Competition between excitonic charge and spin density waves: Influence of electron-phonon and Hund's rule couplings

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(Received 9 July 2015; published 2 September 2015)

We analyze the stability of excitonic ground states in the two-band Hubbard model with additional electron-phonon and Hund's rule couplings using a combination of mean-field and variational cluster approaches. We show that both the interband Coulomb interaction and the electron-phonon interaction will cooperatively stabilize a charge density wave (CDW) state which typifies an "excitonic" CDW if predominantly triggered by the effective interorbital electron-hole attraction or a "phononic" CDW if mostly caused by the coupling to the lattice degrees of freedom. By contrast, the Hund's rule coupling promotes an excitonic spin density wave. We determine the transition between excitonic charge and spin density waves and comment on a fixation of the phase of the excitonic order parameter that would prevent the formation of a superfluid condensate of excitons. The implications for exciton condensation in several material classes with strongly correlated electrons are discussed.

DOI: 10.1103/PhysRevB.92.115106 PACS number(s): 71.10.Fd, 71.35.−y, 71.45.Lr, 71.30.+h

I. INTRODUCTION

Excitonic insulator (EI) phases show a spontaneous coherence between conduction-band electrons and valence-band holes, where the prior formation of bound electron-hole pairs (excitons) is typically triggered by the interband Coulomb interaction. The condensation of excitons in an EI state was theoretically predicted half a century ago to occur in semiconductors (semimetals) with small band gap (band overlap) [1–3]. The condensed excitonic phase can be characterized by a nonvanishing order parameter $\langle c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}} f_{\boldsymbol{k}}\rangle$, where $c^\dagger_{\boldsymbol{k}}$ and $f^\dagger_{\boldsymbol{k}}$ are the creation operators of an electron in the conduction and valence bands, respectively. If the valence-band top and conduction-band bottom are separated by the wave vector $\boldsymbol{Q}$, the system forms a density wave with modulation $\boldsymbol{Q}$. It is important to note that the EI—despite representing a macroscopic, phase-coherent quantum state—does not necessarily feature supertransport properties.

The experimental efforts to establish the EI in weakly correlated bulk materials largely failed. It is only recently that exciton condensation has been addressed in systems with rather strong electronic correlations [4]. In this regard, Tm(Se,Te) was argued to exhibit a pressure-induced excitonic instability, related to an anomalous increase in the electrical resistivity and thermal diffusivity [5,6]. The charge-density-wave (CDW) state observed in $1T$-$TiSe_2$ was claimed to be of excitonic origin [7–14]. In $Ca_{1-x}La_xB_6$, the weak ferromagnetism was interpreted in terms of doped spin-triplet excitons [15–17]. The condensation of spin-triplet excitons was also predicted to occur in the proximity of the spin-state transition [18], of which $Pr_{0.5}Ca_{0.5}CoO_3$ is an example [19,20]. Likewise, the structural phase transition of the layered chalcogenide Ta_2NiSe_5 has been attributed to a spin-singlet EI [21–24]. The spin-density-wave (SDW) state of iron-pnictide superconductors has sometimes been argued to be of the excitonic origin as well [25–28]. Finally, an EI state was suggested in a t_{2g}-orbital system with strong spin-orbit coupling [29].

From the theoretical side, the extended Falicov-Kimball model was considered as a paradigmatic model to describe the EI formation and the closely related phenomenon of electronic ferroelectricity [30–41]. Here the spin degrees of freedom were not taken into account, however. Excitonic phases in strongly correlated spinful systems can be discussed in the framework of two-band Hubbard-type models. Including thereby the Hund's rule coupling is known to stabilize the spin-triplet excitonic phase in the otherwise degenerate spin-singlet and spin-triplet excitonic phases [18–20,28,42,43]. On the other hand, we have shown in our previous work [43] that taking into account electronic interactions only, a spin-singlet excitonic phase cannot be stabilized, which may however be realized in $1T$-$TiSe_2$ and Ta_2NiSe_5, where the importance of electron-phonon coupling was recently pointed out [10–14,23]. Although the spin-singlet excitonic state has been investigated in the spinless multiband model with electron-phonon coupling [12,44,45], not much is known about the role of the electron-phonon coupling played in the excitonic density wave states in the spinful multiband Hubbard model.

Motivated by the recent developments in the field, in this paper, we will thoroughly investigate the stability of the excitonic density wave states in the two-band Hubbard model with additional electron-phonon coupling and Hund's rule exchange. The model is analyzed employing static mean-field theory for the electron-phonon coupling and the variational cluster approximation (VCA) for the electronic correlations. In doing so, we will first show that the interband Coulomb interaction U' and electron-phonon interaction λ cooperatively stabilize the CDW and that a smooth crossover occurs between "excitonic" CDW and "phononic" CDW states, just by increasing the ratio λ/U'. Incorporating the Hund's rule coupling J, an excitonic SDW state competes with the excitonic CDW. The ground-state phase diagram of such extended two-band Hubbard model is determined in the J-λ plane. We will, moreover, pay particular attention to the phase of the order parameter in the presence of the electron-phonon and Hund's rule couplings and show that both electron-phonon coupling and pair-hopping terms fix the phase of the excitonic order parameters, thereby preventing the system from realizing a superfluid. Finally, the implications for exciton condensation in real materials will be discussed.

The paper is organized as follows: In Sec. II, we present our model and briefly outline the methods of calculations. The numerical results will be presented in Sec. III, where electron-phonon interaction, Hund's rule coupling, and pair-hopping effects will be discussed and the ground-state phase diagram is derived. Section IV relates our results to recent experiments and draws conclusions.

II. MODEL AND METHODS

A. Model Hamiltonian

We consider the two-band Hubbard model, supplemented by electron-phonon and Hund's rule coupling terms,

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}^U_{e\text{-}e} + \mathcal{H}^J_{e\text{-}e} + \mathcal{H}_{ph} + \mathcal{H}_{e\text{-}ph}, \tag{1}$$

defined on a two-dimensional square lattice. The noninteracting f/c-band electrons are described by

$$\mathcal{H}_e = \sum_{\boldsymbol{k},\sigma} \varepsilon^f_{\boldsymbol{k}} f^\dagger_{\boldsymbol{k}\sigma} f_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k},\sigma} \varepsilon^c_{\boldsymbol{k}} c^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}, \tag{2}$$

where $f^\dagger_{\boldsymbol{k}\sigma}$ ($c^\dagger_{\boldsymbol{k}\sigma}$) denotes the creation operator of an electron with momentum $\boldsymbol{k}$ and spin σ ($=\uparrow,\downarrow$) in the f (c) band. Within the tight-binding approximation, the dispersion of band α ($=f,c$) is given by $\varepsilon^\alpha_{\boldsymbol{k}} = -2t_\alpha(\cos k_x + \cos k_y) + \varepsilon_\alpha - \mu$, where t_α is the electron hopping integral between the neighboring sites and ε_α is the on-site energy of the α orbital. We assume $\varepsilon_f < 0$ and $\varepsilon_c > 0$, so that the f and c bands correspond to the valence and conduction bands, respectively. The chemical potential μ is fixed to ensure a filling of two electrons per site (half filling), i.e., $\langle n^f_i \rangle + \langle n^c_i \rangle = 2$ with $n^\alpha_i = n^\alpha_{i\uparrow} + n^\alpha_{i\downarrow} = \alpha^\dagger_{i\uparrow}\alpha_{i\uparrow} + \alpha^\dagger_{i\downarrow}\alpha_{i\downarrow}$.

The repulsive Coulomb interaction takes the form

$$\mathcal{H}^U_{e\text{-}e} = U_f \sum_i n^f_{i\uparrow} n^f_{i\downarrow} + U_c \sum_i n^c_{i\uparrow} n^c_{i\downarrow} + U' \sum_i n^f_i n^c_i, \tag{3}$$

where U_α is its intraorbital part and U' gives the interorbital contribution that is responsible for an effective electron-hole attraction and eventually for an excitonic instability in the system. The Hund's exchange interaction is defined by

$$\begin{aligned}\mathcal{H}^J_{e\text{-}e} = &-2J \sum_i \left(\boldsymbol{S}^f_i \cdot \boldsymbol{S}^c_i + \frac{1}{4} n^f_i n^c_i \right) \\ &- J' \sum_i \left(f^\dagger_{i\uparrow} f^\dagger_{i\downarrow} c_{i\uparrow} c_{i\downarrow} + c^\dagger_{i\uparrow} c^\dagger_{i\downarrow} f_{i\uparrow} f_{i\downarrow} \right),\end{aligned} \tag{4}$$

with $\boldsymbol{S}^\alpha_i = \sum_{\sigma,\sigma'} \alpha^\dagger_{i\sigma} \boldsymbol{\sigma}_{\sigma\sigma'} \alpha_{i\sigma'}/2$, where $\boldsymbol{\sigma}$ is the vector of Pauli matrices. J and J' are the strengths of the Hund's rule coupling and pair-hopping term, respectively. J and J' will stabilize a spin-triplet excitonic state [43].

In Eq. (1), we also included the phonon degrees of freedom because the lattice displacements play an important role in the materials under consideration. The electron-phonon coupling becomes particularly important when we address spin-singlet electron-hole excitations. In the harmonic approximation, the phonon part of the Hamiltonian is given by

$$\mathcal{H}_{ph} = \sum_{\boldsymbol{q}} \omega_{\boldsymbol{q}} b^\dagger_{\boldsymbol{q}} b_{\boldsymbol{q}}, \tag{5}$$

where the bosonic operator $b^\dagger_{\boldsymbol{q}}$ creates a phonon with momentum $\boldsymbol{q}$ and frequency $\omega_{\boldsymbol{q}}$ (we have set $\hbar = 1$). The dominant electron-phonon coupling term between a c-f (electron-hole) excitation and lattice displacement is assumed to be

$$\mathcal{H}_{e\text{-}ph} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k},\boldsymbol{q}} \sum_\sigma g_{\boldsymbol{q}} (b_{\boldsymbol{q}} + b^\dagger_{-\boldsymbol{q}}) c^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma} f_{\boldsymbol{k}\sigma} + \text{H.c.}, \tag{6}$$

with coupling constant $g_{\boldsymbol{q}}$ [12,14,44,45].

Throughout the paper, we fix the hopping parameters $t_f = t_c = t$ and use t as the unit of energy. Furthermore, we set $\varepsilon_c/t = -\varepsilon_f/t = 3.2$, so that the noninteracting band structure represents a semimetal with a small band overlap. The conduction-band bottom at $\boldsymbol{k} = (0,0)$ gives rise to an electron pocket, while the valence-band top produces a hole pocket at $\boldsymbol{k} = (\pi,\pi)$, resulting in the modulation vector of the density wave $\boldsymbol{Q} = (\pi,\pi)$; see Ref. [42] for the band dispersion and Fermi surface in the Brillouin zone of the square lattice. For simplicity, we assume $U_f = U_c = U$ and employ $U = 2U' - J$ to suppress the Hartree shift [46]. In this choice, the EI state is stabilized between the band-insulator and Mott-insulator states [42,43]. Moreover, we consider a dispersionless Einstein phonon $\omega_{\boldsymbol{q}} = \omega$ and a momentum-independent electron-phonon coupling constant $g_{\boldsymbol{q}} = g$. Since the strength of the electron-phonon coupling appears in the form $\lambda = g^2/\omega$ in the mean-field approximation used below, we take λ as the electron-phonon coupling parameter in what follows.

B. Mean-field approximation for the phonons

We treat the electron-phonon interaction term $\mathcal{H}_{e\text{-}ph}$ in the mean-field (frozen-phonon) approximation. Introducing the expectation values of the c-f hybridization $\langle c^\dagger f \rangle$ and lattice displacement $\langle b \rangle$, the operators in Eq. (6) are approximated as $b_{\boldsymbol{q}} c^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma} f_{\boldsymbol{k}\sigma} \sim [\langle b_{\boldsymbol{q}} \rangle c^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma} f_{\boldsymbol{k}\sigma} + b_{\boldsymbol{q}} \langle c^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma} f_{\boldsymbol{k}\sigma} \rangle] \delta_{\boldsymbol{q},\boldsymbol{Q}} - \langle b_{\boldsymbol{q}} \rangle \langle c^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma} f_{\boldsymbol{k}\sigma} \rangle \delta_{\boldsymbol{q},\boldsymbol{Q}}$. Since in our model the nesting vector $\boldsymbol{Q} = (\pi,\pi)$ is commensurate with the lattice periodicity, $e^{2i\boldsymbol{Q}\cdot\boldsymbol{r}_i} = 1$ for lattice vectors $\boldsymbol{r}_i$. Hence, we have $b_{\boldsymbol{Q}} = b_{-\boldsymbol{Q}}$ ($b^\dagger_{\boldsymbol{Q}} = b^\dagger_{-\boldsymbol{Q}}$) [12], where $b_{\boldsymbol{Q}}$ and $b_{-\boldsymbol{Q}}$ ($b^\dagger_{\boldsymbol{Q}}$ and $b^\dagger_{-\boldsymbol{Q}}$) annihilate (create) the same phonon. This implies $\langle b_{\boldsymbol{Q}} \rangle = \langle b_{-\boldsymbol{Q}} \rangle = \langle b^\dagger_{\boldsymbol{Q}} \rangle$, and therefore $\langle b_{\boldsymbol{Q}} \rangle$ becomes a real number. In view of $\langle c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}\sigma} f_{\boldsymbol{k}\sigma} \rangle = \langle f^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{Q}\sigma} \rangle^* \neq 0$, we define the complex order parameter of the excitonic CDW as

$$\Phi_c = |\Phi_c| e^{i\theta_c} = \frac{1}{2N} \sum_{\boldsymbol{k},\sigma} \langle c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}\sigma} f_{\boldsymbol{k}\sigma} \rangle, \tag{7}$$

where $|\Phi_c|$ and θ_c are the amplitude and phase of the order parameter, respectively. Then the electron-phonon part in the mean-field approximation is

$$\begin{aligned}\mathcal{H}^{\text{MF}}_{e\text{-}ph} = &\frac{2g}{\sqrt{N}} \langle b_{\boldsymbol{Q}} \rangle \sum_{\boldsymbol{k},\sigma} (c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}\sigma} f_{\boldsymbol{k}\sigma} + f^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{Q}\sigma}) \\ &+ 4g\sqrt{N} (b^\dagger_{\boldsymbol{Q}} + b_{\boldsymbol{Q}}) |\Phi_c| \cos\theta_c \\ &- 8g\sqrt{N} \langle b_{\boldsymbol{Q}} \rangle |\Phi_c| \cos\theta_c.\end{aligned} \tag{8}$$

Introducing $B_{\boldsymbol{q}} = b_{\boldsymbol{q}} + \delta_{\boldsymbol{q},\boldsymbol{Q}}(4g\sqrt{N}/\omega)|\Phi_c|\cos\theta_c$, the phonon Hamiltonian $\mathcal{H}_{ph}$ together with the second term of the right-hand side of Eq. (8) can be diagonalized, yielding $\omega\sum_{\boldsymbol{q}} B^\dagger_{\boldsymbol{q}} B_{\boldsymbol{q}} - 16\lambda N|\Phi_c|^2\cos^2\theta_c$. Hence, from $\langle B_{\boldsymbol{Q}}\rangle = \langle B^\dagger_{\boldsymbol{Q}}\rangle = 0$, we find

$$\langle b_{\boldsymbol{Q}}\rangle = \langle b^\dagger_{\boldsymbol{Q}}\rangle = -\frac{4g\sqrt{N}}{\omega}|\Phi_c|\cos\theta_c. \tag{9}$$

Substituting this expression into Eq. (8), we finally obtain the mean-field electron-phonon Hamiltonian,

$$\mathcal{H}^{\mathrm{MF}}_{e\text{-}ph} = \Delta_p\cos\theta_c\sum_{\boldsymbol{k},\sigma} f^\dagger_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}+\boldsymbol{Q}\sigma} + \mathrm{H.c.} + \frac{N\Delta_p^2}{4\lambda}\cos^2\theta_c, \tag{10}$$

with $\Delta_p = -8\lambda|\Phi_c|$. Using Eq. (10), below we will minimize the grand potential of the system with respect to Δ_p and θ_c.

We define the complex order parameter of the excitonic SDW as

$$\Phi_s = |\Phi_s|e^{i\theta_s} = \frac{1}{2N}\sum_{\boldsymbol{k},\sigma}\sigma\langle c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}\sigma}f_{\boldsymbol{k}\sigma}\rangle, \tag{11}$$

where $|\Phi_s|$ and θ_s are the amplitude and phase of the order parameter, respectively. Because we assume an SDW state with modulation vector $\boldsymbol{Q} = (\pi,\pi)$, where the expectation value $\langle c^\dagger_{i\uparrow}f_{i\uparrow}\rangle$ is in antiphase compared to $\langle c^\dagger_{i\downarrow}f_{i\downarrow}\rangle$ regarding the spatial variation, these two expectation values have opposite signs on the same site. In momentum space, this reads $\sum_{\boldsymbol{k}}\langle c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}\uparrow}f_{\boldsymbol{k}\uparrow}\rangle = -\sum_{\boldsymbol{k}}\langle c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}\downarrow}f_{\boldsymbol{k}\downarrow}\rangle$. We then find, from Eqs. (7) and (9), that $\langle b_{\boldsymbol{Q}}\rangle = \langle b^\dagger_{\boldsymbol{Q}}\rangle \propto \sum_{\boldsymbol{k},\sigma}\langle c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}\sigma}f_{\boldsymbol{k}\sigma}\rangle = 0$, which means that the spin-triplet condensate will not couple to the phonons.

C. Variational cluster approximation

In order to take electron correlation effects into account, we treat the electronic interactions in (1) within the VCA [47,48], which is a quantum cluster method based on the self-energy functional theory [49]. The VCA first introduces disconnected clusters of finite size, for which the cluster self-energy Σ' can be computed exactly. In a next step, out of this, a superlattice is formed as a reference system. By restricting the trial self-energy to Σ', we obtain a certain approximation to the grand potential of the original system,

$$\Omega = \Omega' + \mathrm{Tr}\ln\left(G_0^{-1} - \Sigma'\right)^{-1} - \mathrm{Tr}\ln(G'), \tag{12}$$

where Ω' and G' are the grand potential and Green's function of the reference system, respectively, and G_0 is the noninteracting Green's function; for further details, see Refs. [50,51]. In doing so, the short-range electron correlations within the cluster of the reference system are treated exactly. In our VCA calculation, we take an $L_c = 2\times 2 = 4$ site (eight-orbital) cluster as the reference system and we use exact diagonalization to solve the corresponding quantum many-body problem in the cluster. Within VCA, we can take into account spontaneous symmetry breakings just by adding appropriate Weiss fields to the reference system [48], and take these fields as variational parameters. The Weiss fields for excitonic CDW and SDW states, which are defined by the order parameter Φ_c [in Eq. (7)] and Φ_s [in Eq. (11)], respectively, may be written as

$$\mathcal{H}^{\mathrm{WF}}_{\mathrm{c}} = \Delta_0' e^{i\theta_c}\sum_{\boldsymbol{k},\sigma} f^\dagger_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}+\boldsymbol{Q}\sigma} + \mathrm{H.c.}, \tag{13}$$

$$\mathcal{H}^{\mathrm{WF}}_{\mathrm{s}} = \Delta_s' e^{i\theta_s}\sum_{\boldsymbol{k},\sigma}\sigma f^\dagger_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}+\boldsymbol{Q}\sigma} + \mathrm{H.c.} \tag{14}$$

Here, Δ_0' and Δ_s' are the strengths of the Weiss fields for the excitonic CDW and SDW states generated by $\mathcal{H}^U_{e\text{-}e}$ and $\mathcal{H}^J_{e\text{-}e}$.

According to Eq. (10), we take into account the contribution of the phonons in the mean-field approximation as a one-particle term in the original system. Then, the Hamiltonian describing an excitonic CDW state in the reference system is given by

$$\mathcal{H}'_{\mathrm{c}} = \mathcal{H}_e + \mathcal{H}^U_{e\text{-}e} + \mathcal{H}^J_{e\text{-}e} + \mathcal{H}^{\mathrm{MF}}_{e\text{-}ph} + \mathcal{H}^{\mathrm{WF}}_{\mathrm{c}}, \tag{15}$$

where we note that $\mathcal{H}_e + \mathcal{H}^U_{e\text{-}e} + \mathcal{H}^J_{e\text{-}e} + \mathcal{H}^{\mathrm{MF}}_{e\text{-}ph}$ is the Hamiltonian of the original system and the Weiss field $\mathcal{H}^{\mathrm{WF}}_{\mathrm{c}}$ is added in the reference system. Using $\mathcal{H}'_{\mathrm{c}}$, we calculate the grand potential Ω and optimize the variational parameters Δ_0', Δ_p, and θ_c. The most stable solution with $(\Delta_0',\Delta_p) \neq (0,0)$ corresponds to the excitonic CDW state. Note that we determine the parameters Δ_p and θ_c via the minimization of the grand potential rather than solving the self-consistent equation. Both procedures are equivalent, however, since the order parameter Φ_c calculated, using the Green's function with Δ_p and θ_c optimized via the grand potential calculation in VCA, exactly satisfies the self-consistent condition $\Delta_p = 8\lambda\Phi_c$.

Since the spin-triplet term does not couple to the lattice degrees of freedom within our mean-field approach, the phonons will not affect the excitonic SDW state. Then the Hamiltonian of the reference system describing an excitonic SDW is

$$\mathcal{H}'_{\mathrm{s}} = \mathcal{H}_e + \mathcal{H}^U_{e\text{-}e} + \mathcal{H}^J_{e\text{-}e} + \mathcal{H}^{\mathrm{WF}}_{\mathrm{s}}. \tag{16}$$

Again we calculate the grand potential Ω from the reference Hamiltonian $\mathcal{H}'_{\mathrm{s}}$ and optimize variational parameters Δ_s' and θ_s, where the most stable solution with $\Delta_s' \neq 0$ corresponds to the SDW state.

III. NUMERICAL RESULTS

A. Phase of the order parameters

We first discuss the phase of the different order parameters entering the grand potential. In the spin-singlet excitonic state, the system forms an excitonic CDW at any finite U' and λ due to the perfect nesting of the Fermi surface. Figure 1(a) shows the calculated grand potential Ω as a function of the variational parameters Δ_0' and Δ_p. Obviously the grand potential has a stationary point at $(\Delta_0',\Delta_p) \neq (0,0)$, signaling a CDW ordering. Without electron-phonon coupling, Ω is independent of the phase θ_c, i.e., $\Omega(\theta_c) = \Omega(\theta_c')$. Accordingly, the excitonic CDW state reveals a gapless acoustic phase mode in its excitation spectrum [45]. If, however, the electron-phonon coupling comes into play, the grand potential manifests a dependence on the phase of the (complex) order parameter. In Fig. 1(b), we display the θ_c dependence of Ω; the grand potential takes its minimum at $\theta_c = 0,\pi$. This phase fixation

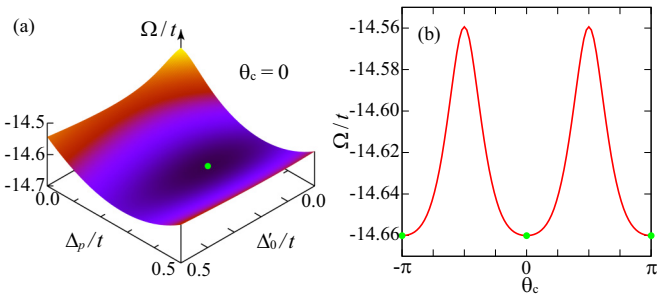

FIG. 1. (Color online) (a) Grand potential Ω as a function of the variational parameters Δ_0' and Δ_p for $U'/t = 4$ and $\lambda/t = 0.15$. (b) θ_c dependence of Ω taken the values of Δ_0' and Δ_p optimized at $\theta_c = 0$. Green dots indicate the stationary points.

may be expected looking at Eq. (10). In our mean-field approximation, the single-particle gap caused by λ is given as $\Delta_p \cos\theta_c$ and is maximized at $\theta_c = 0$. When θ_c is fixed by the electron-phonon coupling, the collective phase mode in the spin-singlet excitonic state becomes massive (see the discussion of the spinless model in Ref. [45]).

In the case of the spin-triplet excitonic state, the excitonic SDW and CDW states are degenerate if the electron-phonon and Hund's couplings are neglected. The Hund's exchange terms $\propto J$ and $\propto J'$ lift this degeneracy and stabilize the SDW state [43]. Note that the θ_s dependence of the grand potential behaves differently in the presence or absence of the pair-hopping term J': For $J' = 0$, the grand potential of the SDW state does not depend on θ_s, i.e., $\Omega(\theta_s) = \Omega(\theta_s')$, whereas Ω depends on θ_s at any finite J'. Again the independence of Φ_s on the phase value θ_s accounts for a gapless excitation spectrum, i.e., an acoustic phase mode. Figure 2 gives the calculated grand potential Ω as a function of the phase θ_s in the presence of the pair-hopping term J'. Indeed we find that Ω has two minima, at $\theta_s = 0, \pi$, which fixes the phase θ_s of Φ_s. It is known that the energy in the presence of the pair-hopping-type exchange interaction shows a phase dependence $\cos 2\theta_s$ [52]. This is why the pair-hopping term J' fixes θ_s and in that way destroys the gapless acoustic phase mode in the spin-triplet excitonic state.

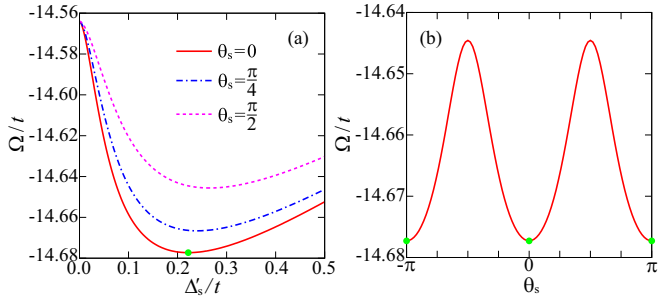

FIG. 2. (Color online) (a) Grand potential Ω as a function of the variational parameter Δ_s' at $U'/t = 4$ and $J/t = J'/t = 1$. (b) θ_s dependence of Ω obtained using the value of Δ_s' optimized at $\theta_s = 0$. Dots mark stable stationary points.

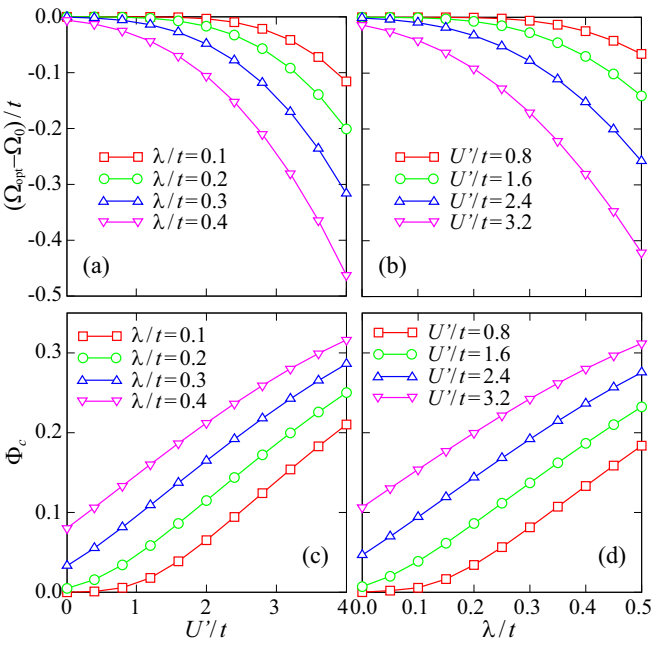

FIG. 3. (Color online) Optimized values of the grand potential $\Omega_{\rm opt}$ in dependence on (a) U'/t and (b) λ/t. Here, Ω_0 is the grand potential in the normal (semimetallic) state. Order parameter Φ_c for the excitonic CDW state as a function of (c) U'/t and (d) λ/t.

B. Excitonic CDW state

Now let us analyze the stability of the CDW state in the presence of the electron-phonon coupling in more detail. In Fig. 3, we present the results for both the optimized grand potential $\Omega_{\rm opt}$ and the order parameter Φ_c when the interband Coulomb interaction U' and the electron-phonon coupling λ are varied. $\Omega_{\rm opt}$ indicates that (i) the symmetry-broken CDW state is lower in energy than the normal state and (ii) the stability of the CDW state is enhanced if U' and λ are increased; see Figs. 3(a) and 3(b). This is corroborated by the behavior of the order parameter Φ_c displayed in Figs. 3(c) and 3(d). We see that the interband Coulomb interaction U' induces and boosts the excitonic CDW state while the electron-phonon coupling λ rather promotes a phononic CDW state (see below). Both, however, cooperatively stabilize a charge-ordered state. In this connection, the electron-phonon coupling lifts the degeneracy of CDW and SDW that exists for $\lambda = 0$.

In the mean-field approximation, the gap parameter of the CDW state, $\Delta_c = (U' + 8\lambda)\Phi_c$, can be separated into two contributions: the excitonic (or interband Coulomb driven) part $\Delta_0 = U'\Phi_c$ and the phononic (or electron-phonon driven) part $\Delta_p = 8\lambda\Phi_c$. Figure 4(a) illustrates the relative magnitude of Δ_0 and Δ_p, in dependence on the ratio $8\lambda/U'$. At $8\lambda/U' \ll 1$, $\Delta_c \simeq \Delta_0 \gg \Delta_p$ and the CDW state, stabilized by the interband Coulomb interaction U', is excitonic by its nature. Increasing $8\lambda/U'$, Δ_0 decreases while Δ_p increases, indicating a smooth crossover to a phononic CDW, which fully develops at $8\lambda/U' \gg 1$, where $\Delta_c \simeq \Delta_p \gg \Delta_0$. In the crossover region $8\lambda/U' \simeq 1$, both excitonic and phononic contributions are equally important.

In Figs. 4(b)–4(e), we show the behavior of the different contributions to the gap parameter Δ_c when U' and λ are varied

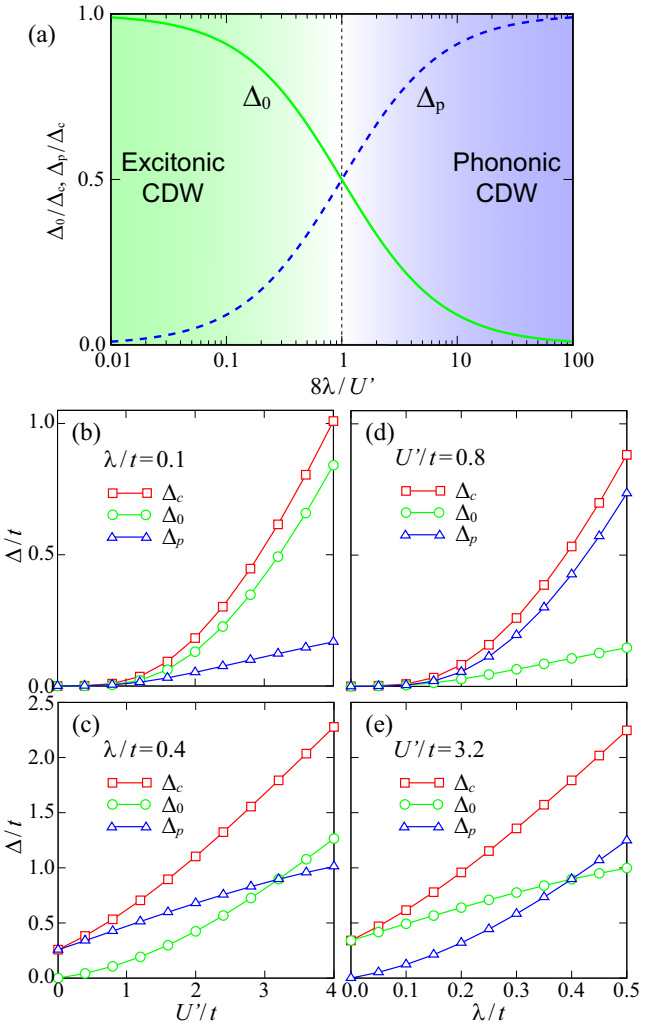

FIG. 4. (Color online) (a) Excitonic gap parameter Δ_0 (solid line) and phononic gap parameter Δ_p (dashed line) divided by the total gap $\Delta_c = \Delta_0 + \Delta_p$. Δ_c, Δ_0, and Δ_p are separately plotted as a function of (b),(c) U'/t and (d),(e) λ/t.

separately. Data are obtained by VCA. Enhancing U'/t (λ/t) at weak λ/t (small U'/t) leads to an increase in Δ_p (Δ_0) as well, since both interactions couple to the same operator-product expectation value $\langle c^\dagger_{\boldsymbol{k}+\boldsymbol{Q}\sigma} f_{\boldsymbol{k}\sigma}\rangle$; see Figs. 4(b) and 4(d). The crossover between excitonic and phononic CDWs can be seen in Figs. 4(c) and 4(e), where a crossing between Δ_p and Δ_0 appears when $U' \simeq 8\lambda$.

C. Excitonic SDW state

We now study the influence of the Hund's rule coupling on the nature of the excitonic phase, and also when an additional electron-phonon coupling acts in the system. Evidently, excitonic CDW and SDW states are degenerate at $J = J' = 0$ and $\lambda = 0$ [42,43]. Any finite J and/or λ lifts this degeneracy. Figure 5 clearly shows that by increasing J, the optimized grand potential $\Omega_{\rm opt}$ for the SDW (CDW) state monotonically decreases (increases); accordingly, the order parameter for the SDW (CDW) phase is enhanced (suppressed). This holds for both $J' > 0$ and $J' = 0$. Clearly the SDW state is stable as

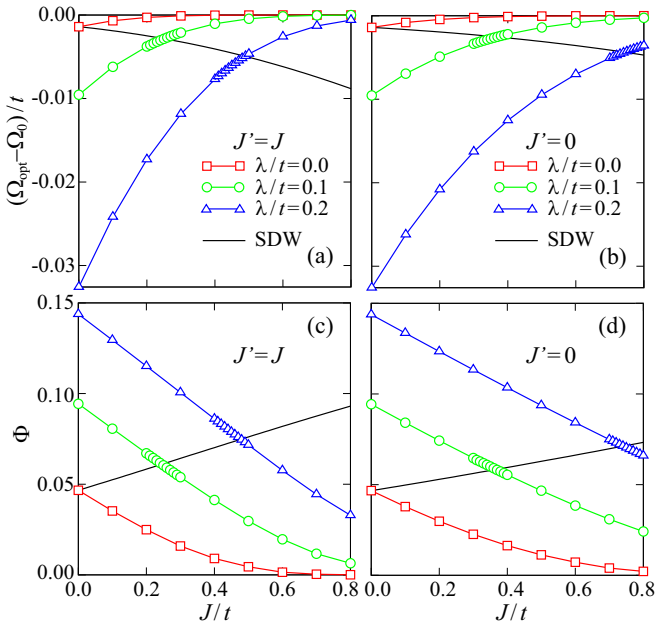

FIG. 5. (Color online) J dependence of the grand potential $\Omega_{\rm opt}$ and the order parameter Φ in the excitonic CDW (symbols) and SDW (solid line) states (a),(c) with ($J' = J$) and (b),(d) without ($J' = 0$) the pair-hopping term, where $U'/t = 2.4$. Ω_0 is the grand potential of the normal semimetallic state.

soon as $\Omega^{\rm SDW}_{\rm opt}$ becomes less than $\Omega^{\rm CDW}_{\rm opt}$. A finite pair-hopping term $\propto J'$ amplifies the tendency towards SDW formation [43].

D. Ground-state phase diagram

The competition between electron-phonon and Hund's rule coupling effects leads to the ground-state phase diagram of the model (1) presented in Fig. 6. Obviously, λ and J tend to establish CDW and SDW phases, respectively, on top of

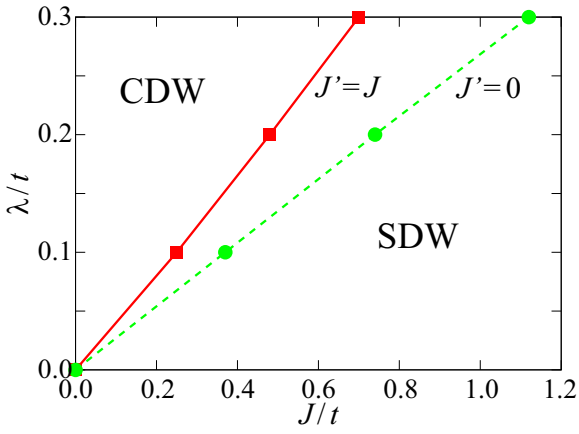

FIG. 6. (Color online) Ground-state phase diagram of the two-band Hubbard model with electron-phonon and Hund's rule couplings showing the stability regions of excitonic CDW and SDW phases. Results are obtained, in the presence ($J' = J$) and absence ($J' = 0$) of the pair-hopping term, by combining the mean-field and VCA approaches, for a two-dimensional (square) lattice at half filling, where $U'/t = 2.4$.

an excitonic state enforced by U'. A finite J' increases the region in the J-λ plane where the excitonic SDW is the ground state. We note that the SDW-CDW transition is a first-order transition, within the limits of our approximations.

IV. DISCUSSION AND CONCLUSIONS

First, let us discuss implications of our findings on materials aspects. The transition-metal chalcogenides $1T$-$TiSe_2$ and Ta_2NiSe_5 have recently been discussed in terms of the spin-singlet EI. In these systems, the valence and conduction bands are formed by orbitals located on different atoms. For example, in $1T$-$TiSe_2$, the $4p$ orbitals of Se ions account for the valence bands and the $3d$ orbitals of Ti ions account for the conduction bands [7–14], and in Ta_2NiSe_5, the $3d$ orbitals of Ni ions form the valence bands and the $5d$ orbitals of Ta ions form the conduction bands [21–24]. Hund's rule coupling, acting between electrons on different orbitals of a single ion and favoring the spin-triplet excitons, is therefore negligible. Rather, in these materials, the electron-phonon coupling is at play and will stabilize a spin-singlet EI state. The interband Coulomb interaction and electron-phonon interaction, which are inherently interrelated in these materials, will cooperatively stabilize the EI CDW, which is predominantly phononic or excitonic depending on the importance of electron-phonon or Coulomb effects.

By contrast, in the iron-pnictide superconductors [26–28] and Co oxides [18–20], the valence and conduction bands are formed by the d orbitals on the (same) transition-metal ions, so that the Hund's rule coupling is expected to be strong. Hence, in these materials, the SDW phase, if really excitonic in origin, is rather triggered by the Hund's rule coupling than by electron-phonon coupling. Then, as our phase diagram suggests, the condensation of spin-triplet excitons will play a major role.

Second, let us comment on the phase of the excitonic order parameters. On the one hand, as we have shown in the preceding section, the electron-phonon interaction stabilizes the spin-singlet excitonic condensate, whereas exchange interactions such as the Hund's rule couplings stabilize a spin-triplet excitonic condensate in the otherwise degenerate excitonic density-wave states. On the other hand, these interactions, in particular the electron-phonon and pair-hopping interactions, will fix the phase of the order parameter of the excitonic state; see Sec. III A. Because the spatial modulations of the CDW and SDW are given by $\cos(\boldsymbol{Q}\cdot\boldsymbol{r}_i+\theta)$, the phase θ may lead to a translational motion of the condensate as a whole [53]. If the energy of the condensate is independent of the phase, maintaining the continuous symmetry of the system with respect to the phase, a gapless acoustic phase mode may appear in the excitation spectrum, allowing for a translational motion of the condensate without loss of energy (i.e., superfluidity), as predicted by Fröhlich in his theory of incommensurate density waves [54]. In real materials, however, excitonic condensation will be influenced by the lattice degrees of freedom or affected by the pair-hopping term. Then the phase of the condensate is fixed and a gap opens for the collective phase mode. This makes realization of excitonic superfluidity in real materials unlikely.

To summarize, we have studied the stability of the excitonic states with charge and spin density modulations in terms of the two-band Hubbard model, supplemented by electron-phonon and Hund's rule interactions, where the static mean-field theory is employed for coupling to the lattice degrees of freedom and the variational cluster approximations for the electron correlations. We have shown that both the interband Coulomb interaction U' and the electron-phonon coupling λ tend to stabilize an excitonic CDW state. While at $\lambda=0$ the excitonic insulator exhibits an acoustic phase mode, any finite λ fixes the phase of the order parameter and therefore eliminates such a gapless excitation related to supertransport properties. The CDW typifies a predominantly excitonic and phononic state for small and large ratios $8\lambda/U'$, respectively. The Hund's rule coupling J, on the other hand, promotes an excitonic SDW phase, which is further stabilized by pair-hopping processes, which also fixes the phase of the order parameter. These results obtained for a generic microscopic model Hamiltonian should contribute to a better understanding of exciton condensation in several material classes with strong electronic correlations.

ACKNOWLEDGMENTS

The authors would like to thank H. Beck, K. Seki, and H. Watanabe for enlightening discussions. T.K. acknowledges support from a JSPS Research Fellowship for Young Scientists. This work was funded in part by a KAKENHI Grant No. 26400349 of Japan. B.Z. and H.F. are supported by Deutsche Forschungsgemeinschaft (Germany) through the Collaborative Research Center 652, Project B5.

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