2-n_{i+1}) \,. \tag{2.2}$$

Furthermore, the finite Mulliken charge-transfer integral gives rise to a hybridization

$$H_{CT} = t \sum_{\substack{\text{all sites}\\ \sigma}} (c_{i\sigma}^{\dagger} c_{i+1\sigma} + c_{i+1\sigma}^{\dagger} c_{i\sigma}) \,, \tag{2.3}$$

where $c_{i\sigma}^{\dagger}$ ($c_{i\sigma}$) is the usual creation (annihilation) operator of electrons at site i with spin σ and $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$.

In Sec. IV the electron-phonon coupling will also be taken into account; first, however, we want to study the properties of this model without possible dimerizations. As mentioned earlier, the on-site Coulomb couplings are large compared to the other characteristic energies (I, A, V, t) in most materials relevant for neutral-ionic transitions, therefore the limit $U_D \to \infty$, $U_A \to \infty$ will be considered in what follows.

In this limit doubly ionized configurations are forbidden and the Hamiltonian can be mapped to a $S=1$ spin chain using the following equivalence between the electronic states and the three states of the spin.

For donors: neutral state $\to |0\rangle$, electron with spin $\uparrow$ missing $\to |1\rangle$, and electron with spin $\downarrow$ missing $\to |-1\rangle$.

For acceptor: neutral state $\to |0\rangle$, electron with spin $\uparrow$ present $\to |-1\rangle$, and electron with spin $\downarrow$ present $\to |1\rangle$.

As is seen, the transfer of a spin-$\uparrow$ electron from the donor to the acceptor $D°A° \to D^{+}A^{-}$ corresponds in the spin language language to an exchange process $|0,0\rangle \to |1,-1\rangle$.

The Hamiltonian can be rewritten in terms of the spin-1 operators as

$$\begin{aligned}
H_{DA} &= I \sum_{\substack{\text{even}\\ \text{sites}}} S_z^2(i) - A \sum_{\substack{\text{odd}\\ \text{sites}}} S_z^2(i) \,, \\
H_C &= -V \sum_{\text{all sites}} S_z^2(i) S_z^2(i+1) \,, \\
H_{CT} &= -\tfrac{1}{2} t \sum_{\substack{\text{all}\\ \text{sites}}} \{ S_z(i) S_z(i+1) [S_+(i) S_-(i+1) + S_-(i) S_+(i+1)] \} \\
&\quad -\tfrac{1}{2} t \sum_{\substack{\text{all}\\ \text{sites}}} \{ [S_+(i) S_-(i+1) + S_-(i) S_+(i+1)] S_z(i) S_z(i+1) \} \,,
\end{aligned} \tag{2.4}$$

where S_+ and S_- are the usual raising and lowering operators. In the original molecular state representation they correspond to removing or adding one electron. The operator S_z measures the state of the ion.

The complicated four-spin interaction in $H_{\rm CT}$ takes care that only those processes are allowed in the charge transfer where the charge and the spin are conserved.

Charge conservation requires $\sum_{\rm even} S_z^2(i) = \sum_{\rm odd} S_z^2(i)$, therefore $H_{\rm DA}$ can be written in the form

$$H_{\rm DA} = \tfrac{1}{2}(I-A)\sum_{\substack{\text{all}\\ \text{sites}}} S_z^2(i) \ . \tag{2.5}$$

III. EXCITATIONS AND PHASE DIAGRAM WITHOUT ELECTRON-PHONON COUPLING

In the limiting case when the transfer integral $t \to 0$ the model becomes a classical one and can be solved exactly.

The ground state will either be completely neutral ($\rm D^\circ A^\circ D^\circ A^\circ \ldots$), in the spin language it is the state $(0,0,\ldots,0)$ with energy $E_N = 0$, or completely ionized $\rm D^+A^-D^+A^- \ldots$ with energy $E_I = (N/2)(I-A) - NV = N(\Delta - V)$, where $\Delta \equiv \frac{1}{2}(I-A)$. The transition between the two regions occurs at $\Delta = V$. In the neutral phase $(\Delta > V)$ the ground state is nondegenerate, in the ionized phase, however, it is highly degenerate due to the spin degeneracy. This spin degeneracy, which has been neglected in some of the earlier works, is important to obtain correctly the low-lying excitations of the system.

There are three kinds of excitations above the ground state which are relevant in understanding the properties of these materials.

(1) Addition or removal of an electron, ΔE_c. This is also $\frac{1}{2}$ of the energy to create an infinitely separated electron-hole pair.

(2) Spin-flip excitations, ΔE_s.

(3) Charge transfer from donor to acceptor without changing the charge or spin, $\Delta E_{\rm CT}$. Note $\Delta E_{\rm CT} < 2\Delta E_C$. $\Delta E_{\rm CT}$ is the threshold for optical absorption.

In the neutral phase the energy to add or remove an electron is simply $\Delta E_C^{(N)} = \Delta$, while in the ionized phase Coulomb energy is also lost, so $\Delta E_C^{(I)} = 2V - \Delta$. Figure 1(a) shows the excitation energies for charge removal.

In order to flip a spin, first an ionized pair has to be created from the neutral phase, after which the spin flip costs no energy; the pair creation costs, however, $\Delta E_s^{(N)} = 2\Delta - V$. In the ionized phase, when all molecules are ionic, it does not cost any energy to flip a spin, so here $\Delta E_s^{(I)} = 0$. As seen from Fig. 1(b), the magnetic gap has a finite jump at the neutral-ionic transition.

Finally, when a charge is transferred from a donor to an acceptor without changing the total charge or spin of the system, it costs an energy $\Delta E_{\rm CT}^{(N)} = 2\Delta - V$ in the neutral phase, while in the ionized phase, where one neutral pair has to be created the energy is $\Delta E_{\rm CT}^{(I)} = 3V - 2\Delta$. These energies are shown in Fig. 1(c). As is seen, the electron-hole pair is bound, i.e., $\Delta E_{\rm CT} < 2\Delta E_C$, due to the Coulomb coupling effect of when the transfer is to first neighbors.

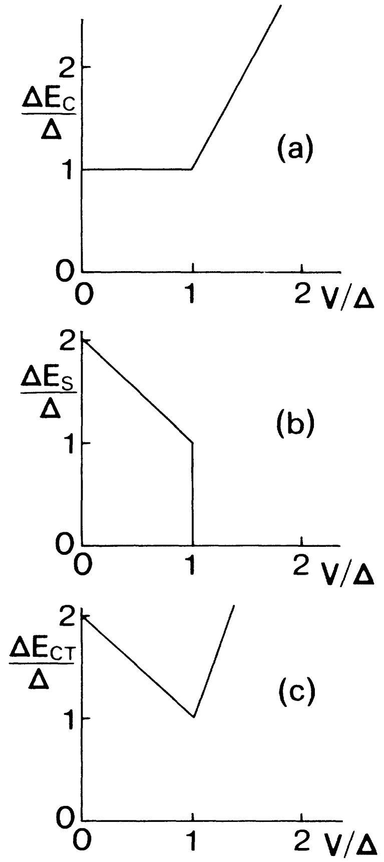

FIG. 1. Excitation energies of a donor-acceptor mixed-stack chain for vanishing charge-transfer integral t. (a) Energy needed to remove or add one electron. (b) Gap for spin-flip excitations. (c) Gap for charge-transfer excitations.

For small t second-order perturbational corrections[16] can be used to understand qualitatively the changes in the location of the transition and in the excitation energies. As has been shown by Soos and Kuwajima,[16] the energy shift per site of the neutral phase is $\Delta E_N = -2t^2/\Delta E_{\rm CT}^{(N)}$. In the ionic phase a $\rm D^+A^-$ pair can be neutralized and reionized either with the same or opposite spin electron, thus leading in second order to an effective exchange Hamiltonian between spin-$\frac{1}{2}$ electrons. The $|1\rangle$ and $|-1\rangle$ states of our spin-1 model are identified with the $|\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ states of the spin-$\frac{1}{2}$ model.

This effective Hamiltonian is

$$H_{\rm eff} = \sum_i [E_0 - \tfrac{1}{2}J_{xy}(\sigma_i^+\sigma_{i+1}^- + \sigma_i^-\sigma_{i+1}^+) + J_z\sigma_i^z\sigma_{i+1}^z] \ , \tag{3.1}$$

with

$$E_0 = -\tfrac{1}{2}\frac{t^2}{\Delta E_{\rm CT}^{(I)}} + \Delta - V \ , \tag{3.2}$$

$$J_{xy} = J_z = 2\frac{t^2}{\Delta E_{\rm CT}^{(I)}} \equiv J \ . \tag{3.3}$$

The energy per site of such an antiferromagnetic spin-$\frac{1}{2}$

chain is[21]

$$\Delta E^{(I)} = E_0 + J(\tfrac{1}{4} - \ln 2) = -2\frac{t^2}{\Delta E_{\mathrm{CT}}^{(I)}}\ln 2 + \Delta - V \;. \tag{3.4}$$

The neutral-ionic boundary is thus shifted to

$$-2\frac{t^2}{\Delta E_{\mathrm{CT}}^{(N)}} = \Delta - V - 2\frac{t^2}{\Delta E_{\mathrm{CT}}^{(I)}}\ln 2 \;. \tag{3.5}$$

Near the transition $\Delta E_{\mathrm{CT}}^{(N)} \simeq \Delta E_{\mathrm{CT}}^{(I)} \simeq \Delta$, and

$$V \simeq \Delta + 2\frac{t^2}{\Delta}(1 - \ln 2) \;. \tag{3.6}$$

In the model where the spin is neglected,[10] the boundary between the neutral and ionic phases remains always at $V = \Delta$.

This calculation shows immediately that at least for small t, the ionic phase behaves like an isotropic Heisenberg antiferromagnet, i.e., there is no gap in the spin-flip excitation spectrum. Moreover, since the ground state is infinitely degenerate, the excitations in that subspace where both charge and spin are conserved, are also gapless.

We expect therefore that $\Delta E_{\mathrm{CT}}^{(I)} = 0$ for any $t \neq 0$ in sharp contrast with $\Delta E_{\mathrm{CT}}^{(I)} = 3V - 2\Delta > 0$ in the $t = 0$ case. The reason is that although a $t = 0$ ground state like $\psi_1 = (1, -1, 1 -1, 1, -1, \ldots)$ is degenerate with an infinite number of other states, e.g., with $\psi_2 = (-1, 1, 1, -1, 1, -1, \ldots)$, an external electromagnetic field does not couple these states. To linear order, the electromagnetic field causes a charge transfer and couples ψ_1 to e.g., $\psi_3 = (0, 0, 1, -1, 1, -1, \ldots)$ with a finite ΔE_{CT}. Once t is finite the ground state will be a linear combination of ψ_1, ψ_2, and ψ_3. As known for the Heisenberg model, the new ground state is still degenerate, corresponding to different linear combinations which can now be coupled by an electromagnetic field. The optical absorption extends then down to zero frequency (although its magnitude may be low for small t) and the gap is $\Delta E_{\mathrm{CT}} = 0$. This remarkable conclusion means that for $t \neq 0$ the ionic phase is a metal (or semimetal) and the *N-I* transition is also an insulator-to-metal transition. This conclusion, however, will be modified when dimerization is allowed for in Sec. IV.

As shown by Soos and Kuwajima,[16] the average charge on the molecules is small on one side

$$\rho_N = \frac{\partial E^{(N)}}{\partial \Delta} = 4\frac{t^2}{(\Delta E_{\mathrm{CT}}^{(N)})^2} \;, \tag{3.7}$$

and close to unity on the other side

$$\rho_I = \frac{\partial E^{(I)}}{\partial \Delta} = 1 - 4\frac{t^2}{(\Delta E_{\mathrm{CT}}^{(I)})^2}\ln 2 \;. \tag{3.8}$$

In order to understand what happens for larger values of the transfer integral, we have performed exact numerical calculations on finite rings containing up to 12 molecules, calculating the ground-state as well as low-lying excitations. A finite-system extrapolation procedure is used to describe the behavior of the infinitely long chains.

Starting from an originally neutral configuration of the finite ring [from state $(0, 0, \ldots, 0)$ in the spin language], the transfer integral will mix in all other states which have total spin and total charge equal to zero. When the eigenvalue problem in this subspace is solved, it turns out that the ground state is always invariant under translation with the donor-donor distance, i.e., it is a $k = 0$ momentum mode. The average charge on the D (or A) molecules is therefore the same. This charge, i.e., the ionicity is shown in Figs. 2 and 3 for two different values of the transfer integral, for different chain lengths.

When t/Δ is small, the ionicity rises very drastically near $V \approx \Delta$. In the limit when $N \rightarrow \infty$ a finite jump will appear, indicating a first-order transition. Usually in first-order transitions the rounding of a finite jump occurs in a range whose width shrinks as N^{-d}, where d is the dimensionality. In the present case this shrinking is much faster, probably similar to to that in the one-dimensional quantum Ising model, for which it was shown[22] that instead of N^{-d} the behavior is $N^{-\alpha}e^{-AN}$ with $\alpha = \frac{3}{2}$. In our case a similar form describes reasonably the sudden rise of the slope in the ionicity with $\alpha \simeq 2$. The position of this sudden change is in agreement with the perturbational calculation, Eq. (3.6).

For larger values of the charge-transfer integral the behavior is different. Although the ionicity changes appreciably for a relatively narrow range of V values, as seen in Fig. 3, it will be a smooth function even in the limit $N \rightarrow \infty$. Therefore the concept of neutral-to-ionic transition based on the value of the average charge is meaningless. If we look, however, at the ground-state and low-lying excitations, a phase transition can still be found. Figures 4–6 show the gaps to the lowest-lying excited states of the three different kinds, mentioned earlier, namely the energy to remove an electron and the energy of spin-flip excitations and charge-transfer excitations. In Figs. 5 and 6 one can clearly distinguish two regimes. At $t = 0.5\Delta$ for $V < 1.4\Delta$ both the spin-flip and charge-transfer excitations have a finite gap. However, above about 1.4Δ both of these excitation energies scale to zero as $1/N$, indicating a highly degenerate ground state which is critical in the sense that correlations will decay with power law and not exponentially. The transition to this gapless regime is probably Kosterlitz-Thouless–like. The energy to remove an electron (Fig. 4) is finite on both

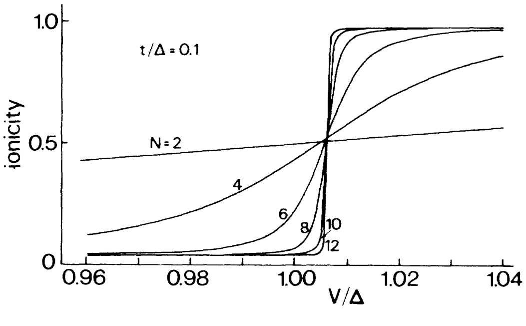

FIG. 2. Average charge on donor or acceptor molecules for varying first-neighbor Coulomb interaction at $t = 0.1\Delta$, calculated for increasing chain length N.

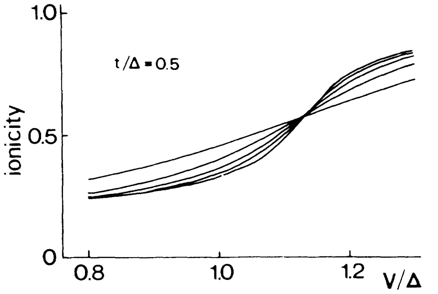

FIG. 3. Average charge on donor or acceptor molecules for varying first-neighbor Coulomb interaction at $t=0.5\Delta$, calculated for increasing chain lengths.

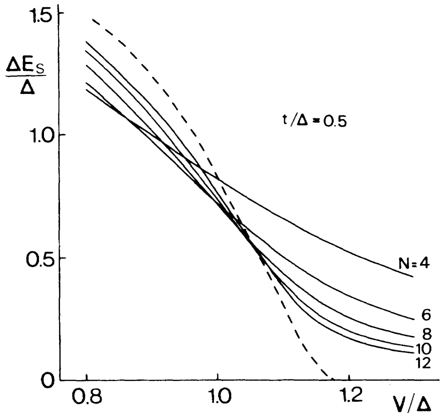

FIG. 5. Energy of spin-flip excitations in finite chains for $t=0.5\Delta$. The dashed curve is the infinite-chain result obtained from a simple $1/N$ scaling.

sides of the transition; however, a sharp dip develops, which, in the limit $N\rightarrow\infty$ will dip to zero at the transition.

To better see the difference between large t and small t behavior, we show in Figs. 7–9 the same excitation energies for $t/\Delta=0.1$. The energy to remove an electron has a sharp dip here as well; however, it stays finite even in the thermodynamic limit at the transition point. The charge-transfer and spin-flip excitation energies vanish as $1/N$ in the quasi-ionized phase in agreement with the mapping to the Heisenberg antiferromagnet. A finite jump appears in these excitation energies at the transitions point.

The transition from the quasineutral to the quasi-ionic phases, or more precisely, between the phase where the ground state is nondegenerate and the phase with a highly degenerate ground state, has been determined for different values of t using different procedures. The first approach is to find that value of V where the charge-removal energy has a minimum. The second is to locate the point beyond which the spin-flip excitations scale as $1/N$ and are therefore gapless in the infinite system. Thirdly, a similar calculation can be carried out for the charge-transfer excitations. Within the accuracy of the calculations all the three methods give the transition at the same place. It is more difficult to determine whether the transition is of first or second order, because of the uncertainty in the extrapolation procedure where the charge-removal energy first vanishes, or when the jump in the spin-flip or charge-transfer excitation gaps will vanish. A rough estimate is that this happens at about $t/\Delta\simeq 0.3$, $V/\Delta\simeq 1.06$. From these results we can construct the phase diagram shown in Fig. 10. This phase diagram is in good agreement with that obtained by Soos and Kuwajima[16] using the diagrammatic valence-bond method, although they did not calculate all low-lying excitations. Their calculation neglected the possibility of dimerization, as we have done until now. They speculate, however, that dimerization hardly affects the neutral-ionic interface. As we will see in the next section, this is not always the case.

IV. THE EFFECT OF ELECTRON-PHONON COUPLING

Since experimentally it is clear that dimerization is associated with the N-I transitions, it is important to take

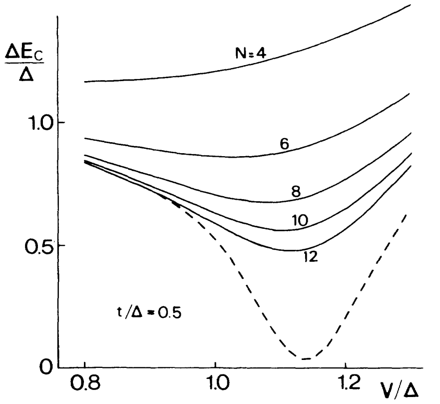

FIG. 4. Energy needed to remove (add) one electron from (to) a neutral chain of finite length N for $t=0.5\Delta$. The dashed curve is the infinite chain result obtained from a simple $1/N$ scaling.

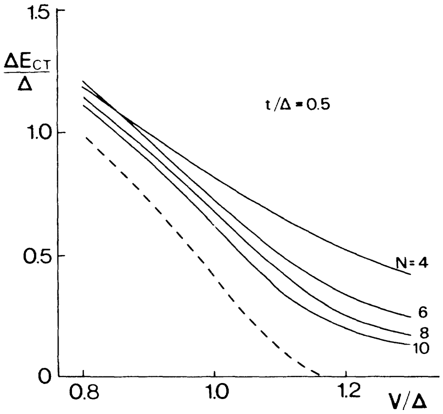

FIG. 6. Energy of charge-transfer excitations in finite chains for $t=0.5\Delta$. The dashed curve is the infinite-chain result obtained from a simple $1/N$ scaling.

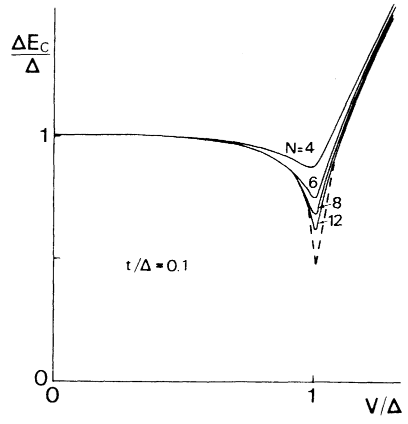

FIG. 7. The same as Fig. 4, except that $t=0.1\Delta$.

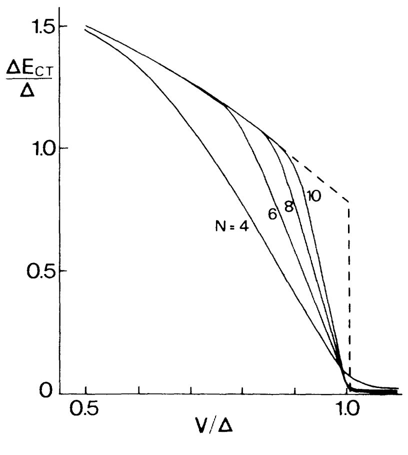

FIG. 9. The same as Fig. 6, except that $t=0.1\Delta$.

into account the effect of electron-phonon coupling. From the mapping of the ionic phase to a spin-$\frac{1}{2}$ Heisenberg antiferromagnet, for which we know that it undergoes spin-Peierls transition, the dimerization of the ionic phase is easily understood at least for small t, where the mapping is valid. The question we have to ask is whether for larger t the quasi-ionic phase is always dimerized or not and what happens in the quasineutral phase.

We assume here the adiabatic limit where the phonon frequency is much smaller than the gap ΔE_{CT}. As found below ΔE_{CT} is always finite when dimerization is allowed for. Experimentally the optical gap is $\Delta E_{\mathrm{CT}}>1$ eV,[1] which is indeed high compared with phonon frequencies of $\lesssim 0.2$ eV.[4] We thus consider the phonons as a classical field and modulate t and V alternately corresponding to a dimerized situation, i.e.,

$$\begin{aligned} t &\to t(1\pm\delta)\ , \\ V &\to V(1\pm\alpha\delta)\ , \end{aligned} \tag{4.1}$$

where δ is the relative displacement of the molecules, and α is a proportionality factor. If the relative displacement of the molecules is transversal,[12] the overlap integral varies more than the Coulomb coupling does. We therefore consider first the case $\alpha=0$. Later we will also consider another limiting case when t and V are changed equally, i.e., $\alpha=1$.

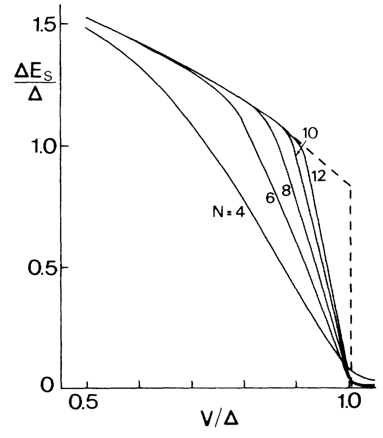

FIG. 8. The same as Fig. 5, except that $t=0.1\Delta$.

The elastic energy due to the distortion of the lattice will be considered classically as

$$E_{\mathrm{elastic}}=\tfrac{1}{2}K\delta^2\ . \tag{4.2}$$

In order to find the ground state, we will have to minimize the total energy with respect to δ. This will give the boundary between a nondimerized and a dimerized ground state. The results are shown in Figs. 11 and 12 for the two cases $\alpha=0$ and $\alpha=1$.

In both cases the behavior is very similar, namely for any value of K there is a phase boundary in the (t,V) plane separating a nondimerized, quasineutral phase from a dimerized, quasi-ionic one. For very small values of t and not too small K the transition will be of first order, as seen in Fig. 13. The energy of the ground state has two minima as a function of the dimerization for fixed t and V. As V increases, the minimum corresponding to the

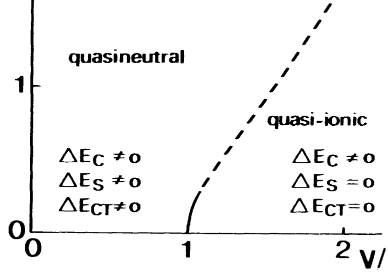

FIG. 10. Phase boundary between the quasineutral and quasi-ionic states in the (t,V) plane. The solid curve indicates first-order transition, while dashed curve indicates second-order transition.

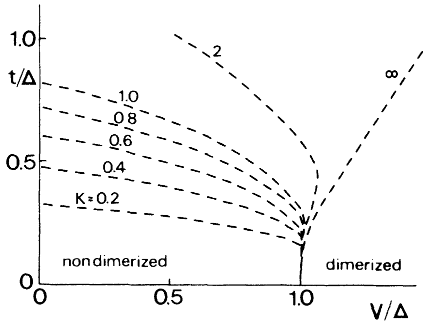

FIG. 11. Phase boundary between the nondimerized and dimerized states in the (t,V) plane for different elasticity constants K, assuming that only the hopping integral is modulated by the dimerization. The solid curve indicates first-order transition, while dashed curve indicates second-order transition.

dimerized state becomes lower. This happens at a V value which is somewhat smaller than the V where the transition would take place without dimerization. The average charge on the molecules jumps at the transition; however, it saturates slower than without dimerization. When for the same t value a somewhat smaller K (a softer lattice) is chosen, the transition occurs at an even smaller value of V and the transition becomes smooth; the average charge changes from the quasi-neutral value to the quasi-ionic one over an extended range, as shown in Fig. 14. The finite-size calculation is not sufficiently precise to determine the location of the points where the first-order transition goes over into a second-order transition; however, the location of the transition, irrespective whether it is of first or second order, is obtained within a few percent.

Beyond about $t \simeq 0.3\Delta$ where the transition without dimerization is of second order, the transition for any value of K will stay of second order and the change in the average charge can spread over a wide region of V.

As seen from the phase diagram, when the dimerization is taken into account, the location and the physical meaning of the transition line are considerably modified. In the abscence of dimerization this line had the significant property, that it separated a singlet ground state from a phase in which both the spin-flip and charge-transfer excitations were gapless, and along the transition line the energy to remove an electron costs little or no energy. In the presence of dimerization all that changes drastically. In Figs. 15–17 we show the lowest excitation energies for charge-removal, spin-flip, and charge-transfer excitations, assuming that the lattice does not relax during the excitation, i.e., the dimerization is the same in the excited state as in the ground state. These excitation energies remain always finite; hence the high degeneracy of the ground state is lifted. It is expected that at least in that regime where the dimerization transition is of second order, there is a soft mode in the system. When the ion dynamics is

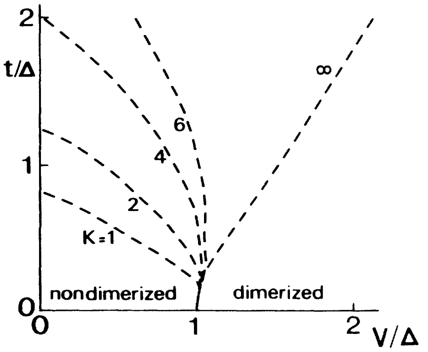

FIG. 12. The same as Fig. 11, except that both the hopping integral and the first-neighbor Coulomb coupling are modulated by the dimerization.

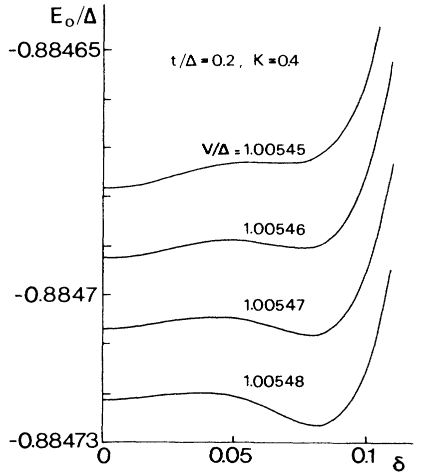

FIG. 13. Ground-state energy for a ring with $N=12$ sites for $t=0.2\Delta$, $K=0.4$ as a function of dimerization for different values of V.

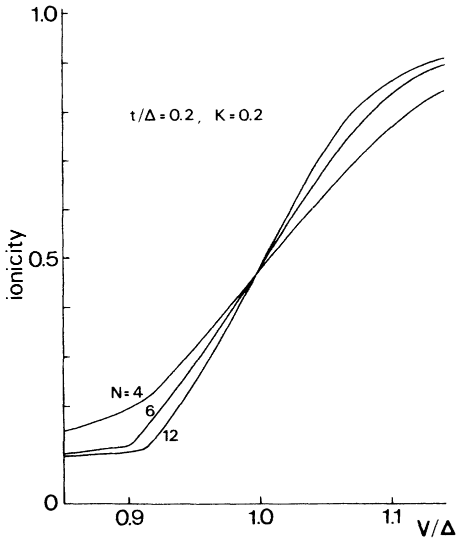

FIG. 14. Average charge on donor or acceptor molecules for varying first-neighbor Coulomb interaction at $t=0.2\Delta$, $K=0.2$, calculated for increasing chain lengths. It is assumed that dimerization modulates the hopping integral only.

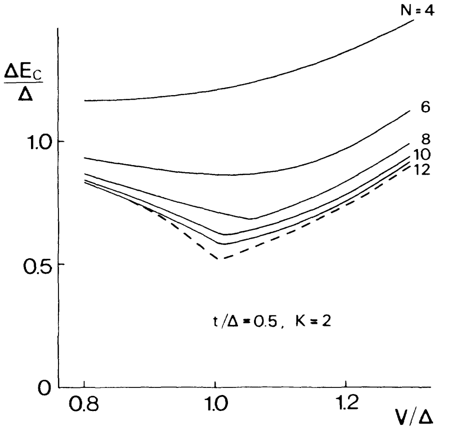

FIG. 15. The same as Fig. 4, except that the lattice can dimerize with $K=2$, assuming that only the hopping integral is modulated.

restored solitonlike excitations[11,14,17] will be of importance; for these, however, calculation on longer chains would be necessary to accommodate a soliton pair.

V. DISCUSSION AND CONCLUSIONS

In the present paper we have studied a model for the neutral-ionic transition for mixed-stack organic solids. As it is known from earlier works, the ionization energy of the donor-acceptor pair, the one-site and intersite Coulomb energies, the charge-transfer integral between the donors and acceptors, and the electron-phonon coupling allowing for the dimerization of the chain are all important if a realistic description of the transition is aimed at. In our model we have taken all these interactions into account, with the simplification that the on-site Coulomb energy is assumed to be much larger than the other characteristic energies and therefore is taken to be infinite to eliminate doubly ionized sites. Furthermore the electron-phonon interaction is treated in the adiabatic limit, i.e., the phonons are treated classically by allowing for a modulation of the donor-acceptor distance.

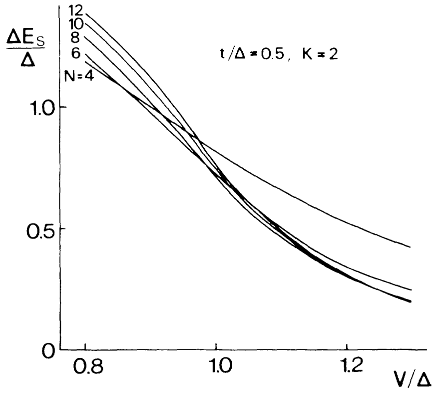

FIG. 16. The same as Fig. 5, except that the lattice can dimerize with $K=2$.

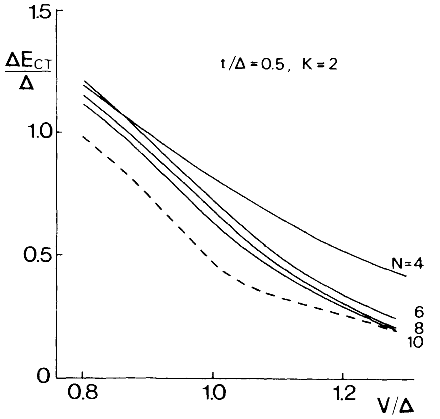

FIG. 17. The same as Fig. 6, except that the lattice can dimerize with $K=2$.

In this way we take a more general model than that considered by Soos and Kuwajima[16] where the electron-phonon coupling was neglected, or that by Bruinsmaa *et al.*[10] who neglected both the electron-phonon coupling and the spin degrees of freedom. Our model is thus the same as studied by Avignon *et al.*,[20] Girlando and Painelli,[19] and Nagaosa.[18]

We agree with these authors that the Peierls distortion is the most characteristic feature of the transition, in fact the dimerization is the proper order parameter as suggested by Horovitz and Schaub,[11] and not the charge transfer or the magnetic gap. Our treatment is, however, more general than theirs, studying the complete phase diagram and the low-lying excitations.

The real-space renormalization-group approach[20] gives a set of excitation energies, but it cannot give all the low-lying excitations, e.g., the spin-flip excitations. The shift of the phase boundary due to dimerization has not been considered by Avignon *et al.*[20] in the regime where the transition is of first order. When the transition is of second order, their phase diagram seems to imply that there are three possible phases: nondimerized quasineutral, dimerized quasineutral, and dimerized quasi-ionic. Contrary to this, we find, as shown in Fig. 14, that together with the appearance of dimerization the ionicity starts to increase immediately, although it may reach its saturation value for large V only.

The work by Girlando and Painelli[19] and by Nagaosa[18] is closest to ours. In both of these works finite chains are studied as was done by us; however, a general phase diagram is not given. In Ref. 19 the intersite Coulomb interaction was treated in a mean-field approximation. The work of Nagaosa has one feature which we could not calculate, namely he studied lattice-relaxed excitations, i.e., solitons.

The most important results of the present analysis are as follows. We have worked out the phase diagram for the neutral-ionic transition for arbitrary values of the charge-transfer integral and the intersite Coulomb energy. When the electron-phonon coupling is neglected quasineutral and quasi-ionic phases are identified. The former has a nondegenerate ground state, all excitations have a finite gap. In the quasi-ionic phase the spin-flip excitations and charge-transfer excitations (with no change in the total spin and charge) are gapless; it costs, however, a finite energy to remove an electron. On the phase boundary between the quasineutral or quasi-ionic phases this latter energy goes to zero or remains finite depending on whether the transition is of second or first order. At the same time the average charge on the molecules changes continuously or has a jump at the transition point. The location of the transition is in agreement with the results of the diagrammatic valence-bond calculation.[16]

Optical absorption which probes charge-transfer excitations would show a zero gap in the ionic phase. The matrix elements for absorption might, however, be small at low frequency and the absorption then peaks at a finite frequency.[23] The gap is then still at zero frequency, but the system is technically a semimetal.

The results change drastically when electron-phonon interaction and the possibility of Peierls distortion is taken into account. There are still two phases; they are, however, characterized by the absence or presence of dimerization. For small values of the transfer integral and not too soft crystals the transition is still of first order with a jump in the average charge. For larger values of t or for softer crystals the transition becomes a second order; the order parameter is the dimerization and the increase of the average charge is spread over a larger range of parameters. It is important to notice that the model can account for only one phase transition which is characterized by the appearance of the dimerization. When this is a first-order transition, the ionicity jumps at the same time, otherwise the ionicity changes smoothly without any additional transition. It could be, in principle, that the first-order line continues after meeting the second-order line, and terminates in a critical end point. If so, a second-order dimerization transition could be followed by a first-order ionicity jump, as seems to happen in TTF-CA under pressure.[15] In our model, however, this does not happen. Both theory and experiment require further study to clarify the possibility of two successive transitions.

Throughout this paper it was assumed that $\Delta > 0$, i.e., without the Coulomb interaction and hopping, the molecules would be neutral. For $\Delta < 0$, a small-t expansion shows that the system is expected to be always ionic and therefore is expected to be dimerized. However, Avignon *et al.*[20] claim a nondimerized ionic phase in a region with $\Delta < 0$. We have checked the $\Delta < 0$ case with our finite-size calculation. Contrary to the real-space renormalization results,[20] our results indicate that the system will always be dimerized, as expected physically.

In addition to shifting the phase boundary, dimerization has a drastic effect on the excitation spectra. In particular, the charge-transfer (optical absorption) and spin-flip gaps become finite in the quasi-ionic phase. The system is then a semiconductor rather than a semimetal. We could not study soliton excitations[11,18] due to the limitation on the chain length. Solitons may lower the above excitation gaps through nonadiabatic processes.

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