Phase Competition, Solitons, and Domain Walls in Neutral–Ionic Transition Systems

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Phase competition and excitations in the one-dimensional neutral–ionic transition systems are theoretically studied comprehensively. From the semiclassical treatment of the bosonized Hamiltonian, we examine the competition among the neutral (N), ferroelectric-ionic (Iferro) and paraelectric-ionic (Ipara) states. The phase transitions between them can become first-order when the fluctuation-induced higher-order commensurability potential is considered. In particular, the description of the first-order phase boundary between N and Iferro enables us to analyze N–Iferro domain walls. Soliton excitations in the three phases are described explicitly and their formation energies are evaluated across the phase boundaries. The characters of the soliton and domain-wall excitations are classified in terms of the topological charge and spin. The relevance to the experimental observations in the molecular neutral–ionic transition systems is discussed. We ascribe the pressure-induced crossover in tetrathiafulvalene-p-chloranil (TTF-CA) at a high-temperature region to that from the N to the Ipara state, and discuss its consequence.

1. Introduction

Neutral–ionic (NI) phase transition systems have been attracting interest over the past decades since the discovery of rich physical phenomena.1–5 These compounds are composed of two kinds of molecules stacked alternately, where the valences of the donor (D) and acceptor (A) molecules are nominally described as D0A0 and D+A−, in the neutral (N) and ionic (I) states, respectively. The material most intensively studied is tetrathiafulvalene-p-chloranil (TTF-CA), which resides in the competing region of the two states and exhibits the NI phase transition2 by changing temperature and/or pressures. The phase diagram on the plane of temperature and pressure was experimentally determined,6–8 in which three different states have been assigned: the ferroelectric-ionic (Iferro) state, the paraelectric-ionic (Ipara) state, and the N state. Schematic illustrations of these states are depicted in Fig. 1. In the N state, both the D and A sites become closed-shelled and thus the electronic spin degree of freedom is inactive; it is a band insulator (BI). In the Iferro state, the lattice is dimerized and spin-singlets are formed between electrons on D and A. In this case, the dimers formed by the D+ and A− molecules can be regarded as electric dipoles and thus the system shows ferroelectric properties. Then the Ipara state, in which there is no static lattice dimerization, is in a paraelectric state. One can assign this state as a Mott insulator with an activated spin degree of freedom. In TTF-CA, the Iferro phase locates at low temperatures in the entire pressure range, whereas a crossover from N to Ipara is seen at high temperatures with an increase in pressure. Note that, in actual materials, the valence becomes partial as D+ρ and A−ρ in all the phases, owing to the quantum nature of electrons, i.e., the hopping integrals between sites. The NI transition/crossover is characterized by the sudden change in ρ.

| phase | lattice | spin | uopt |
|-------|---------|------|------|
| N     | D0A0    | D+A− | 0    |
| Iferro| D+D−    | D+D− | uopt |
| Ipara | D+D−    | D+D− | 0    |

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Fig. 1. (Color online) Schematic view of three states observed in the NI transition systems. D and A stand for the donor and acceptor molecules, respectively, where the HOMO of the former and the LUMO of the latter are drawn. The red ellipses in the N and Iferro states represent the singlet formation of the spins. In the Ipara state, the semiclassical picture of the spin degree of freedom is the antiferromagnetic ordering, i.e., spin-density-wave (SDW). In the Iferro state, the lattice dimerization becomes finite, while in the Ipara state the SDW order parameter becomes finite in the semiclassical picture.
One of the key factors in the NI transition systems is the emergence of the multi-stable structure in the free energy, coupled to lattice deformation. This is seen in the first-order nature of the N-to-I_{ferro} transition; near there, characteristic domain walls between the two states are stabilized and contribute to the physical phenomena. Moreover, related to this fact, it has been recognized that the various states can be controlled by photo-irradiations, and that TTF-CA is one of the best target materials realizing photo-induced phase transitions.

Theoretical analyses of the phase competition and excitations in the NI transition systems have been performed in detail by Nagaosa and Takimoto applying Monte Carlo calculations to a microscopic model for the electron-lattice coupled system. In particular, the fundamental excitations are interpreted as soliton formations that can be described by the phase-field description of the order parameters. Various quantum calculations have been performed so far. Nevertheless, there are still issues to be clarified: For example, the description of the three phases seen in the experiments and their competitions from a microscopic point of view needs to be elaborated, since early works mainly focus on low-pressure states, namely, N and I_{ferro}. Another important aspect is the multi-stable character stressed above, which is realized numerically but has not been reproduced from the analytical phase-field approach. These are the points that we discuss in this paper.

Another motivation here is the recent experimental progress in high-pressure measurements on TTF-CA. As a function of pressure in the high-temperature phases, it has been observed that the resistivity exhibits a characteristic suppression around the crossover region between the N and I_{para} states, at which the spin excitations also show an abrupt change in behaviors. A theoretical analysis of soliton excitations has been performed motivated by these findings.

In this paper, we perform a comprehensive theoretical analysis of the phase competitions and excitations, on the basis of a microscopic interacting electron model taking into account the electron–phonon coupling, by paying special attention to the multi-stable properties. We follow the semiclassical analysis developed in Refs. 18, 19, 26, and 30. In Sect. 2, we introduce the model and apply the bosonization method to obtain the phase-variable description of the Hamiltonian. In Sect. 3, the ground-state properties of the semiclassical phase Hamiltonian are analyzed by searching the potential minima. In Sect. 4, the soliton and domain excitations are analyzed. A summary and discussions are given in Sect. 5.

### 2. Model Hamiltonian and Bosonization

We consider the standard one-dimensional Hubbard-type model for NI transition systems such as TTF-CA, which can describe all the three states shown in Fig. 1. The Hamiltonian is given by

\[ H = H_e + H_{e-ph} + H_{ph}, \]

where \( c_{j,\sigma} \) is the annihilation operator of electron on the \( j \)-th site with spin \( \sigma \), and \( n_{j,\sigma} = c_{j,\sigma}^\dagger c_{j,\sigma} \). The site-alternating potential reflecting the alternation of the D and A molecules along the chain direction is represented by \( \Delta \). We assume \( \Delta > 0 \) without losing generality. The couplings \( U \) and \( V \) represent the on-site and nearest-neighbor Coulomb interactions, respectively; \( H_e \) is sometimes called the ionic (extended) Hubbard model. The quantity \( u_j \) represents the lattice distortion; \( H_{e-ph} \) is the electron–phonon coupling term and the parameter \( K_{ph} \) is the spring constant. Here, we consider the classical phonon and focus only on the bond-alternating (\( q = \pi \)) distortion. The average electron density is set as half-filling, taking into account the HOMO of D and the LUMO of A molecules, as shown in Fig. 1.

#### 2.1 Bosonized Hamiltonian

Here, we represent the Hamiltonian in terms of bosonic phase-field variables. By setting the lattice constant as \( a \), the charge and spin density operators can be represented as

\[ n_j = \frac{\sin(2K_Fx + \theta) \cos \phi}{a}, \]

\[ S_j = \frac{\cos(2K_Fx + \theta) \sin \phi}{a}, \]

where \( \theta (\phi) \) represents the charge (spin) phase. The Fermi momentum is \( K_F = \pi/(2a) \).

The Hamiltonian density of the electron part is given by

\[ \mathcal{H}_e = \frac{\nu_p}{4\pi} \left[ K_p (2\pi \Pi_\theta)^2 + \frac{1}{K_p} (\partial_x \theta)^2 \right] \]

\[ + \frac{\nu_\sigma}{4\pi} \left[ K_\sigma (2\pi \Pi_\theta)^2 + \frac{1}{K_\sigma} (\partial_x \phi)^2 \right] \]

\[ - \frac{g_\Delta}{2\pi^2a^2} \sin \theta \cos \phi \]

\[ - \frac{g_c}{2\pi^2a^2} \cos 2\theta + \frac{g_s}{2\pi^2a^2} \cos 2\phi \]

\[ - \frac{g_{cs}}{2\pi^2a^2} \cos 2\theta \cos 2\phi, \]
where $K_p$ and $K_\sigma$ are the Tomonaga–Luttinger parameters for the charge and spin degrees of freedom. The operators $\Pi_\theta$ and $\Pi_\phi$ are phase fields conjugate to $\theta$ and $\phi$, respectively. The couplings are given as $g_\Delta = 4 \pi \Delta a$, $g_c = (U - 2V) a + O(U^2, UV, V^2)$, $g_{cs} = (U - 2V) a + O(U^2, UV, V^2)$, and $g_{cs} = -2V a + O(U^2, UV, V^2)$. The Peierls-type electron–phonon coupling term and the lattice Hamiltonian densities read

$$\mathcal{H}_{e-ph} = -\frac{ug_\Delta}{2\pi^2 a^2} \cos \theta \cos \phi,$$

$$\mathcal{H}_{ph} = \frac{K_{ph}}{2a^2},$$

where $g_\Delta = 8\pi \rho a$.

As pointed out by Sandvik et al., higher-order commensurability can be important in altering the character of phase transitions. The corresponding term is expressed as

$$\mathcal{H}'_c = -\frac{g_{2c}}{2\pi^2 a^2} \cos 4\theta,$$

where $g_{2c} > 0$. This term effectively represents the four-body interaction, which is absent in the microscopic Hubbard-type Hamiltonian; however, it can be generated through the renormalization-group (RG) procedure. The RG equation for $g_{2c}$ is given by

$$\frac{d}{dt}[g_{2c}] = (2 - 8K_p)g_{2c} + cg_{c}^2 + c'g_{2c},$$

where $l$ is the scaling parameter of the short-distance cutoff ($a \to a e^{it}$), and $c$ and $c'$ are positive numerical constants. Since the couplings $g_c$ and $g_{cs}$ are generally finite, the $g_{2c}$ term can become finite with a positive sign [$g_{2c}(l) > 0$] through the RG procedure $l \to \infty$. Eventually, this term can be relevant when $K_p < 1/4$ and can alter the second-order phase transition into the first-order one. This could be confirmed by analyzing the RG explicitly; however, we assume this term to be a priori throughout this paper, since as we will see below it drives the phase transition between N and $I_{ferro}$ to the first order, consistent with results of the experiments.

Semiclassical analysis is performed by neglecting the phase fields $\Pi_\theta$ and $\Pi_\phi$. Then the semiclassical Hamiltonian is

$$\mathcal{H}_{c1} = -\frac{v_p}{4\pi K_p} (\partial_\theta)^2 + \frac{v_\sigma}{4\pi K_\sigma} (\partial_\phi)^2 + \frac{1}{2\pi^2 a^2} V(\theta, \phi, u).$$

The potential term is given by

$$V(\theta, \phi, u) = -g_\Delta \sin \theta \cos \phi - g_c \cos 2\theta + g_{cs} \cos 2\phi - 2g_{2c} \cos 4\theta - g_{cs} \cos 2\theta \cos 2\phi - ug_\Delta \cos \theta \cos \phi + \frac{K_{ph}}{2} a^2,$$

where we have set

$$\tilde{K}_{ph} \equiv 2\pi^2 a^2 \frac{K_{ph}}{a}.$$

We will investigate its ground-state properties and excitations in Sects. 3 and 4, respectively.

### 2.2 Order parameters

In order to characterize the N, $I_{ferro}$, and $I_{para}$ states in the following, let us introduce order parameters. Following the arguments in Ref. 26, we can consider the spin-density-wave (SDW), bond-charge-density-wave (BCDW), and bond-spin-density-wave (BSDW) states. They are characterized by the following order parameters:

$$\mathcal{O}_{SDW} \equiv (-1)^j (n_{j,\uparrow} - n_{j,\downarrow}),$$

$$\mathcal{O}_{BCDW} \equiv (-1)^j (c_{j,\uparrow}^\dagger c_{j+1,\uparrow} + c_{j+1,\uparrow}^\dagger c_{j,\uparrow} + H.c.),$$

$$\mathcal{O}_{BSDW} \equiv (-1)^j (c_{j,\uparrow}^\dagger c_{j+1,\uparrow} - c_{j+1,\uparrow}^\dagger c_{j,\uparrow} + H.c.).$$

The BCDW order parameter corresponds to the Peierls dimerization operator.

Furthermore, to characterize low-energy excitations, it is convenient to introduce topological charges $Q$ and $S_z$ for the charge and spin sectors, which we use to classify the soliton and domain-wall excitations. They are given by

$$Q = \frac{1}{\pi} \int dx \partial_\theta, \quad S_z = \frac{1}{2\pi} \int dx \partial_\phi.$$
The potential is rewritten as
\[
V(\theta, \phi, u_{opt}) = -g_\Delta \sin \theta \cos \phi \\
- \tilde{g}_c \cos 2\theta + \tilde{g}_s \cos 2\phi - g_{2c} \cos 4\theta \\
- \tilde{g}_{cs} \cos 2\theta \cos 2\phi,
\]
where the coupling constants are renormalized as
\[
\tilde{g}_c \equiv g_c + \frac{g_s^2}{8K_{ph}},
\]
\[
\tilde{g}_s \equiv g_s - \frac{g_s^2}{8K_{ph}},
\]
\[
\tilde{g}_{cs} \equiv g_{cs} + \frac{g_s^2}{8K_{ph}}.
\]
Here, we neglect the term \(-\frac{g_s^2}{8K_{ph}}\), which merely gives a constant contribution.

The resulting potential Eq. (3.2) is reduced to the same form as that for the purely electronic ionic extended Hubbard model without lattice distortion,\cite{26,33} i.e., \(H_c [Eqs. (2.1a)]\) whose phase-field description is \(H_c [Eq. (2.3a)]\) added by the higher-order term \(H'_c [Eq. (2.4)]\). In Ref. 26, \(H_c\) was analyzed, including the semiclassical treatment for the ground state, which we can directly extend.

Let us make the correspondence between the phases discussed in previous works and those observed in the NI transition systems. They are characterized by the optimized lattice distortion \(u_{opt}\) and the SDW order parameter \(\langle \mathcal{O}_{SDW} \rangle\). The correspondence is summarized in Fig. 1. In the N phase, which corresponds to the BI,\cite{25,26} there is neither lattice dimerization nor spin ordering, i.e., \(u_{opt} = 0\), \(\langle \mathcal{O}_{SDW} \rangle = 0\). The \(I_{\text{ferro}}\) state is characterized by the finite lattice dimerization \(u_{opt} \neq 0\), i.e., \(\langle \mathcal{O}_{SDW} \rangle \neq 0\), while the spin ordering is absent owing to the spin-singlet formation: \(\langle \mathcal{O}_{SDW} \rangle = 0\). In the \(I_{\text{para}}\) phase, the spin fluctuation develops owing to the absence of the lattice distortion \(u_{opt} = 0\). In the semiclassical picture, such a Mott insulating state is simply described by the SDW ordering and gives \(\langle \mathcal{O}_{SDW} \rangle \neq 0\). If we take into account the fluctuation effects for the spin mode in terms of the RG method, the SDW ordered phase may be regarded as the paramagnetic state with predominant spin correlations.\cite{26,32} Namely, the positive coupling \(u_s\) becomes marginally irrelevant and renormalized to zero \(g_s \to 0\), indicating the absence of locking potential for the spin phase variable \(\phi\): the paramagnetic gapless spin-liquid state.

When there is finite electron–phonon coupling, the one-dimensional Mott insulating state (i.e., the \(I_{\text{para}}\) state) is always unstable owing to the Peierls instability in the ground state \((T = 0)\). Thus, with decreasing temperature, the phase transition occurs from the paramagnetic \(I_{\text{para}}\) state into the state with static lattice dimerization \(I_{\text{ferro}}\) state) where spin-singlets are formed. This is seen in the form of the effective coupling for the spin mode \(\tilde{g}_s\) given by Eq. (3.3b). Once the electron–phonon coupling is introduced, the effective coupling \(\tilde{g}_s\) turns negative at sufficiently low energy or temperature, and then the effective coupling \(\tilde{g}_s\) flows to \(-\infty\). This situation corresponds to the spin-singlet formation and then the SDW correlations decay exponentially. Therefore the \(I_{\text{para}}\) state is unstable at \(T = 0\) for finite electron–phonon coupling. However, this is not the case if we consider the states at finite temperatures, since the temperature plays a role of cutoff of the RG equation, and then the effective coupling \(\tilde{g}_s\) can be positive. Thus the obtained \(I_{\text{para}}\) state in our semiclassical treatment should be regarded not as a zero-temperature phase but as a finite-temperature phase, which in fact is the case in experiments for NI transition systems.

We can find the stable points in the potential Eq. (3.2), by assuming spatially uniform solutions. As mentioned above, we can follow the analysis in Ref. 26 but here the higher-order \(g_{2c}\) term \(H'_c [Eq. (2.4)]\) is included. The positions of the locked phase fields \(\theta\) and \(\phi\) are determined from the saddle-point equations \(\partial V(\theta, \phi, u_{opt})/\partial \theta = \partial V(\theta, \phi, u_{opt})/\partial \phi = 0\). The solutions of the saddle-point equations yield the following four states \((\alpha_\theta\) and \(\alpha_\phi\) are nonuniversal constants), which are qualitatively the same as those in Ref. 26:

(i) N state: The phase fields are locked at \((\theta, \phi) = (\frac{\pi}{2}, 0), (\frac{3\pi}{2}, \pi)\) (modulo 2\(\pi\)). In this case, \(u_{opt} = 0\) and \(\langle \mathcal{O}_{SDW} \rangle = 0\).

(ii) \(I_{\text{ferro}}\) state: The phase fields are locked at \((\theta, \phi) = (\frac{\pi}{2} + \alpha_\theta, 0)\) or \((-\frac{\pi}{2} + \alpha_\theta, \pi)\). The lattice dimerization order parameter becomes finite \((u_{opt} \propto \cos \theta \cos \phi \neq 0)\) while \(\langle \mathcal{O}_{SDW} \rangle = 0\).

(iii) \(I_{\text{para}}\) state: The phase fields are locked at \((\theta, \phi) = (0, \pm \frac{\pi}{2})\) or \(\pi, \pm \frac{\pi}{2})\). The SDW order parameter becomes finite \((\langle \mathcal{O}_{SDW} \rangle \propto \cos \theta \sin \phi \neq 0)\), while \(u_{opt} = 0\).

(iv) BSDW state: The phase fields are locked at \((\theta, \phi) = (\frac{\pi}{2}, 0 \pm \alpha_\phi)\) or \(\frac{3\pi}{2}, \pm (\pi - \alpha_\phi)\).

The positions of the locked phase fields \(\theta\) and \(\phi\) and the corresponding states are shown in Fig. 2. In the present analysis, we do not focus on the BSDW phase since this is not observed experimentally in TTF-CA. Additionally, the BSDW state cannot have a true long-range order since the phase locking of \(\phi\) is prohibited, except in the spin-gapped case with \(\langle \phi \rangle = 0\) (mod \(\pi\)), owing to the spin-rotational SU(2) symmetry.\cite{26}

The analysis without the higher-order term \((g_{2c} = 0)\) yields the phase diagram in Fig. 10 of Ref. 26, where the “BI”, “BCDW”, and “SDW” phases correspond to the N, \(I_{\text{ferro}}\), and \(I_{\text{para}}\) states, respectively. Owing to the presence of the \(\tilde{g}_{cs}\) term that couples the charge and spin phase variables, the direct transition between N and \(I_{\text{para}}\) occurs in a finite parameter range and its phase transition is of the first order. However, the transition between N and \(I_{\text{ferro}}\) was found to always be of the second order, and then the experimental observations in TTF-CA could not be reproduced. The introduction
of the $g_{2c}$ term changes it to a first-order transition. Once the $g_{2c}$ term is introduced, although analytical evaluations of the phase boundaries are complicated, here we obtain the phase diagram for a finite value of $g_{2c}$ by numerically finding the potential minima of $V(\theta, \phi, u_{\text{opt}})$, as shown in Fig. 3. We find that the phase boundary between the N and $I_{\text{ferro}}$ states becomes of the first order in contrast to the previous analysis, owing to the presence of the higher-order commensurability term $\sim \cos 4\theta$. In other words, near the first-order phase boundary, a multi-stable character between the N and I states is seen, then the NI domain walls can be discussed as in the next section.

Incidentally, the phase boundary between the $I_{\text{para}}$ and $I_{\text{ferro}}$ states also becomes of the first order. This first-order behavior is seen even for $g_{2c} = 0$ and can be ascribed to the spin-charge coupling $g_{cs}$ term. As already clarified in Ref. 26, this first-order behavior is an artifact due to the semiclassical treatment and changes into the second-order transition if we take into account the fluctuation effect in terms of the RG method. This is consistent with the spin-Peierls transition in the $S = 1/2$ Heisenberg chain coupled with lattice distortions, where the gapless spin liquid turns into a spin-gapped dimerized state. It shows a second-order phase transition in general. It is also consistent with the experiments where the $I_{\text{para}}$-$I_{\text{ferro}}$ transition as a function of temperature is continuous, in contrast with the first-order nature of the N-$I_{\text{ferro}}$ transition.

4. Soliton and Domain Formations

In this section, we examine the excited states, namely, the soliton and domain formations. By taking into account the spatial variations of the phase fields $\theta$ and $\phi$ and also of the lattice distortion, our semiclassical Hamiltonian density [Eq. (2.6)] is given by

$$
\mathcal{H}_{c3} = \frac{\nu}{4\pi K_\rho} [\partial_x \theta(x)]^2 + \frac{\nu}{4\pi K_\rho} [\partial_x \phi(x)]^2 + \frac{1}{2\pi^2 a^2} V(\theta(x), \phi(x), u(x)),
$$

where the spatial variation of the lattice distortion is now explicitly shown $[u \to u(x)]$. The lattice distortion $u(x)$ can again be determined from the variational approach:

$$
u_{\text{opt}}(x) = \frac{g_3}{K_{ph}} \cos \theta(x) \cos \phi(x).$$

In the semiclassical approach, possible soliton/domain excitations from the ground state are described as variational solutions of the following simultaneous equations

$$
0 = \frac{\pi \nu a^2}{K_\rho} \frac{d^2 \theta(x)}{dx^2} + g_3 \cos \theta(x) \cos \phi(x)
- 2g_c \sin 2\theta(x) - 4g_{2c} \sin 4\theta(x).$$
versal values of the minima of the potential. In both excitations, the topological charge ble. One is the charge soliton, and the other is the spin soliton.

The characters of all the possible excitations discussed in the following are summarized in Table I. In the following, we show results for the fixed condition $g_{\Delta} = 1$, $\tilde{g}_{cs} = -0.2$, $g_{2c} = 0.1$, $v_{p} = v_{s} = 2$, $K_{p} = 0.3$, and $K_{s} = 1$.

4.1 Soliton excitations

By solving Eq. (4.3) numerically, we can analyze possible excitations. We obtain various types of excitations depending on the choice of the parameters. The typical soliton excitations in the three phases are shown in Fig. 4, showing the spatial variations of the phase fields $\{a\}$, $\{d\}$, $\{g\}$ and the order parameters $\{(b)\}$, $\{(e)\}$, $\{(h)\}$ as well as the trajectories in the $(\theta, \phi)$ plane $\{(c)\}$, $\{(f)\}$, $\{(i)\}$.

The soliton excitations in the N and I$_{\text{ferro}}$ states are consistent with those discussed in Ref. 17. Namely, in the N state, a possible soliton is the so-called polaron excitation. The polaron is described by the local lattice distortion and order parameters $\{(b)\}$, $\{(e)\}$, $\{(h)\}$ as well as the trajectories in the $(\theta, \phi)$ plane $\{(c)\}$, $\{(f)\}$, $\{(i)\}$.

In the I$_{\text{para}}$ state, the soliton excitation connecting potential minima along the $\theta$ direction is the charge soliton. Note that the charge soliton profile on the $\theta$--$\phi$ plane largely deviates from a straight line. Owing to this fact, as seen in Fig. 4(h), it is accompanied by the local lattice distortion. In this sense, this charge soliton is different from the charge excitation in the prototypical one-dimensional Mott insulator. We can also consider the spin soliton, which connects the potential minima along the $\phi$ direction. The spin soliton is accompanied by the local lattice distortion as well. However, note that this behavior is in contrast to the charge soliton: In the case of the charge soliton, the lattice distortion disappears if the soliton profile is the straight line on the $\theta$--$\phi$ plane (i.e., $\langle \phi \rangle = \pi/2 \mod \pi$), while the spin soliton always carries the lattice distortion even if the spin soliton profile is described by the straight line (i.e., $\langle \phi \rangle = 0 \mod \pi$). This is because of the presence of the term $\cos \theta(x) \cos \phi(x)$ in Eq. (4.2). We find $\cos \langle \phi \rangle = 0$ in the case of a straight-line charge soliton, while $\cos \langle \theta \rangle = \pm 1$ in the case of a straight-line spin soliton. Furthermore, we also observe a charge-spin coupled excitation, connecting the minima, e.g., $\langle \theta, \phi \rangle = (0, \pi/2)$ and $\langle \pi, \pi/2 \rangle$: This carries $|Q| = 1$ and $|S_{z}| = 1/2$. Its profile shown in the dashed line in Fig. 4(i) is different from the isolated charge or spin solitons and then we call this “charge+spin” soliton. When we decrease $\tilde{g}_{c}$, the profile of this charge+spin soliton smoothly connects to that of the charge soliton.

4.2 Soliton formation energies

From the results above, we evaluate the soliton formation energies across the NI phase boundaries, keeping in mind the experimental system showing the phase transition/crossover by changing temperature and pressure. In particular, we pay attention to the possible excitations contributing to the electric conductivity.

The results for soliton excitations across the boundary between the N and I$_{\text{para}}$ states are shown in Fig. 5(a). For small $\tilde{g}_{c}$, the system is in the N phase and the fundamental excitation is given by the polaron. For large $\tilde{g}_{c}$, the system is in the I$_{\text{para}}$ state and the possible excitations are charge, spin, and charge+spin solitons. We observe that the excitation energy of charge+spin soliton is always slightly larger than that of the charge soliton. In the I$_{\text{para}}$ state, the spin soliton does not carry a charge and thus does not contribute to electric conductivity. Thus electric conduction is possible through excitations of the polaron soliton and the charge and charge+spin solitons in the N and I$_{\text{para}}$ phases, respectively. As seen in Fig. 5(a), all of their excitation energies become sufficiently suppressed, monotonically toward the phase boundary. On the phase boundary ($\tilde{g}_{c} = 0.4$), the excitation energy of the polaron and that of the charge soliton coincide.

The soliton excitation energies across the boundary between the N and I$_{\text{ferro}}$ states are shown in Fig. 5(b). In the I$_{\text{ferro}}$ state, both the charge and spin solitons are responsible for the electric conductivity, since both carry the topological (fractional) charge $Q$. With increasing $\tilde{g}_{c}$, the polaron excitation energy decreases. On the other

| Excitation       | Charge $|Q|$ | Spin $|S_{z}|$ | Lattice distortion | Ref. |
|------------------|-------------|-------------|-------------------|------|
| Polaron in N     | 1           | 1/2         | Local distortion* | 17   |
| SS in I$_{\text{ferro}}$ | $2\alpha_{p}/\pi$ | 0         | Phase change      | 17,19 |
| CS in I$_{\text{ferro}}$ | $1 - 2\alpha_{p}/\pi$ | 1/2       | Phase change      | 17,19 |
| CS in I$_{\text{para}}$ | 1          | 0           | Local distortion* |      |
| SS in I$_{\text{para}}$ | 0          | 1/2         | Local distortion  |      |
| CSS in I$_{\text{para}}$ | 1          | 1/2         | Local distortion* |      |
| N--I$_{\text{ferro}}$ DW | $\alpha_{p}/\pi$ | 0         | Zero to Finite    |      |
| N--I$_{\text{para}}$ DW | 1/2         | 1/4         | Local distortion  |      |
| I$_{\text{ferro}}$--I$_{\text{para}}$ DW | $1/2 - \alpha_{p}/\pi$ | 1/4       | Finite to Zero    |      |
Fig. 4. (Color online) Soliton excitations in different phases: N (a-c), I\(_{\text{ferro}}\) (d-f), and I\(_{\text{para}}\) (g-i). The parameters are chosen as \((\tilde{g}_c, \tilde{g}_s) = (0.1, 0.1)\) for the N state, \((1.0, -0.5)\) for the I\(_{\text{ferro}}\) state, and \((1.0, 0.1)\) for the I\(_{\text{para}}\) state. The spatial variations of the phase fields \(\theta\) and \(\phi\) are shown in (a), (d), and (g). The variations of the order parameters \(u_{\text{opt}}\) and \(\langle \mathcal{O}_{\text{SDW}} \rangle\) are shown in (b), (e), and (h). The corresponding trajectories on the plane of \(\theta\) and \(\phi\) are shown by the solid lines in (c), (f), (i), where the other possible trajectories are indicated by the dashed lines.

hand, in the I\(_{\text{ferro}}\) phase, the charge-soliton excitation energy increases, while that of the spin soliton decreases. Such a behavior is seen as well in the case of \(g_c = g_s = g_{cs} = g_{2c} = 0\), which corresponds to the results of Ref. 30. This is seen in the dashed lines in Fig. 5(b): the polaron excitation energy smoothly connects to the spin-soliton excitation energy across the phase boundary. In the present case with \(g_{2c} \neq 0\), there is a gap between them owing to the first-order nature of the phase transition.

In both cases above, just at the phase boundaries, there are relations between the soliton formation energies of the two phases when approaching from both sides of the critical values. There, domain-wall excitations become possible as discussed in previous works, which we discuss in the next subsection.

4.3 Domain walls

In this subsection, we analyze the possible excitations at the phase boundaries. At the phase boundaries, domain excitations become possible in addition to the soliton excitations. In previous theoretical and experimental works, the domain wall between the N and I states (abbreviated as NIDW) has been discussed as a possible fundamental excitation near the NI phase transition point. However, the explicit descriptions of the NIDW were not given in terms of the phase-field \((\theta, \phi)\) description as mentioned in Sect. 1, since the multi-stable character of the N and I\(_{\text{ferro}}\) states could not be realized. In the present analysis, in contrast, the multi-stable structure of the potential is realized by taking into account the higher-order commensurability potential and thus it is now possible to give explicit descriptions.
of NIDW.

Figure 6 shows lowest-energy excitations on the various phase boundaries with the boundary conditions $Q = 2$ and $S_z = 0$. Owing to the finite value of $Q$, they can carry electronic currents when an electric field is applied. In the following, possible excitations are analyzed in the respective cases.

### 4.3.1 N–I$_{\text{para}}$ boundary

At the phase boundary between the N and I$_{\text{para}}$ states, the only stable excitation is the NIDW [Figs. 6(a)–6(c)]. In this case, the potential $V(\theta, \phi, u_{\text{opt}})$ takes minima at, e.g., $(\theta, \phi) = (\pi/2, 0)$ (corresponding to the N state) and $(\theta, \phi) = (0, \pi/2)$ (corresponding to the I$_{\text{para}}$ state). The NIDW is described by the excitation connecting these minima. In order to distinguish this from the NIDW discussed in the next subsection, we call this “N–I$_{\text{para}}$ DW”. As we will see below, this N–I$_{\text{para}}$ DW smoothly connects to the polaron in the N phase [Fig. 4(c)] or to the charge soliton in the I$_{\text{para}}$ phase [Fig. 4(i)] if we move away from the phase boundary. This is the reason why the polaron excitation energy and the charge-soliton excitation energy coincide at the boundary [Fig. 5(a)]. Here it is worth noting that the lattice distortion occurs locally at the N–I$_{\text{para}}$ DW. This is natural since the polaron in the N phase and the charge soliton in the I$_{\text{para}}$ phase both have such a character.

The polaron in the N phase can be considered as a confined particle of the pair of the local lattice distortion $u > 0$ and $u < 0$. The N–I$_{\text{para}}$ DW can be regarded as a dissociation of this pair of lattice distortion, i.e., the single polaron is deconfined into two N–I$_{\text{para}}$ DWs at the phase boundary and the I$_{\text{para}}$ state emerges as an intervening state between them, as shown in Fig. 7(a). This picture is in accord with the observation that the single polaron carries the charge $|Q| = 1$ and the spin $|S_z| = 1/2$, while the single N–I$_{\text{para}}$ DW carries $|Q| = 1/2$ and $|S_z| = 1/4$. Similarly, approaching from the I$_{\text{para}}$ phase, the charge soliton is dissociated to a pair of N–I$_{\text{para}}$ DW, as shown in Fig. 7(b). This picture is also in accord with the
conservation of the topological charge and spin.

4.3.2 $N{-}\text{I}_{\text{ferro}}$ boundary

At the phase boundary between the N and I\text{ferro} states, two kinds of excitations are possible [Figs. 6(d)–6(f)]. One is the NIDW, sometimes called\textsuperscript{17} the lattice relaxed (LR-) NIDW, and the other is the spin soliton. In this case, the potential takes minima at, e.g., $(\theta, \phi) = (\pi/2, 0)$ and $(-\pi/2, \pi)$ (corresponding to the N state) and $(\theta, \phi) = (\pi/2 \pm \alpha, 0)$ and $(-\pi/2 \pm \alpha, \pi)$ (corresponding to the I\text{ferro} state). The NIDW is described by the excitation connecting the minima, e.g., $(\theta, \phi) = (\pi/2, 0)$ and $(-\pi/2 - \alpha, 0)$. This can be called “$N{-}\text{I}_{\text{ferro}}$ DW”. On the other hand, the spin soliton is described by the excitation connecting the minima, e.g., $(\theta, \phi) = (\pi/2 - \alpha, 0)$ and $(-\pi/2 + \alpha, \pi)$, where we assumed $\alpha > 0$.

When we approach the phase boundary from the N state, we can observe that the single polaron (connecting $(-\pi/2, \pi)$ and $(\pi/2, 0)$) splits into two $N{-}\text{I}_{\text{ferro}}$ DWs and the single spin soliton [see Fig. 8(a)]. Then at the $N{-}\text{I}_{\text{ferro}}$ boundary, we can obtain the relation

$$\Delta_{\text{polaron}} = 2\Delta_{N{-}\text{I}_{\text{ferro}}\text{DW}} + \Delta_{\text{spin}},$$

(4.4)

where $\Delta_{\text{polaron}}$, $\Delta_{N{-}\text{I}_{\text{ferro}}\text{DW}}$, and $\Delta_{\text{spin}}$ are the respective formation energies. Therefore the gap in energy of the polaron and spin excitations observed in Fig. 5(b) can be understood as $2 \times \Delta_{N{-}\text{I}_{\text{ferro}}\text{DW}}$.

On the other hand, when we approach the phase boundary from the I\text{ferro} state, the single charge soliton splits into two $N{-}\text{I}_{\text{ferro}}$ DWs [see Fig. 8(b)]. Thus we obtain

$$\Delta_{\text{charge}} = 2\Delta_{N{-}\text{I}_{\text{ferro}}\text{DW}},$$

(4.5)

where $\Delta_{\text{charge}}$ is the formation energy of the charge soliton. These pictures are in accord with the neutrality of the topolog-
Fig. 8. (Color online) Generations of the N–Iferro DWs when approaching the N–Iferro boundary from the N state (a) and from the Iferro state (b), where we fixed $g_s = -0.5$. The notations are the same as those in Fig. 7. The polaron in the N state (a) splits into two N–Iferro DWs and a single spin soliton, where the lattice-distorted region of the polaron is expanded and changes into the Iferro state. The charge soliton in the Iferro state (b) splits into a pair of the N–Iferro DWs and a single N–Iferro DW. The notations are the same as those in Fig. 5(b), both interpretations indicate that the resistivity minimum to coincide with the transition point between the N and Ipara states. This paramagnetic Mott insulating state is a finite temperature phase which is unstable toward the spin-Peierls dimerization, i.e., the Iferro state, as was discussed in Sect. 3 as well. The first-order N–Ipara phase boundary is expected to turn into a crossover at high temperatures, since there is no symmetry breaking now because the corresponding Mott insulating state has no spin ordering. From these correspondences, our results are consistent with the experimental phase diagram, as well as with recent numerical results.27

Next, we discuss the characteristic behavior of resistivity, where a sharp minimum as a function of pressure was observed in the high-temperature crossover region between the N and Ipara states.6,28,29 In the low-pressure N state, the lowest-energy excitation is the polaron that carries a charge. Therefore, the rapid decrease in soliton formation energy seen in Fig. 5 toward the phase boundary is consistent with the decrease in the resistivity in experiments. On the other hand, as for the Iferro state, it was claimed in Ref. 17 that the activation energy in conductivity is determined by the larger excitation energy of the spin or charge soliton, i.e., by the rate-determining step. In Ref. 30, in contrast, the activation energy was considered to be determined by the sum of excitation energies of charge and spin solitons. If we apply these interpretations to the present results across the N–Iferro boundary [Fig. 5(b)], both interpretations indicate that the resistivity takes a minimum away from the N–Iferro boundary. Instead, the soliton formation energies across the N–Ipara boundary [Fig. 5(a)] suggest the resistivity minimum to coincide with the transition point between the N and Ipara states. This is because, in the Ipara state, the low-energy excitations carrying electric current are the charge and charge+spin solitons, both showing a monotonic and steep increase in formation ener-
gies by going away from the phase boundary. The distinction of the two scenarios is possible by experimentally determining the pressure where the phase transformation takes place and comparing with the pressure for the resistivity minimum. The former can be extracted, e.g., by analyzing the pressure dependence of the charge transfer $\rho$, although it is a crossover, which seems to support the latter interpretation.\(^{29}\)

Here we briefly discuss the magnitude of the excitation gap at the boundary between the $N$ and $I_{\text{para}}$ states. In TTF-CA, the minimum activation energy was evaluated as $E \approx 0.055$ eV.\(^{30}\) To make a qualitative comparison between this activation energy and the present results, we should take into account the quantum fluctuations in the electron parts of the Hamiltonian and go beyond the adiabatic treatment of the lattice distortion. In addition, the excitation gap at the boundary sensitively depends on the magnitude of the dynamically-generated $g_{\text{sc}}$ term in Eq. (2.5), whose qualitative estimation is difficult. Here let us just argue about possible roles of the quantum fluctuations due to the $\Pi_{\sigma}$ and $\Pi_{\rho}$ terms in Eq. (2.3a), and the effect of phonon dynamics. The present semiclassical treatment of the electron part can be justified when $K_{\rho} \ll 1$ ($\nu = \rho, \sigma$). It is known that the soliton formation energy is reduced when quantum fluctuations are included: For example, the soliton formation gap induced only by the $g_{\text{sc}} \cos 2\theta$ term (simple quantum sine-Gordon model), which is given by $\sim \sqrt{g_{\text{sc}}}$ in the classical limit, is given by $g_{\text{sc}}^{1/(2-2K_{\rho})}$ for a general value of $K_{\rho}(<1)$.\(^{38,39}\) As for the spin part, the excitation gap in the $I_{\text{para}}$ vanishes if we take the $1D$ quantum fluctuation effects into account, as discussed before. Regarding the dynamical phonon, we can expect that the excitation gap will sufficiently be reduced if the gap is smaller than the Debye frequency, as has been indicated in the context of the spin-Peierls chain.\(^{40}\) All these effects can be taken into account by using the RG method,\(^{41,42}\) whose application to the full Hamiltonian in this case for the quantitative evaluation of the soliton excitation gap is left for future works.

We note that the character of spin excitations at the $N$--$I_{\text{ferro}}$ boundary is completely different from that at the $N$--$I_{\text{para}}$ boundary. In the former, the elementary spin excitation is a spin soliton, which essentially should show an activation behavior in the spin susceptibility in the dilute limit. In the latter, it will be paramagnetic excitations as seen in the Heisenberg spin chain; therefore every D and A site carries effective $S = 1/2$ interacting along the chain. Nevertheless, we note that the temperature dependence of spin susceptibility can largely deviate from the Bonner–Fisher behavior, owing to the renormalization effects by the terms absent in the simple Hubbard model but present here, e.g., the site-alternating potential term and the electron–phonon coupling. In fact, in tetrathiafulvalene-$p$-bromanil (TTF-BA),\(^{35}\) the spin susceptibility in the $I_{\text{para}}$ phase shows paramagnetic behavior above the transition temperature to the $I_{\text{ferro}}$ ground state, but does not follow the Bonner–Fisher behavior. In addition, as shown in Sect. 4.1, we found that the spin soliton in the $I_{\text{para}}$ state is accompanied by local lattice distortion. In this sense, our spin soliton excitation is different from the conventional spinon excitations, and can be regarded as a “spin-polaron” excitation. The local/dynamic lattice distortions have actually been observed in the high-temperature crossover region in TTF-CA under pressure in the optical measurements,\(^{3}\) whose relevance to such a novel excitation might be an interesting future problem.

Finally, let us comment on experimental observations of photo-induced phenomena in NI systems, especially in the $I_{\text{ferro}}$ phase of TTF-CA, which is prominent among many. In Ref. 10, an $I_{\text{ferro}}$-to-$N$ conversion into stable macroscopic $N$ domains induced by pulse optical excitations is reported. A notable point is that, when the temperature is just below the transition temperature $T_{\text{NI}}$, the conversion occurs irrespective of the excitation density by light, whereas at low temperature, a high density is needed. This is consistent with the multi-stable structure of free energy discussed in this paper and with the stability of $N$--$I_{\text{ferro}}$ DW just at the transition point. In our calculations, when the system is deeply in the $I_{\text{ferro}}$ phase, DW excitations are not stable; they will pair annihilate into a polaron excitation [the inverse process of Fig. 8(a)], and therefore multiplication of the excited $N$ state is hampered. However, since the present calculations are based on classical phonons, its direct application to one-dimensional “string” excitations implicated in experiments is not straightforward, but may rather serve to describe the macroscopic domain of the $N$ state in the $I_{\text{ferro}}$ background observed at a later time scale of the order of 100 ps; the oscillation of such a domain is suggested in Ref. 10.

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