Carriers binding to excitons: Crystal-field excitations in doped Mott-Hubbard insulators

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We address the role played by orbital degeneracy in doped Mott-Hubbard insulators. We observe that in all but the simplest systems the carriers bind to *d-d* excitons because of Hund's-rule interactions. These three-particle bound states have distinct spectroscopic signatures and at least in one case these seem already confirmed experimentally. If the crystal-field gaps become of the order of the kinetic energy of the carriers, doping might tend to stabilize phases characterized by a finite occupation of *d-d* excitons in the ground state. If the total spin of both the carrier state and the spin background are at maximum, the relevant excitons do not involve a change in spin. As a consequence, the orbital channel can be in the first instance considered independently from the spin channel and we find an exciton-carrier coupling that in essence interpolates between the carrier-spin-wave couplings of the *t-J* model and the conventional couplings to optical phonons. We work out in detail a case involving high-spin holes in a cupratelike system and we show that the exciton-carrier coupling tends to stabilize an orthorhombic type of orbital order. On the other hand, if either the carriers or the background are in a low-spin state, the relevant excitons also change total spin locally and more-exotic order parameters are possible. We analyze in detail the case of a nickelate close to the high-spin–low-spin transition where we show that doping will tend to stabilize an ordering related to superpositions of low-spin and high-spin states, characterized by an overall spin-rotational invariance. We argue that such a state might be realized in *n*-type La_2NiO_4.

I. INTRODUCTION

Taking the theory of correlated fermions literally, this subject could be to a large extent understood by considering ensembles of effective hydrogen atoms. With few exceptions ($1/N$ theory for Ce intermetallics,[1] the quadrupolar Kondo effect,[2] some work in itinerant magnetism[3]) orbital degeneracy is not considered explicitly, in favor of a description in terms of spin degeneracy alone. In many cases it is possible to argue that orbital degeneracies are irrelevant, as for instance seems established for the high-T_c superconductors.[4] However, very little is known about specific effects of orbital degeneracy in correlated systems in situations where it does matter.

In this paper we will address the role of orbital degeneracy in doped Mott-Hubbard insulators. In fact, van Vleck's "crystal-" or "ligand-field"[5] theory deals with the complications introduced by orbital degeneracy in the undoped insulators. In contrast to the spin degrees of freedom, the continuous symmetry of the atomic angular momentum states is explicitly broken by the lattice. At the same time, the presence of more than one orbital channel introduces states with different spin multiplicities. Accordingly, crystal-field and exchange gaps appear in the ionic excitation spectra, which are typically much smaller than the (Hubbard) gap in the charge excitation spectrum. Hence, in addition to the spin waves, so-called crystal-field or *d-d* excitons are found inside the Hubbard charge gap, with multiplicities, etc., determined by the point symmetry groups of the lattice.

Except for the spin-degenerate case, barely anything is known about what happens when such a system is doped with carriers. We will approach this problem from a strong-coupling perspective, not only in the sense of the on-site (monopole) Coulomb interaction (U) being large compared to the hopping (t), but also with respect to the actual values of the crystal-field and exchange splittings. If $t \rightarrow 0$, the carrier ($d^{n\pm1}$) charge state will have a multiplet spectrum with gaps comparable in magnitude to the crystal-field and exchange splittings at half-filling (d^n). As long as these gaps are large compared to the bandwidth of the carriers, the local exchange- and crystal-field interactions will determine the symmetry of the carrier state. This "projective renormalization" involving the excitonic gaps is much more robust than one might expect. For instance, in the high-T_c cuprates the excess holes are predominantly localized on the oxygen ions. Nevertheless, as Zhang and Rice[6] showed, the symmetry of the carrier state follows at least approximately the symmetries associated with the d^8 state of Cu.

It is well known that the balance between the Hund's-rule exchange coupling and the crystal-field energy determines whether the ground state of an insulator is low-spin (large crystal field) or high spin (large Hund's-rule coupling). This balance might work out quite differently depending on the charge state of the $3d$ ion. In other words, the symmetry of the carrier state can be drastically different from that of the spin background in which the carrier moves. van Elp *et al.*[7] pointed out an extreme example recently. CoO has a high-spin ($S=\frac{3}{2}$) d^7 ground

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state. Upon hole doping (with Li), the carrier corresponds with a Co d^6 state which is particularly sensitive to crystal-field splittings because the low spin state has a filled shell configuration. van Elp *et al.* find that the carrier ground state is indeed of the $S=0$ variety[7] and because single-particle hopping is only possible when the difference between the background and carrier spin is $\frac{1}{2}$, the carriers in hole doped CoO are completely localized.

As we will discuss in Sec. II, this becomes comprehensible if viewed from the following perspective: the two-body Hund's-rule interaction binds the crystal-field excitations of the d^n background to the carriers. The carriers are in fact hole- (or electron-) exciton bound states. These three-particle bound states are (at least superficially) related to the three-particle resonances proposed by Ruckenstein and Varma[8] in the context of high-T_c superconductivity. Guided by the assertion that a condensation of charge-transfer excitons might occur in the cuprates at higher doping concentration[9] these authors posed the question whether the anomalies of the metallic state could be caused by singularities in the three-particle (exciton-hole) vertex. Although this physics cannot be addressed in the present (strong-coupling) context, the existence of exciton-hole bound states is now unambiguous. Moreover, it is straightforward to show that these bound states should have clear spectroscopic signatures ("excitonic satellites"). As we show in Sec. II, strong experimental evidence already exists in favor of these *d-d* exciton-carrier composites.

Additional complications arise because the ground-state multiplets of the different charge states are not only characterized by their orbital character, but also by the total spin. The simplest situation arises when both the carrier state and the state of the background are characterized by maximum total spin ("high-high spin"). In this case, the relevant exciton only involves a change in orbital character. On the other hand, especially in more covalent materials (e.g., oxides), the background might be in the high-spin state and the carrier in the low-spin state (or vice versa) as in the example of van Elp *et al.*,[7] and this involves excitons which carry, in addition, a change in locally conserved total spin ("high-low spin").

In the high-high spin cases, the spins of the carrier and the background differ by no more than $\frac{1}{2}$ and single-particle hopping is therefore possible in all cases. Especially near the beginning and end of the 3*d* series, hopping might be allowed in the high-low spin cases as well. If the crystal-field and exchange splittings are much larger than the kinetic scales (hopping and superexchange), only spin degrees of freedom are left and the strong-coupling models are of the *t-J* variety. As we discussed elsewhere,[10] the high-low spin situation can be modeled with the large(r) S generalizations of the usual (spin-degenerate) *t-J* model.[11] However, for the high-high spin systems a novel variety of *t-J* like models is found. We showed elsewhere that the simplest model of this kind (triplet carriers in a doublet background) is radically different from the usual *t-J* model (e.g., absence of a quasiparticle pole in two dimensions).[10]

At half-filling, crystal-field excitations are unimportant for the macroscopic physics of the vast majority of Mott-Hubbard insulators. The reason is that the couplings are of the order of J (superexchange) which is usually much smaller than typical crystal-field splittings. Only if these latter splittings get small are effects of the orbital degrees of freedom expected. This happens frequently in rare-earth systems (where this subject is called "singlet-singlet" or "singlet-triplet" models[12]), while in the 3*d* series only a small number of Cu compounds have been identified to exhibit "orbital" effects, which were analyzed in the seminal work by Kugel and Khomskii.[13] We argue that in the doped Mott-Hubbard systems these "orbital" effects are more frequent. The reason is that the Hund's-rule coupling can force the carriers into orbital configurations which strongly reduced the hopping probabilities. This kinetic-energy deficit can be partly restored by mixing in crystal-field excitons in the ground state. Hence, in the doped systems the crystal-field splittings have to be compared with transfer-matrix elements which are usually much larger than spin-spin interactions.

Because the orbital channel is strongly tied to the details of the lattice structure, the resulting physics is less generic than in the case of the spin-only problem. For no other reason than to keep the length of this paper finite, we limit ourselves to perovskite planes and we assume in addition that the higher-lying multiplets of the carrier charge state can always be neglected. Under these assumptions, the same excitons which bind to the carriers play a role in the delocalization process. In the high-high spin situation, this exciton does not change total spin and in this case generalizations of the *t-J* model are derived where the dynamics in orbital and spin channel are relatively independent. We analyze this in more detail in Sec. III using as a specific example of triplet holes in cuprate perovskite planes where the active exciton is of the tetragonal $(x^2-y^2 \rightarrow 3z^2-1)$ variety. Neglecting the spin channel altogether, we derive a classical phase diagram which bears some resemblances to the phase diagrams suggested in the context of the charge-transfer excitons. For increasing doping, a strongly first-order transition occurs (accompanied by phase separation) into a state with a finite occupancy of excitons in the d^9 background. The carrier-exciton couplings have some features in common with conventional electron-phonon couplings. At the same time, this problem bears some resemblances to that of holes delocalizing in uniaxial spin systems. The kinetic hole-exciton coupling favors ferro-orbital orderings, while the kinetic exchange at half-filling stabilizes staggered orbital configurations.[13]

Our findings in Sec. III largely confirm the simple intuition of what to expect from orbital degrees of freedom. The high-low spin problem offers in this respect a more interesting problem. Now the active exciton changes the local total spin and the excitonic and spin degrees of freedom cannot be considered separately at all. In Sec. IV we analyze the problem of a Nickelate which is close to the high-spin–low-spin transition, doped with low-spin carriers. We first analyze the (Kugel-Khomskii–like) problem at half-filling and we find, besides the usual Néel state, the possibility of an order parameter which is related to a mixture of the low-spin and the high-spin states

which at the same time obeys spin-rotational invariance. Especially in the n-type case, the carriers can gain kinetic energy when low-spin excitons are admixed in the high-spin background (or vice versa). In the neighborhood of the low-spin–high-spin transition this might cause a novel phase, characterized by a coexistence of Néel ordered normal spins and ferromagnetically ordered pseudospins.

II. *d-d* EXCITONS, CARRIERS, AND SPECTROSCOPY

Probably the most striking property of the Mott-Hubbard insulators (MHI) is the separation of spin and charge. Although it costs an energy of order U (on-site Coulomb interaction) to create a charge excitation, the spins can be excited at arbitrarily low energies, because the latter excitation does not violate the constraint of local charge neutrality. In all but the simplest MHI this is not the whole story. Besides the spins, it is also possible to change the orbital angular momentum state of the $3d$ ions, without invoking a charge excitation. The difference with the spin waves is that these excitations are massive, because the symmetry in orbital angular momentum space is explicitly broken by the lattice. However, the crystal-field energies are often much smaller than U and, accordingly, these excitations show up within the electronic band gap and are commonly referred to as crystal-field (or *d-d*) excitons. The same complications arise with regard to the carriers induced by doping, which in principle can be also internally excited. This would be all rather harmless, were it not for the atomic Hund's-rule interaction (J_H). This interaction, is in the end, responsible for the binding of the exciton to the carrier. To stay close to familiar grounds, let us consider a cupratelike situation. We assume a two-dimensional (2D) square lattice of $3d^9$ ions like a half-filled (undoped) high-temperature superconductor. The holes occupy $3d_{x^2-y^2}(x)$ orbitals in the ground state. Neglecting t_{2g} states, the *d-d* exciton involves the promotion of a hole to a $3d_{3z^2-1}(z)$ state, i.e., $x \rightarrow z$ with an exciton energy E_z. Upon p-type doping and in the strong-coupling limit (the hopping t much less than all other energy scales), the additional hole would have the choice to form one of the following local states,

$$
\begin{aligned}
|S_a\rangle &= |x\uparrow x\downarrow\rangle \ , \\
|T_1\rangle &= |x\uparrow z\uparrow\rangle \ , \\
|S_b\rangle &= (1/\sqrt{2})(|x\uparrow z\downarrow\rangle - |x\downarrow z\uparrow\rangle) \ ,
\end{aligned}
\tag{1}
$$

as well as the other spin components of the triplet states, $|T_m\rangle$ (in the notation of the D_{4h} point group, $|S_a\rangle \sim {}^1A_1$, $|T_m\rangle \sim {}^3B_1$, and $|S_b\rangle \sim {}^1B_1$). In the cuprates it is usually assumed that an additional hole doubly occupies the $|S_a\rangle$ state (and the Zhang-Rice singlet[6] is formed). However, it could as well be that instead the local triplet state $|T_m\rangle$ would be favored. In the absence of the Hund's-rule coupling, putting a hole into the z orbital would be a costly excitation, regardless the presence of the holes. However, J_H can only act if the holes of the d^8 state occupy different orbital channels, a situation which can only be realized if a *d-d* exciton is excited at the site of the hole. Schematically,

$$
|S_a\rangle + (x \rightarrow z) \rightarrow |T_1\rangle \ , \tag{2}
$$

and the right side is favored, if $J_H > E_z$. In other words, the exciton binds to the carrier, if the attractive interaction (J_H) overcomes the exciton energy (E_z). Binding more excitons to the hole is no issue here. A second exciton leads to a state $|zz\rangle$ which is again a singlet, destabilized by the Hund's-rule interaction, and more is not possible.

To convince oneself that this three-particle bound state is not merely semantics, it is helpful to consider the single electron spectral function (SES). If the quasiparticles are composite objects, the SES will reflect this, as for instance in the form of vibronic progressions in the case of small polarons (electrons bound to phonons). The most appropriate definition of a noninteracting analog in the present context is possibly the Koopmans theorem spectrum, derived from a Hartree-Fock calculation for the undoped system. This spectrum is in some important respects correct (e.g., it respects the Mott-Hubbard gap), but by keeping the additional hole(s) in extended states the binding to excitons is prohibited. We imagine an orbital degenerate system with on-site electron-electron interactions (in obvious notation) described by,[14]

$$
\begin{aligned}
H_C = \sum_i \Big[& (U+2J_H)(n_{ix\uparrow}n_{ix\downarrow} + n_{iz\uparrow}n_{iz\downarrow}) + U\sum_\sigma n_{ix\sigma}n_{iz-\sigma} \\
& + (U-J_H)\sum_\sigma n_{ix\sigma}n_{iz\sigma} - \frac{1}{2}J_H \sum_\sigma d^\dagger_{ix,\sigma}d_{ix,-\sigma}d^\dagger_{iz,-\sigma}d_{iz,\sigma} + E_z \sum_{i\sigma}(n_{iz,\sigma} - n_{ix,\sigma}) \Big] \ ,
\end{aligned}
\tag{3}
$$

and a hopping part of the form,

$$
H_K \sim t \sum_{\langle ij\rangle,\sigma} \left[d^\dagger_{ix\sigma}d_{jx\sigma} + \frac{1}{\sqrt{\alpha_0}}(d^\dagger_{ix\sigma}d_{jz\sigma} + \text{H.c.}) + \frac{1}{\alpha_0}d^\dagger_{iz\sigma}d_{jz\sigma} \right] \ , \tag{4}
$$

where the hopping in H_K takes place between the nearest neighbors, i and J ($\langle ij\rangle$ restricts the sum in (4) to nearest neighbors), while $\alpha_0 = 3$ for tight-binding $d_{x^2-y^2}$ and d_{3z^2-1} orbitals,[15] and smaller for more complicated orbitals. The last term in Eq. (3) is the crystal-field energy parametrized by a single parameter E_z. For large U/t the Koopmans theorem spectrum would be as indicated in Fig. 1(a) for a site with a $|x\uparrow\rangle$ state occupied (in hole

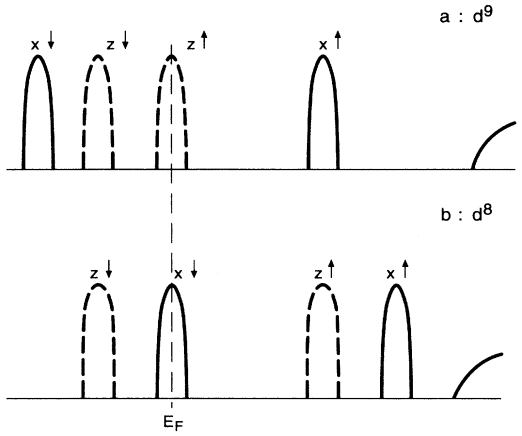

FIG. 1. Schematic Hartree-Fock spectral densities for hole-doped (a) d^9 and (b) d^8 systems. The solid and dashed lines indicate that the holes are polarized parallel (in $d_{x^2-y^2}$) and perpendicular (in d_{3z^2-1} orbital) to the planes, respectively.

notation). At half-filling, Hartree-Fock correctly produces the x-like upper Hubbard band (UH). The lower Hubbard band (LH) splits up because of E_z and J_H and it depends on the relative magnitude of these parameters which subband gets first occupied under doping. For $E_z > 3J_H$ this would be the $x\downarrow$ band (corresponding with Zhang-Rice singlets), while otherwise the hole goes into the "high-spin" $z\uparrow$ subband.

Now consider the correct SES in the strong-coupling limit, focusing on the unoccupied states. For the low-spin holes, the overall structure of the Hubbard bands would be similar to the Koopmans spectrum. However, for the high-spin holes a new peak appears [Fig. 2(a)]. By removing a hole (adding an electron), the triplet may be broken up in two ways: $|T_m\rangle + |k\rangle \rightarrow |x\rangle$ or $|T_m\rangle + |k\rangle \rightarrow |z\rangle$, where $|k\rangle$ is an electron in the vacuum. In the first process, the local d^9 ground state is restored and the corresponding spectral weight is found in the vicinity of the Fermi-energy (E_F) (Refs. 16 and 17). However, in the second process a d-d exciton is excited in the final state, giving rise to spectral weight centered at the exciton energy E_z. This is very similar to the phonon progressions found in small polaron systems, except that in our case only one boson binds to the fermion.

Although these triplet holes might appear a bit exotic, they would be the rule were it not that further complications enter. In the case of the cuprates, the holes have predominantly $O(2p)$ character, screening the Hund's-rule interaction to an extent that possibly the crystal-field splitting dominates.[19] In fact, the only evidence disfavoring high-spin holes in the cuprates comes from x-ray absorption measurements, involving the same kind of reasoning as leading to Fig. 2. It is the absence of significant doping induced absorptions in the c direction in the best available data,[18] both at the OK and CuL edges, which argues against populating the ground state with excitons under doping.

It is in fact expected that triplet holes win out if the ligand content to the LH band decreases by choosing more electronegative ligands like, e.g., fluorine. The same goal can be achieved by going to the left in the $3d$ series; the CT energy gradually increases while U tends to decrease.[20] For instance, NiO is considered a borderline case. Although it seems now established that the holes in, e.g., $Ni_{1-x}Li_xO$ are low-spin ($|x\uparrow x\downarrow z\uparrow\rangle$ or $|z\uparrow z\downarrow x\uparrow\rangle, {}^2E$),[21] for a long time it was believed that a high-spin hole state involving a $t_{2g}\sim t$ hole, of the form $|x\uparrow x\uparrow t\uparrow\rangle ({}^4T_2)$, was realized instead.[22,23] This latter situation (likely to occur in other Ni compounds) is basically similar to that of the triplet holes in the cuprates [Fig. 2(c)]. The only difference is that there are now three ways to end up in the $N+1$ ground state by removing the t_{2g} holes (dashed band) and only two ways to end up in $N+1$ states with a $|x\uparrow z\uparrow\rangle$ $({}^3A_2) \rightarrow |e\uparrow t\uparrow\rangle ({}^3T_2)$ ($e=x,z$) exciton excited, by removing the e_g holes, reducing the weight of the exciton "satellite."

In the examples discussed so far, we have considered cases where both the localized spins and the holes are in their maximum total spin state. Accordingly, we had only to consider the excitation of orbital degrees of freedom, factorizing out spin dependences. However, crystal-field excitations might also involve a change of the "internal" total spin of the localized states. Except

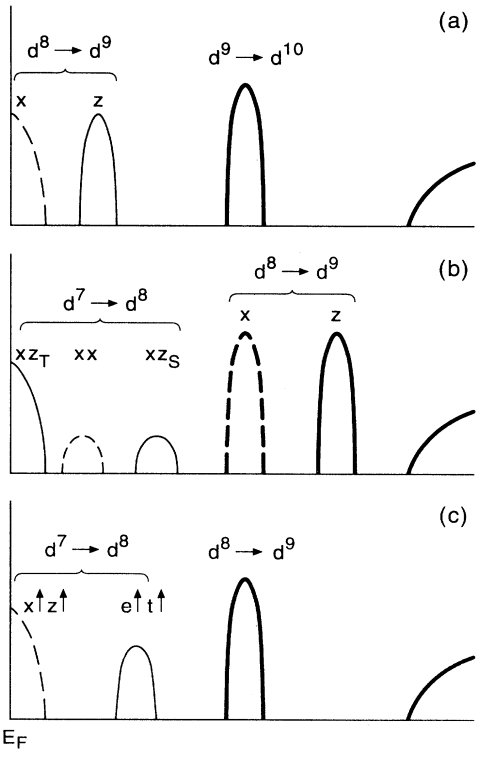

FIG. 2. The real unoccupied single-particle spectral weight for (a) a d^9 system with triplet holes, (b) a high-spin d^8 system with low-spin and (c) high-spin holes, respectively. The full and the dashed lines have the same meaning as in Fig. 1. Notice the extra "exciton satellites," reflecting the binding of the holes to excitons.

for the trivial cuprate situation, these excitons become important if one considers low(er)-spin holes in a high-spin background. To make the principle clear, let us consider the simple and experimentally relevant example of doped La_2NiO_4. We neglect the t_{2g} states and the relevant crystal-field excitations are $|T_m\rangle \rightarrow |S_a\rangle$ and $|T_m\rangle \rightarrow |S_b\rangle$ [Eq. (1)], which both change local total spin from $S=1$ to 0. At half-filling, the Hubbard bands of the Koopmans spectrum would be split by the tetragonal crystal field [Fig. 1(b)]. Note that, in contrast to the Cu triplet hole case, the spectrum of the d^8 states is now correct, because the holes were allowed to bind to the excitons in the high-spin Hartree-Fock ground state. Upon doping, the holes go into the $x\downarrow$-band forming $S=\frac{1}{2}$ states. In the real spectrum again exciton "satellites" show up:

$$\begin{aligned} |x\uparrow x\downarrow z\sigma\rangle + |k\rangle &\rightarrow |T_m\rangle \ , \\ &\rightarrow |S_a\rangle \ , \\ &\rightarrow |S_b\rangle \ , \end{aligned}$$

with relative weight 3, 1, and 1, corresponding with the creation of a low-energy excitation, and shake-offs involving the (low-spin) $|S_a\rangle$ and $|S_b\rangle$ excitons, respectively [see Fig. 2(b)]. Hence, in this case we find binding of the hole to a linear combination of two excitons, both having a local total spin-state different from the ground state and mutually different by their orbital content. In fact, van Elp *et al.*[24] already deduced the spectrum presented schematically in Fig. 2(b), arguing that the different weights of the "exciton" satellites in the O*K*-edge and inverse photoemission experiments could explain the vast difference in appearance of the gap region in these two experiments.

III. *t-J* MODELS FOR HIGH-SPIN SYSTEMS

A. General *t-J* models

The most relevant experimental question is whether these three-particle bound states are merely a spectroscopic curiosity, or if this physics also has macroscopic consequences. If the crystal-field energies and/or exchange splittings become of the order of the carrier bandwidth, the *d-d* excitons start to play an explicit role themselves. The reason is that the hopping couples the holes to these excitonic degrees of freedom, in a similar way as it couples holes to spin flips in the usual *t-J* model. The difference is that the atomic orbital momentum invariance has been explicitly broken, and therefore the excitations are massive. Further, the hole-exciton couplings are less symmetric and are more like the coupling of electrons to optical phonons.[25]

The hopping process is related to the single electron spectral function. If the carrier leaves a site, the three-particle bound state is broken up, as in photoemission, but as an added complication one has now to take care of the way in which the moving carrier binds to a *d-d* exciton at the next site where it enters. Obviously, the relevant excitons are of the same variety as those showing up in the SES. Accordingly, there are two different situations to consider. First, the simpler case of high-spin holes moving in a high-spin background, where the *d-d* excitations carry only the orbital momentum, considered below; second, the more complicated situation where total spin S is not at its maximum, which we discuss in the next section.

Let us again consider the triplet hole in a cupratelike system, approaching the carrier delocalization from a strong-coupling (*t-J* model) perspective, assuming in addition that the singlet-triplet splitting is much larger than the transfer integral, so that the singlets can be neglected in first instance. For the moment we neglect spin dependences. According to Eq. (4), the triplet hole can only delocalize in the x background by the hopping of its z component:

$$|xz\rangle_i |x\rangle_j \rightarrow |x\rangle_i |xz\rangle_j \ ,$$

with hopping amplitude t/α_0. On the other hand, in the z background the hole propagates by the hopping of its x component

$$|xz\rangle_i |z\rangle_j \rightarrow |z\rangle_i |xz\rangle_j \ ,$$

with amplitude t. Hence, the hole increases its kinetic energy by an amount $\sim(\alpha_0-1)t/\alpha_0$ when the background is changed from x^2-y^2 to $3z^2-1$. In other words, the exciton-hole bound state hops better to a site where an exciton is already present, a generic effect due to overlap (Franck-Condon–like) factors. Equally vital are the cross terms in Eq. (4), giving rise to:

$$|xz\rangle_i |x\rangle_j \rightarrow |z\rangle_i |xz\rangle_j \ ,$$

with amplitude $t/\sqrt{\alpha_0}$. Because orbital angular momentum is not conserved during the hopping, the hole can polarize the orbital background. Summarizing, the hopping between the neighboring sites occurs in one of the following ways:

$$\begin{aligned} (T_i,x_j) &\xrightarrow{t/\alpha_0} (x_i,T_j) \ , \\ (T_i,x_j) &\xrightarrow{t/\sqrt{\alpha_0}} (z_i,T_j) \ , \\ (T_i,z_j) &\xrightarrow{t/\sqrt{\alpha_0}} (x_i,T_j) \ , \\ (T_i,z_j) &\xrightarrow{t} (z_i,T_j) \ . \end{aligned} \tag{5}$$

The crystal-field excitation is more similar to a phonon and dissimilar to a spin, although the strong coupling via the hopping itself resembles the spin-hole coupling in *t-J* models. One sees immediately that this leads to strong attractive interactions. If the hole hops in the x background, it will leave behind a wake of z-polarized d^9 states and this increases the kinetic energy of the other holes. One can look at this as a ligand-field effect for extended holes, expected to lead at some point to structural instability.

Elsewhere we discussed how the (triplet) spin of the hole affects the hopping in the ($S=\frac{1}{2}$) spin background.[10] Compared to the usual singlet hole, the triplet

hole carriers an internal spin degree of freedom, and the hopping amplitude now depends on the relative orientation of the carrier spin and the spin on the site where the carrier arrives. We found (i and j are neighboring sites; 1, 0, and -1 stand for the m_z states of the hole):[10]

$$\begin{aligned}
&(1_i,\uparrow_j)\xrightarrow{t}(\uparrow_i,1_j)\ ,\\
&(1_i,\downarrow_j)\xrightarrow{t/\sqrt{2}}(\uparrow_i,0_j)\ ,\\
&(0_i,\uparrow_j)\xrightarrow{t/2}(\uparrow_i,0_j)\ ,
\end{aligned}\tag{6}$$

and the other five hops obtained from the above by time-spin reversal. It is convenient to describe the triplet holes as products of SU(3) Schwinger bosons ($a^\dagger_{im_s}$) and auxiliary fermions ($h_i^\dagger$) representing the internal spin degree of freedom ($m_z=1,0,-1$) and the charge of the holes, respectively.[10] The SU(2) Schwinger bosons, describing the $S=\frac{1}{2}$ spin background, occur now in two flavors, describing the two possible orbital polarizations ($b^\dagger_{i,x,n}$ and $b^\dagger_{i,z,n}$). In this representation, combining the findings in Eqs. (5) and (6), we arrive at the following hopping model for the triplet holes

$$H_t=\frac{t}{2}\sum_{\mathrm{i},\delta}\sum_{m,n=-1/2}^{1/2}\left\{\left[b^\dagger_{\mathrm{i}+\delta,z,n}+\frac{(-1)^{\delta\cdot\mathbf{y}}}{\sqrt{\alpha_0}}b^\dagger_{\mathrm{i}+\delta,x,n}\right]\left|\sum_{\pm}\sqrt{(3/2\pm m)(3/2\pm n)}\,a^\dagger_{\mathrm{i},m\pm1/2}a_{\mathrm{i}+\delta,n\pm1/2}\right|\right.$$
$$\left.\times\left[b_{\mathrm{i},z,n}+\frac{(-1)^{\delta\cdot\mathbf{y}}}{\sqrt{\alpha_0}}b_{\mathrm{i},x,n}\right]h_\mathrm{i}h^\dagger_{\mathrm{i}+\delta}+\mathrm{H.c.}\right\}.\tag{7}$$

Notice that for the x^2-y^2 orbital the parity is different along the x and y directions in the square lattice, while the $3z^2-1$ orbital has one sign in the plane. This introduces the different signs for the $x\rightarrow z$ hoppings in the x and y directions ($\mathbf{y}$ is the unit vector pointing in the y direction). By similar reasoning, but now pertaining to the virtual hopping processes at half-filling, one finds the exchange part of the Hamiltonian, being here a generalization of the so-called Kugel-Khomskii Hamiltonian.[13] In terms of the SU(2) flavored Schwinger bosons[26] we define spin operators (with the standard commutation relations $[X^a,X^b]=i\epsilon^{abc}X^c$), given by

$$\begin{aligned}
&S^+_{i,xx}=b^\dagger_{ix\uparrow}b_{ix\downarrow}\ ,\\
&S^+_{i,zz}=b^\dagger_{iz\uparrow}b_{iz\downarrow}\ ,\\
&S^+_{i,xz}=b^\dagger_{ix\uparrow}b_{iz\downarrow}+b^\dagger_{iz\uparrow}b_{ix\downarrow}\ ,\\
&S^z_{i,xx}=\tfrac{1}{2}(b^\dagger_{ix\uparrow}b_{ix\uparrow}-b^\dagger_{ix\downarrow}b_{ix\downarrow})\ ,\\
&S^z_{i,zz}=\tfrac{1}{2}(b^\dagger_{iz\uparrow}b_{iz\uparrow}-b^\dagger_{iz\downarrow}b_{iz\downarrow})\ ,\\
&S^z_{i,xz}=\tfrac{1}{2}(b^\dagger_{ix\uparrow}b_{iz\uparrow}+b^\dagger_{iz\uparrow}b_{ix\uparrow}-b^\dagger_{ix\downarrow}b_{iz\downarrow}-b^\dagger_{iz\downarrow}b_{ix\downarrow})\ ,
\end{aligned}\tag{8}$$

and spin-independent operators,

$$\begin{aligned}
&n_{i,-}=\tfrac{1}{2}(b^\dagger_{ix\uparrow}b_{ix\uparrow}+b^\dagger_{ix\downarrow}b_{ix\downarrow}-b^\dagger_{iz\uparrow}b_{iz\uparrow}-b^\dagger_{iz\downarrow}b_{iz\downarrow})\ ,\\
&T_{i,xx}=\tfrac{1}{2}(b^\dagger_{ix\uparrow}b_{iz\uparrow}+b^\dagger_{ix\downarrow}b_{iz\downarrow}+b^\dagger_{iz\uparrow}b_{ix\uparrow}+b^\dagger_{iz\downarrow}b_{ix\downarrow})\ ,
\end{aligned}\tag{9}$$

and we find the Hamiltonian,

$$H_J=\sum_{\langle\mathrm{i}\delta\rangle}\left[2J_{\mathrm{i}\delta}\left[\mathbf{S}_{\mathrm{i},xx}+\frac{1}{\alpha_0}\mathbf{S}_{\mathrm{i},zz}+\frac{(-1)^{\mathbf{y}\cdot\delta}}{\sqrt{\alpha_0}}\mathbf{S}_{\mathrm{i},xz}\right]\cdot\left[\mathbf{S}_{\mathrm{i}+\delta,xx}+\frac{1}{\alpha_0}\mathbf{S}_{\mathrm{i}+\delta,zz}+\frac{(-1)^{\mathbf{y}\cdot\delta}}{\sqrt{\alpha_0}}\mathbf{S}_{\mathrm{i}+\delta,xz}\right]\right.$$
$$\left.\times\left[n_{\mathrm{i},-}+\frac{(-1)^{\mathbf{y}\cdot\delta}}{\sqrt{\alpha_0}}T_{\mathrm{i},xz}\right]\left[n_{\mathrm{i}+\delta,-}+\frac{(-1)^{\mathbf{y}\cdot\delta}}{\sqrt{\alpha_0}}T_{\mathrm{i}+\delta,xz}\right]\right]-\sum_\mathrm{i}\left[E_z+\frac{zJ}{\alpha_0^2}\right]n_{\mathrm{i},-}\ ,\tag{10}$$

omitting for simplicity the terms coming from the Hund's-rule splitting of the intermediate (d^8) state.[26] Equations (7) and (10) (augmented with a constraint term prohibiting double occupancy) constitute the generalized t-J model for the triplet hole, including the crystal-field excitation.

How general is the model given by Eqs. (7) or (10), even in the context of high-spin holes and high-spin backgrounds? Unfortunately, this kind of Hamiltonian reflects the specific way in which the orbital angular symmetry is broken by the crystal structure, and it therefore depends strongly on the system under consideration. The triplet hole case, as discussed above, is characterized by orbital degrees of freedom which directly overlap with each other in the square lattice. Let us reformulate the argument leading to Eqs. (7) and (10) in a more precise way. Usually one considers as relevant basis states in the cuprates the x^2-y^2 orbitals on the Cu ions and the σ bonding $O(2p)$ orbitals [Fig. 3(a)]. According to the Zhang-Rice mapping,[6] the oxygen orbitals can be integrated out and the effective (singlet) hole hops with a transfer matrix element $t\propto t_\sigma^2/\Delta E$, where ΔE is the

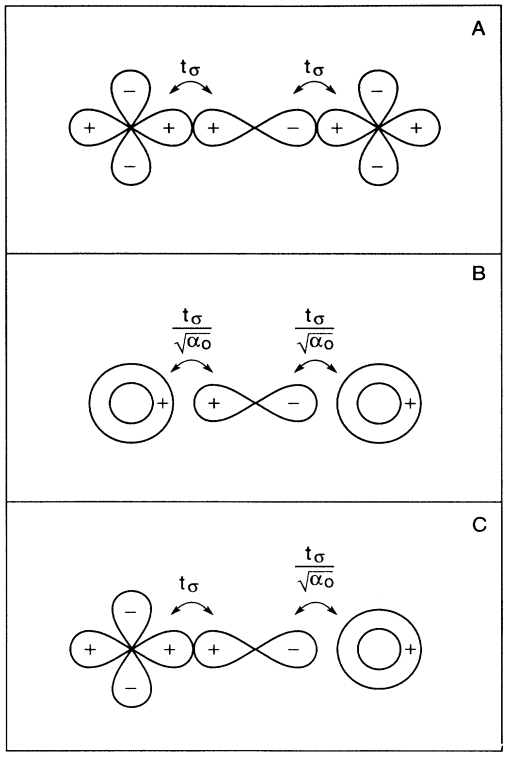

FIG. 3. The hopping possibilities for a planar d^9 system. Hopping can involve only (a) $d_{x^2-y^2}$, or (b) d_{3z^2-1} orbitals, (c) but cross terms are also possible.

relevant gap. However, in the considered geometry of a CuO_2 plane in a high-temperature superconductor, the $3z^2-1$ orbital overlaps as well with the σ bonding $O(2p)$ orbital and, accordingly, the hole within the effective z orbital, occupied in the triplet state, hops also in the plane with an amplitude $t/\sqrt{\alpha_0}$ [Fig. 3(c)]. Finally, the x and z orbitals also overlap with each other [Fig. 3(c)], giving rise to the "polarization" cross terms in Eq. (7). To see that this is not generic consider the otherwise rather similar problem of a high-spin hole ($|x\uparrow z\uparrow t\uparrow\rangle$) in a high-spin background ($|x\uparrow z\uparrow\rangle$) in a nickel compound with a rock-salt structure. For clarity, we consider only a 2D rock-salt layer. This layer can be considered as a superposition of two perovskite layers, where the metal ions of one of the layers is located in the middle of the empty squares of the other, sharing the counter ions, as in NiO (see Fig. 4). Inside each perovskite layer, the σ- and π-type orbitals are orthogonal [Figs. 4(a) and (b)] and the hole can hop in either of these channels with hopping matrix elements $t\propto t_\sigma^2/\Delta E$ and $t/\alpha_t\propto t_\pi^2/\Delta E$, for σ and π hopping, respectively. On the contrary, the only way to get from one of the perovskite sublattices to the other is by a term mixing the σ and π channels:

$$t/\sqrt{\alpha_t}\propto t_\sigma t_\pi/\Delta E$$

[Fig. 4(c)]. We find the following transitions in the subspace in which only high-spin holes (e^2t) and high-spin background states (e^2,et) are allowed, labeling the two perovskite sublattices with A,B:

$$\begin{aligned}
&(e^2t_{iA,B},e^2_{j,A,B})\xrightarrow{t/\alpha_t}(e^2_{i,A,B},e^2t_{jA,B})\,,\\
&(e^2t_{iA,B},et_{jA,B})\xrightarrow{t}(et_{iA,B},e^2t_{jA,B})\,,\\
&(e^2t_{iA,B},e^2_{jB,A})\xrightarrow{t/\sqrt{\alpha_t}}(et_{iA,B},e^2t_{jB,A})\,,\\
&(e^2t_{iA,B},et_{jB,A})\xrightarrow{t/\sqrt{\alpha t}}(e^2_{iA,B},e^2t_{jB,A})\,.
\end{aligned}\tag{11}$$

As in the case of the triplet hole, the Hund's-rule coupling forces the hopping to come from the orbital with the smaller overlap, thus reducing the effective hopping. By occupying the exciton the full hopping gets restored. The cross terms are interesting: the only way to get from one sublattice to the other is by exciting an exciton. In other words, if the crystal-field energy is infinite, a hole is confined to one of the sublattices and the Hilbert space splits into two degenerate sets of states, each belonging to one of the perovskite sublattice. For finite crystal fields, the holes can escape their sublattice by exciting the *d-d* excitons, which on their turn increase the kinetic energy for intrasublattice hopping. It seems unavoidable that a Jahn-Teller–like instability has to occur.

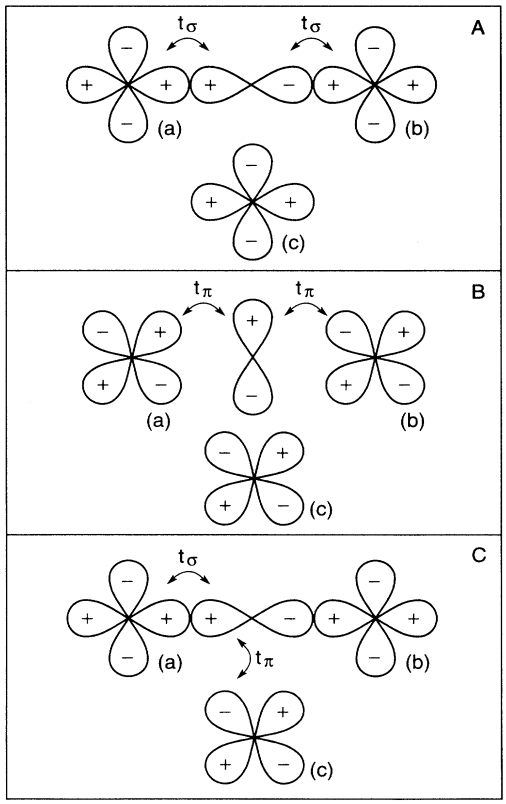

FIG. 4. Hopping possibilities for e_g and t_{2g} holes in a cubic environment. The hopping via p_σ and p_π orbitals couples the (a) $d_{x^2-y^2}$ and d_{xy} orbitals, respectively. (c) Only via cross hoppings is it possible to come from atom (a) to atom (c). These hoppings are forbidden if the crystal-field energy is infinite (see text).

B. Spinless model

To get some feeling for the nature of the structural instabilities occurring in this context, let us reconsider the relatively simple model for triplet holes in cupratelike situations, given by Eqs. (7) and (10). The difficulty is in the spin channel. Although it is by now established that apparently the problem of an isolated singlet hole in the 2D quantum antiferromagnet is solved by linear spin-wave theory together with a self-consistent Born approximation for the hole-magnon couplings,[27] it is not clear at all how to treat the finite hole-density problem, not to speak of the triplet hole problem where we showed that, even for an isolated hole, simple perturbation theory diverges.[10] At the same time, the orbital dependence of the hopping is the same in every spin channel [see Eq. (7)] and it seems reasonable to assume that the spin dependences in the hopping problem can be neglected in the first instance, if the interest is in the orbital channel. After all, in the hopping Hamiltonian the orbital dynamics is the same in all spin channels. The spinless variant of Eq. (7),

$$H=t\sum_{i,\delta}\left[b_{iz}+\frac{(-1)^{\delta\cdot y}}{\sqrt{\alpha_0}}b_{ix}\right]f_i^\dagger f_{i+\delta}\left[b_{i+\delta,z}^\dagger+\frac{(-1)^{\delta\cdot y}}{\sqrt{\alpha_0}}b_{i+\delta,x}^\dagger\right]+E_z\sum_i b_{iz}^\dagger b_{iz}+\sum_i\lambda_i\left[\sum_{\xi=x,z}b_{i\xi}^\dagger b_{i\xi}+f_i^\dagger f_i-1\right], \tag{12}$$

using slave bosons $(b_{ix}^\dagger, b_{iz}^\dagger)$ to represent the orbital degrees of freedom. Further, we included Langrange multipliers (λ_i) to enforce the usual local constraint at finite dopings. Neglecting the dynamics of the crystal-field excitations [as follows from Eq. (10) (Ref. 26)], the exciton can be modeled by a single oscillator.

The spinless model given by Eq. (12) is simpler than, for instance, a t-J model, because the excitation is massive. This mass sets a short length scale and it is expected that a semiclassical approximation should be qualitatively correct. Such an approximation is in the present context of the slave-boson mean-field (MF) variety,[28] obtained by replacing the b's by scalars $\langle b\rangle$. In addition, the local constraint (λ_i) is replaced by a global one (i.e., $\lambda_i=\lambda$). In this approximation, the physical vacuum in which the hole hops is like

$$|\Phi_0\rangle=\prod_i(\alpha_{ix}b_{ix}^\dagger+\alpha_{iz}b_{iz}^\dagger)|0\rangle\ . \tag{13}$$

Except for the amplitudes of the $\langle b\rangle$'s, which we have assumed to be uniformly distributed, there is also an issue of the relative phases of the x and z d^9 states. We checked the uniform [Fig. 5(a)], as well as the staggered version of the phasing [Fig. 5(b)], and we find that the former yields lower energies in the whole parameter space. For the uniform distribution of the $\langle b\rangle$'s we obtain a MF free energy at carrier concentration $n=\sum_k^{\rm occ}1$,

$$\mathcal{F}_{\rm MF}=\eta^2b^2E_z+\lambda[b^2(1+\eta^2)+n-1]-\frac{1}{\beta}\int\frac{d^2k}{(2\pi)^2}\ln(1+e^{-\beta E_{\mathbf{k}}})\ , \tag{14}$$

where the quasiparticle energies are

$$E_{\mathbf{k}}=\lambda+ztb^2\left[\left(\eta^2+\frac{1}{\alpha_0}\right)\gamma_{\mathbf{k}}+\frac{2\eta}{\sqrt{\alpha_0}}\gamma_{\mathbf{k}}^-\right]\ . \tag{15}$$

We have parametrized the boson mean fields by $\langle b_x\rangle=b$ and $\langle b_z\rangle=\eta b$, while

$$\gamma_{\mathbf{k}}=\frac{1}{z}\sum_\delta\exp(-i\mathbf{k}\cdot\delta)$$

and

$$\gamma_{\mathbf{k}}^-=\frac{1}{z}\sum_\delta(-1)^{y\cdot\delta}\exp(-i\mathbf{k}\cdot\delta)$$

stand for the structure factors (z is the coordination number). There are three possible saddle points. Either the d^9 background is of pure x^2-y^2 [with $\mathcal{F}_{\rm MF}=(1-n)E_+/\alpha_0$ at $T=0$, where $E_+=(zt/N)\sum_{\mathbf{k}}^{\rm occ}\gamma_{\mathbf{k}}$], or of pure $3z^2-1$ character [$\mathcal{F}_{\rm MF}=(1-n)(E_++E_z)$], or, finally, a mixed state where both orbitals are occupied is possible. At zero temperature, the saddle-point equations yield

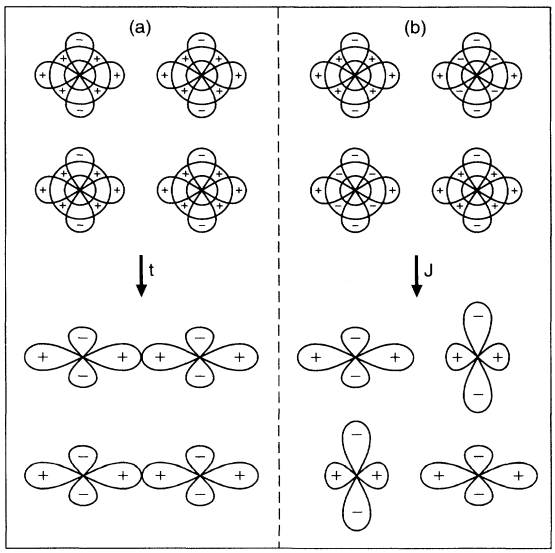

FIG. 5. (a) In d^9 systems the hopping of the triplet hole tends to stabilize a uniform relative phasing of the $d_{x^2-y^2}$ and d_{3z^2-1} orbitals. This implies a strengthening of the bonds along one direction (x or y) in the perovskite plane, leading to an orthorhombic lattice distortion. (b) On the other hand, superexchange processes at half-filling tend to favor a staggering of the phases if the orbital degrees of freedom are involved, leading to distortions as found in K_2CuF_4.

$$b^2=(1-n)/(1+\eta^2)\ ,$$

$$\eta=\frac{-E_-}{\sqrt{\alpha_0}(E_z+\lambda+E_-)}\ , \tag{16}$$

$$\lambda=-\frac{1}{2}\left\{\frac{(\alpha_0+1)E_+}{\alpha_0}+E_z+\left[\left[\frac{(\alpha_0+1)E_+}{\alpha_0}+E_z\right]^2-\frac{4}{\alpha_0}(E_+^2+E_+E_z-E_-^2)\right]^{1/2}\right\},$$

where $E_-=(zt/N)\sum_{\mathbf{k}}^{\mathrm{occ}}\gamma_{\mathbf{k}}^-$. The saddle point is rather unconventional, as the stability of the different phases ("mixed," and "pure" x and z) is directly related to the shape of the Fermi surface. In the "pure" phases, the Fermi surface has the fourfold symmetry of the square lattice and, accordingly, E_- vanishes. In order to have both orbitals simultaneously occupied ($0<\eta<\infty$), E_- has to be finite, implying that the k_x and k_y directions in the Brillouin zone have to become inequivalent. Taking $\eta\neq 0$, one finds that the Fermi surface becomes an ellipse (with E_F being the Fermi energy),

$$\frac{E_F-\lambda}{2ztb^2}=\left[\frac{1}{\sqrt{\alpha_0}}+\eta\right]^2\cos k_{F,x}+\left[\frac{1}{\sqrt{\alpha_0}}-\eta\right]^2\cos k_{F,y}\ , \tag{17}$$

and E_- is therefore automatically nonzero. The reason for this symmetry breaking is that if the x and z states are uniformly phased, hybrid orbitals are formed with larger overlaps in, e.g., the x direction than in the y direction [see Fig. 5(a)]. The system gains kinetic energy E_- because the $x\leftrightarrow z$ hopping term in Eq. (12) contributes on average, at the cost of the kinetic energy E_+ in the diagonal ($x\leftrightarrow x$ and $z\leftrightarrow z$) channels. Therefore, the orbital mixing will only pay off above some critical hole concentration.

Equations (16) can be solved by fixing E_F (grand-canonical ensemble) and iterating η and λ until a self-consistent solution is found. In Fig. 6 we show the zero-temperature free energies obtained in this way as a function of the number of holes, $\langle n\rangle$, for $E_z=|t|$ and $\alpha_0=3$. For $\langle n\rangle\simeq 0.4$ substantial energy is gained by distorting the Fermi surface but this mixed phase saddle point ceases to exist for smaller hole concentrations, where the pure x phase gets stable. By applying the Maxwell construction (dashed line), one finds a region where the system phase separates in a hole-rich mixed-phase and a hole-poor x phase. In this way we obtain the zero-temperature phase diagram as shown in Fig. 7, as a function of $\langle n\rangle$ and $E_z/|t|$. Up to rather large values of E_z the free energies behave similarly to Fig. 6 (the shaded area indicates phase separation), except that the stabilization energy of the mixed phase becomes rapidly insignificant (dashed lines). The mixed phase is most stable at $E_z/|t|\sim 0.75$ where the x and z phases would be degenerate in the absence of the orbital mixing. Finally, for small values of $E_z/|t|$ and small doping the carriers accumulate in a pure $3z^2-1$ phase, while at larger dop-

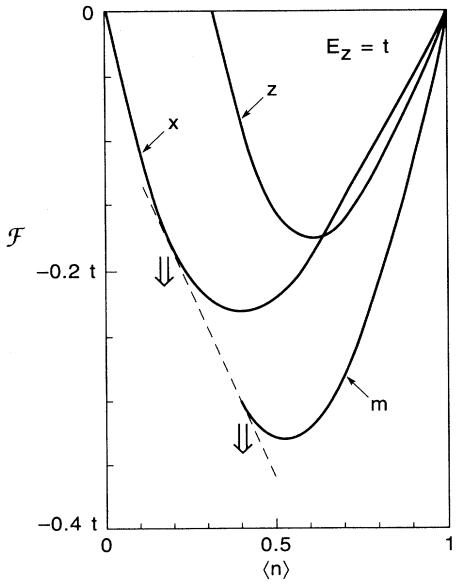

FIG. 6. The zero-temperature free energy following from the mean-field theory for the spinless d^9 triplet-hole model as a function of hole concentration, n. x, z, and m indicate the free energies of the pure $d_{x^2-y^2}$, pure d_{3z^2-1} and the mixed orbital phase, as indicated in Fig. 5(a), respectively. From the Maxwell construction (dashed line) a region of phase separation follows.

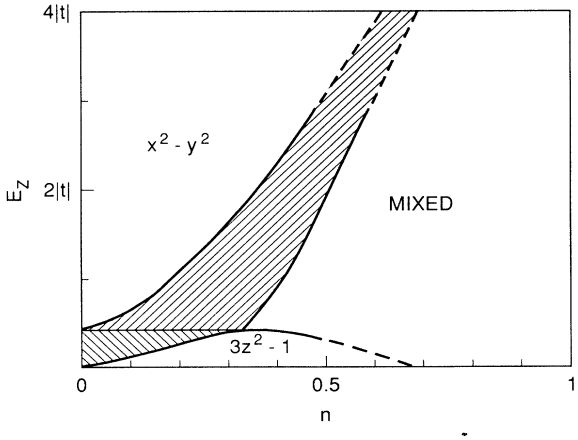

FIG. 7. Mean-field phase diagram for the spinless d^9 triplet-hole model as a function of the crystal-field energy E_z and hole concentration, n. The shaded areas indicate regions of phase separation between the pure and mixed phases.

ings a weakly first-order phase transition follows to the mixed phase, with a rather insignificant x^2-y^2 admixing.

In Fig. 8 we show the relative weight of the z states,

$$\langle n_z \rangle = \langle b_z \rangle^2 / (\langle b_x \rangle^2 + \langle b_z \rangle^2) .$$

This weight grows gradually in the mixed state for decreasing E_z and is only weakly dependent on the doping, demonstrating again the strongly first order nature of the phase transition.

The above picture is most probably too oversimplified to account for the physical reality. What are the complications? First, we have neglected completely the half-filling superexchange Hamiltonian, as given by Eq. (10). In fact, from the seminal work of Kugel and Khomskii[13] it is known (and experimentally confirmed[13]) that already at half-filling phenomena occur, similar to those we just discussed as induced by doping. Also at half-filling the pure z state should become more favorable for decreasing E_z.[26] As Kugel and Khomskii showed,[13] a new phase occurs in the vicinity of this point, which is similar to the orbital mixed state stabilized by the holes, except that the relative phasing of the orbitals is now staggered, as indicated in Fig. 5(b). However, this new phase is stable only in the presence of the Hund's-rule coupling J_H, acting in the d^8 intermediate state, in addition giving rise to a ferromagnetic superexchange between the spins. Even in zeroth order it is therefore no longer possible to treat the spin and orbital degrees of freedom as independent. As we showed elsewhere, also the excitations at half-filling involve mixing of spin and orbital degrees of freedom.[26] In other words, if the "spin" part of our generalized t-J model is taken seriously, it is no longer possible to treat the orbital degrees of freedom independently of the spin subsystem and the existing couplings will tend to favor ferromagnetism.

A further complication involves the phonons. It has been shown that the electron-phonon (EP) coupling gives a half-filling an effective electron-electron interaction of the form,[29]

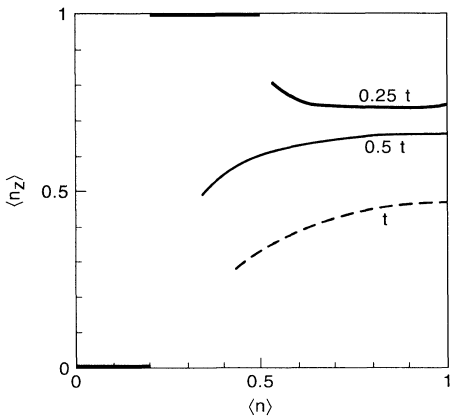

FIG. 8. The relative d_{3z^2-1} occupancy of the d^9 states, $\langle n_z \rangle$, as a function of triplet-hole concentration n for different values of the crystal-field splitting, E_z. The discontinuities in $\langle n_x \rangle$ come from the strong first-order nature of the phase transitions.

$$H_{EP} \sim \sum_{\mathbf{q}} [K_n(\mathbf{q}) n_{\mathbf{q},-} n_{-\mathbf{q},-} + K_t(\mathbf{q}) T_{\mathbf{q},xz} T_{-\mathbf{q},xz}] , \quad (18)$$

where $n_{\mathbf{q},-}$ and $T_{\mathbf{q},xz}$ are the Fourier transforms of the operators $n_{i,-}$ and $T_{i,xz}$, defined by Eqs. (9) and introduced in Hamiltonian (10), and $K_t[\mathbf{q}=(\pi,\pi)]>0$ dominates in a cuprate perovskite structure. Physically this means that the EP coupling also tends to favor an orbital mixed phase of the staggered variety [as shown in Fig. 5(b)].[29] The Cu—O bond length shrinks or increases, depending on whether the bonds get stronger (large lobes) or weaker (small lobes), and the perovskite plane is subject to an antiferrodistortive "quadrupolar" instability. Hence, the EP and purely electronic interactions drive the system in the same direction and it is in fact not clear what is cause and effect in situations where this instability actually occurs [as in, e.g., K_2CuF_4 (Ref. 13)]. The EP couplings are also expected to feedback positively[30] on the electronic instability in the hole-doped systems [Fig. 5(a)], causing a ferrodistortive (orthorhombic) instability. Hence, keeping in mind that if not only because of electrostatic reasons,[31,32] holes tend to renormalize the crystal-field energy downwards, one expects the hole induced ferrodistortive instability to compete with the antiferrodistortive tendency coming from Eqs. (10) and (18). This should lead to superstructures with a larger period. In fact, the superstructures proposed by Krekels *et al.*[33] to occur in oxygen deficient $YBa_2Cu_3O_7$ exactly match this expectation. Also, the anomalous dynamics of the apical oxygens, which has been proposed to explain extended x-ray-absorption fine structure (EXAFS)[34] and neutron scattering data[35] of a variety of high-T_c cuprates, seems to point in this direction. These structural data and the polarized x-ray absorption measurements[18] are in contradiction and we feel that a final verdict about the relevance of triplet holes for high-T_c superconductivity has to be postponed until the experimental situation is clarified.

IV. NONMAXIMAL SPINS

In the previous section we have considered the case that the total spin of both the carrier and the antiferromagnetic background are at their maxima. However, one can imagine a variety of situations where the spin state of either the carriers or the background are not at maximum. The simplest situation of this sort is the one described by the standard t-J model, which is rather exceptional because no internal degree of freedom is related to the total spin state of the background spins. If the background spins are instead composite objects, one encounters again the crystal-field excitations. The example of a doped nickelate, as discussed in Sec. II [see Figs. 1(b) and 2(b)] might further clarify this.

A. Spin Hamiltonian

To keep matters as simple as possible, we again imagine the 2D perovskite planes as in, e.g., La_2NiO_4. The local total spin state is not clear before hand. Usually Ni^{2+} is in the high-spin state, which is defined in operator form in terms of the ("d^9") Schwinger bosons introduced in the

previous section, $b^{\dagger}_{i,x\sigma}$ and $b^{\dagger}_{i,z\sigma}$ as follows:

$$B^{\dagger}_{i,1}=b^{\dagger}_{ix\uparrow}b^{\dagger}_{iz\uparrow}\ ,$$
$$B^{\dagger}_{i,0}=(1/\sqrt{2})(b^{\dagger}_{ix\uparrow}b^{\dagger}_{iz\downarrow}+b^{\dagger}_{ix\downarrow}b^{\dagger}_{iz\uparrow})\ , \tag{19}$$
$$B^{\dagger}_{i,-1}=b^{\dagger}_{ix\downarrow}b^{\dagger}_{iz\downarrow}\ .$$

On the other hand, the tetragonal distortion will tend to stabilize low-spin states of the form,

$$A^{\dagger}_{i}=b^{\dagger}_{ix\uparrow}b^{\dagger}_{ix\downarrow}\ , \tag{20}$$

corresponding with a triplet to singlet d-d exciton, with energy $E_S=J_H-E_z$. The issue is what happens when this energy gets of the order of the hopping integral and/or of the superexchange, in other words, if the system is close to a high-spin–low-spin transition.

In order to gain some intuition it is instructive to consider first this problem at half-filling. The situation is qualitatively different from that considered so far, as the virtual processes leading normally to superexchange turn out to couple here as well the high- and low-spin states. As we will show and discuss in more detail elsewhere,[36] incorporating the low-spin states in the usual superexchange considerations yields a "spin" Hamiltonian of the form,

$$H_J=2J\sum_{i\delta}\{[\mathbf{S}_i+(-1)^{\delta\cdot y}\sqrt{\alpha_1}\tilde{\mathbf{S}}_i]\times[\mathbf{S}_{i+\delta}+(-1)^{\delta\cdot y}\sqrt{\alpha_1}\tilde{\mathbf{S}}_{i+\delta}]+\alpha_2 n_i(A)n_{i+\delta}(A)\}+E_S\sum_i n_i(A)\ , \tag{21}$$

where α_1 and α_2 are nonuniversal parameters. If $\alpha_0=3$, one finds $\alpha_1=\frac{3}{8}$ and $\alpha_2=\frac{1}{4}$, while the superexchange interaction is $J=8t^2/9U$. The number operators are defined as

$$n_i(A)=A^{\dagger}_i A_i\ ,$$
$$n_i(B_m)=B^{\dagger}_{i,m}B_{i,m}\ , \tag{22}$$

and $\mathbf{S}_i$ is the conventional spin operator, represented for $S=1$ by

$$S^{+}_i=\sqrt{2}(B^{\dagger}_{i,1}B_{i,0}+B^{\dagger}_{i,0}B_{i,-1})\ ,$$
$$S^{z}_i=n_i(B_1)-n_i(B_{-1})\ . \tag{23}$$

The $\tilde{\mathbf{S}}_i$ operators are unusual and show up in Eq. (21) because of the mixing of the low- and high-spin sectors by the kinetic exchange. These new operators can be written as

$$\tilde{S}^{+}_i=\sqrt{2}(B^{\dagger}_{i,1}A_i-A^{\dagger}_i B_{i,-1})\ ,$$
$$\tilde{S}^{z}_i=-(A^{\dagger}_i B_{i,0}+B^{\dagger}_{i,0}A_i)\ . \tag{24}$$

Together with the spin operators they obey an SO(4) (dynamical) algebra,

$$[S^a,S^b]=2\epsilon_{abc}S^c\ ,$$
$$[S^a,\tilde{S}^b]=2\epsilon_{abc}\tilde{S}^c\ , \tag{25}$$
$$[\tilde{S}^a,\tilde{S}^b]=2\epsilon_{abc}S^c\ .$$

The SO(4) symmetry is, however, broken by the ligand fields [e.g., $(-1)^{\delta\cdot y}\sqrt{\alpha_1}\to 1$ and E_S, $\alpha_2\to 0$ would yield an SO(4) symmetric Hamiltonian] and the only remaining continuous symmetry is SU(2), the spin rotation. Still, $\tilde{\mathbf{S}}_i$ transforms like a vector under spin rotation [Eq. (25)], although it is not a spin variable in the usual sense.

The problem given by the Hamiltonian (21) appears to be conceptually similar to the so-called singlet-triplet models which have been proposed in the context of crystal-field excitations in rare-earth systems.[12] We emphasize, however, that the physical origin is completely different. In the rare earths, the spin-orbit coupling dominates and the resulting total angular momenta, $\mathbf{J}_i$, couple by (dipolar) interactions, while the crystal field induces a small local coupling between states with different values of J. In our case, the orbital momentum is quenched, while the states with different total spin S interact via kinetic exchange.

The simplest way to proceed to get qualitative answers concerning the nature of the ground state is by implementing a classical spin approximation. It is asserted that the ground state at half-filling can be written as

$$|\Phi_0\rangle=\prod_i(b_{i,1}B^{\dagger}_{i,1}+b_{i,0}B^{\dagger}_{i,0}+b_{i,-1}B^{\dagger}_{i,-1}+a_i A^{\dagger}_i)|0\rangle\ , \tag{26}$$

where the $b_{i,m}$'s can be parametrized by two angles, θ_i and ϕ_i per site, as follows,

$$\begin{pmatrix} b_{1,i}\\ b_{0,i}\\ b_{-1,i}\end{pmatrix}=b_i\begin{pmatrix} e^{-i\phi_i}\cos^2(\theta_i/2)\\ \sqrt{2}\sin(\theta_i/2)\cos(\theta_i/2)\\ e^{i\phi_i}\sin^2(\theta_i/2)\end{pmatrix} \tag{27}$$

while the two Schwinger bosons, a_i and b_i, satisfy the local constraint that $a_i^2+b_i^2=1$. Using this parametrization one finds that the expectation values for the spin operators are

$$\langle S^z_i\rangle=b_i^2\cos(\theta_i)\ ,$$
$$\langle S^x_i\rangle=b_i^2\sin(\theta_i)\cos(\phi_i)\ , \tag{28}$$
$$\langle S^y_i\rangle=b_i^2\sin(\theta_i)\sin(\phi_i)\ ,$$

with θ_i and ϕ_i characterizing the orientation of the spin at site i. Classically, the spinlike nature of the $\tilde{\mathbf{S}}_i$ operators becomes transparent and follows automatically from the ansatz (26),

$$\langle\tilde{S}^z_i\rangle=\sqrt{2}a_i b_i\sin(\theta_i)\ ,$$
$$\langle\tilde{S}^x_i\rangle=-\sqrt{2}a_i b_i\cos(\theta_i)\cos(\phi_i)\ , \tag{29}$$
$$\langle\tilde{S}^y_i\rangle=-\sqrt{2}a_i b_i\cos(\theta_i)\sin(\phi_i)\ .$$

The phases in $\langle\tilde{S}^x_i\rangle$ and $\langle\tilde{S}^y_i\rangle$ are still arbitrary and we have chosen them here in such a way that the classical spins correctly reproduce two local invariants of the SO(4) algebra,[36]

$$\mathbf{S}_i^2+\tilde{\mathbf{S}}_i^2=3\ , \tag{30}$$

$$\mathbf{S}_i \cdot \tilde{\mathbf{S}}_i = 0 \ . \tag{31}$$

With the above parametrization we may call the spins $\tilde{\mathbf{S}}_i$ pseudospins because they do not change the sign under reflection in the (xy) plane. They are locally perpendicular to the original spins, $\mathbf{S}_i$ [see Eq. (31)].

Setting the phase $\phi=0$ in (27), the classical free energy of the "spin" Hamiltonian in Eq. (21) takes the following form on a square lattice:

$$\mathcal{F}_J = 2J \sum_{i\delta} [b_i b_{i+\delta}(b_i b_{i+\delta} + 2\alpha_1 a_i a_{i+\delta})\cos(\Delta\theta_{i\delta}) + \alpha_2 a_i^2 a_{i+\delta}^2] + E_S \sum_i a_i^2 \ , \tag{32}$$

where $\Delta\theta_{i\delta}=\theta_i-\theta_{i+\delta}$. This favors a staggered order parameter for both $\mathbf{S}_i$ and the "spin" component of $\tilde{\mathbf{S}}_i$, while the "orbital" components of the latter (a,b) will take uniform values. Apart from the high-spin $(b^2=1)$ and low-spin $(a^2=1)$ phases with free energies $\mathcal{F}(\mathrm{HS})=-zJ$ and $\mathcal{F}(\mathrm{LS})=zJ\alpha_2+E_S$, respectively, we find a third possible saddle point involving a mixture of the low- and high-spin phases, characterized by the amplitude of the low-spin state,

$$\langle n(A)\rangle = a^2 = \frac{1-\alpha_1+E_s/2zJ}{1-2\alpha_1-\alpha_2} \ , \tag{33}$$

and the classical free energy at $T=0$,

$$\mathcal{F}_J = zJ\alpha_2 - E_S - zJ\frac{(\alpha_1+\alpha_2+E_S/2zJ)^2}{2\alpha_1+\alpha_2-1} \ . \tag{34}$$

The region of existence of this mixed phase is determined by the physical condition for the amplitude, $0\le a^2\le 1$. Such a mixed state is favored if $2\alpha_1+\alpha_2>1$. For $\alpha_0=3$ this mixed state does not exist in the present approximation (is on the verge of stability since $2\alpha_1+\alpha_2=1$), while one expects that for physically allowed values this number is generally less than one. In fact, as we will show elsewhere,[36] a mixed state becomes stable in the neighborhood of the transition from high- to low-spin phase, if the local problem is treated fully quantum mechanically, while the nonlocal interactions are treated classically. This latter mixed phase is different from the one obtained within the ansatz (26) in the sense that only $\tilde{\mathbf{S}}_i$ acquires an expectation value with a staggered ordering of these pseudospins [Fig. 9(b)], while $\langle \mathbf{S}_i \rangle = 0$. Moreover, it can be shown that this mixed phase is stable against Gaussian fluctuations.[36]

B. Hole doping

Let us now consider what happens under doping. First, consider p-type doping (of, e.g., La_2NiO_4) where the hole goes into a low spin state, like

$$|\sigma\rangle \equiv |x\uparrow x\downarrow z\sigma\rangle \ .$$

If $E_S/t\to\infty$, the hoppings would be as in Eq. (6), with the larger spin now associated with the background. However, allowing for the low-spin states (20) as well, we find in addition the transitions

$$\begin{aligned} (A_i,\uparrow_j) &\xrightarrow{t/\alpha_0} (\uparrow_i, A_j) \ , \\ (A_i,\uparrow_j) &\xrightarrow{-t/\sqrt{\alpha_0}} (\downarrow_i, B_{j,1}) \ , \\ (A_i,\downarrow_j) &\xrightarrow{t/\sqrt{\alpha_0}} (\uparrow_i, B_{j,-1}) \ , \end{aligned} \tag{35}$$

with the other possibilities obtained by spin and/or time reversal. Collecting those we find the following hopping Hamiltonian expressed in terms of the B_{im} and A_i operators defined in Eqs. (19) and (20), and auxiliary fermions representing the carrier $h^\dagger_{i,\sigma}$,

$$\begin{aligned} H_t = t \sum_{i\delta} [& X^\dagger_{i+\delta,+} h^\dagger_{i,\uparrow} h_{i+\delta,\uparrow} X_{i,+} + X^\dagger_{i+\delta,-} h^\dagger_{i,\downarrow} h_{i+\delta,\downarrow} X_{i,-} + (X^\dagger_{i+\delta,-} B_{i,1} + B^\dagger_{i+\delta,-1} X_{i,+}) h^\dagger_{i\uparrow} h_{i+\delta,\downarrow} \\ & + (X^\dagger_{i+\delta,+} B_{i,-1} + B^\dagger_{i+\delta,1} X_{i,-}) h^\dagger_{i\downarrow} h_{i+\delta,\uparrow} + B^\dagger_{i+\delta,1} B_{i,1} h^\dagger_{i,\uparrow} h_{i+\delta,\uparrow} + B^\dagger_{i+\delta,-1} B_{i,-1} h^\dagger_{i,\downarrow} h_{i+\delta,\downarrow}] \ , \end{aligned} \tag{36}$$

with

$$X^\dagger_{i,\pm} = \frac{B^\dagger_{i,0}}{\sqrt{2}} \pm \frac{1}{\sqrt{\alpha_0}} (-1)^{\delta\cdot y} A^\dagger_i \ . \tag{37}$$

Together with Eq. (21) it defines the t-J model for nonmaximal spins,

$$H_{tJ} = H_t + H_J \ . \tag{38}$$

The physical content of the hopping Hamiltonian Eq. (36) is rather interesting. On the one hand, it shows that the hole in the high-spin background can only delocalize by exciting spin flips. On the other hand, the hopping in the low-spin background is hindered because the hole can only delocalize there by the hopping of its "wrong" $(3z^2-1)$ orbital component, in analogy with the "x" phase of the d^9 triplet-hole problem. Terms like Eqs. (35b) and (35c) are novel. In analogy to the "polarization hops" of the d^9 problem [see Eq. (5)], this variety of hoppings excites low-spin excitons in a high-spin background, or vice versa. The physics is now more complicated because a change of local spin is involved and it is therefore no longer possible to treat the "exciton" and "spin" sectors as independent from each other, even in zeroth order.

As we discussed elsewhere,[10] the problem of the propagation of $(S=\frac{1}{2})$ holes in the high-spin $(S=1)$ background is in general more complicated than that in the usual (singlet-hole) t-J model.[11] The reason is that new hopping possibilities arise for higher spin, in addition to the usual hoppings of the singlet-hole model as given in Eq. (6), which eventually lead to multiple spin flips. The

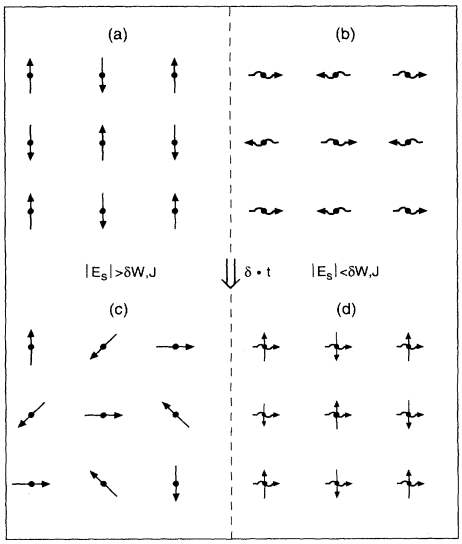

FIG. 9. The nature of the semi-classical ground states of a d^8 system. At half-filling, near the (a) high-spin and low-spin transition a novel phase might occur which is characterized by mixtures of local total spin states (wiggly arrows) (b), carrying a net spinlike momentum [$\tilde{\mathbf{S}}_i$, Eq. (24)]. Upon doping, the competition is between (c) high-spin states of the spiral-variety and (d) states characterized both by a high-spin momentum and a nonzero expectation value of $\tilde{\mathbf{S}}_i$. The spins are antiparallel while the delocalization of the (low-spin) holes tend to favor parallel alignment of the pseudospins.

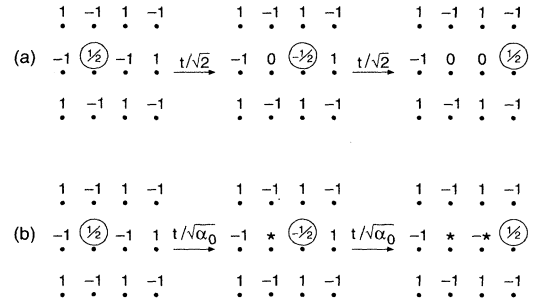

FIG. 10. Stringlike hopping histories in a $S=1$ background. (a) Without invoking excitons, the usual string of spin flips is left behind by the moving hole. The hole can also leave behind a string of low-spin excitons [stars in (b)], if the system is near the low-spin–high-spin transition. Because of the local total spin coherence, the phase of the exciton relative to the background is determined by the spin ordering. This effect is responsible for the ferro-alignment of the pseudospins.

delocalization of an isolated singlet hole is well understood[11] and the key aspect is the so-called string potential:[37] in the (classical) Néel background every hop creates two (in 2D) ferromagnetic spin bonds, giving rise to a confining potential between the reversed spin (at the origin) and the charge of the hole. Similar hopping histories occur as well in the case of the $S=\frac{1}{2}$ hole in the $S=1$ background, except that the overall kinetic energy is reduced by a factor $\sqrt{2}$ [Fig. 10(a)]. This loss in kinetic energy is partly compensated by the other hoppings, which however lead directly into higher energy spin configurations involving double local spin flips. In this rather complicated manner the classical ($S\rightarrow\infty$) limit is approached,[38] where the kinetic-energy cost for the hopping in the Néel background becomes of order t itself.[39]

Instead of creating spin flips ($B^{\dagger}_{i,0}$ states) in the high-spin phase, the moving carrier can also create "strings" of singlet excitons, as indicated in Fig. 10(b). In the neighborhood of the low-spin–high-spin transition these excitations are not costly and the delocalizing hole or electron will tend to populate these singlet states, while simultaneously spin flips are created. In other words, at least on the semiclassical level this has to involve again the pseudospins of Eq. (24). As in the undoped case, because a change in total spin is involved, it is impossible to separate the low- and high-spin sectors. For instance, the spontaneous symmetry breaking leading to the Néel state background influences the excitonic sector, where it leads to a staggering of the phases of the low-spin excitons excited by hopping [Fig. 10(b)]. The latter will have consequences for the relative orientations of the pseudospins.

Using Eq. (27), neglecting again the second spin angle (ϕ_i) and transforming the hole wave functions by a canonical transformation,

$$\begin{bmatrix} h^{\dagger}_{i\uparrow} \\ h^{\dagger}_{i\downarrow} \end{bmatrix} = \begin{bmatrix} \cos(\theta_i/2)\sin(\theta_i/2) \\ -\sin(\theta_i/2)\cos(\theta_i/2) \end{bmatrix} \begin{bmatrix} h^{\dagger}_{1i} \\ h^{\dagger}_{2i} \end{bmatrix}, \tag{39}$$

we obtain the semiclassical version of the hopping Hamiltonian given by Eq. (36) for holes,

$$H^h_t = t\sum_{i\delta}\left\{\cos\left[\frac{\Delta\theta_{i\delta}}{2}\right]\left[b^{\dagger}_{i+\delta}b_i h^{\dagger}_{i,1}h_{i+\delta,1} + \frac{a^{\dagger}_{i+\delta}a_i}{\alpha_0}(h^{\dagger}_{i,1}h_{i+\delta,1} + h^{\dagger}_{i,2}h_{i+\delta,2}) - \frac{(-1)^{\delta\cdot y}}{\sqrt{\alpha_0}}(a^{\dagger}_{i+\delta}b_i h^{\dagger}_{i,1}h_{i+\delta,2} + b^{\dagger}_{i+\delta}a_i h^{\dagger}_{i,2}h_{i+\delta,1})\right] - \sin\left[\frac{\Delta\theta_{i\delta}}{2}\right]\left[\frac{(-1)^{\delta\cdot y}}{\sqrt{\alpha_0}}(a^{\dagger}_{i+\delta}b_i - b^{\dagger}_{i+\delta}a_i)h^{\dagger}_{i,1}h_{i+\delta,1} + \frac{a^{\dagger}_{i+\delta}a_i}{\alpha_0}(h^{\dagger}_{i,1}h_{i+\delta,2} - h^{\dagger}_{i,2}h_{i+\delta,1})\right]\right\} \tag{40}$$

The meaning of the different hoppings becomes clear in the semiclassical limit. The transformation introduced in Eq. (39) rotates the hole spins in a direction parallel to that of the local spins and the "1" states correspond to this reference frame with hole states decreasing the length of the local spin by $\frac{1}{2}$ unit, while the "2" states involve a change by $\frac{3}{2}$ unit. In the high-spin phase only the former can hop and the hopping amplitude is $\propto\cos(\Delta\theta_i)$, i.e., at maximum for parallel spins and diminishing in the Néel phase. It is well known that the competition between the ferromagnetic tendency due to the hopping and the antiferromagnetic exchange at half-filling gives rise to either uniform canting of the spins,[39] or to a spiral spin structure[40] [Fig. 9(c)]. In the low-spin phase, on the contrary, holes with both spin directions can hop and both "1" and "2" states show up in the terms $\propto a^2$ in Eq. (40) and these terms are invariant under the transformation Eq. (39).

The new physics is hidden in the terms which appear in the mixed phase and are $\propto ab$. These terms come in two varieties: (i) the ones $\propto\cos(\Delta\theta_i)$, describing the mixing of the two hole sectors, and (ii) the terms at maximum in the Néel state [$\propto\sin(\Delta\theta_i)$], propagating the "high-spin" holes. These latter terms will turn out to be the important ones and they describe hopping histories as indicated in Fig. 10: if the spin components of the wiggly spins are antiferromagnetic, the hole (or electron) propagates optimally in the region of the mixed phase $\propto abt$ as long as the relative phasing of the high- and low-spin states [$\mathrm{sgn}(a_i b_i)$] is staggered on the lattice. These "spin" and "orbital" staggerings cancel each other [Eq. (29)] and, as a consequence, the carrier delocalization favors in this channel a parallel alignment of the pseudospins, while the normal spins remain antiparallel, as in Fig. 9(d).

In order to further quantify these findings we considered the following possibilities: the classical (Ising-like) "orbital" variables, a_i and b_i, may have either uniform phases ["ferro-orbital" (FO)], or the sign of $a_i\times b_i$ may be staggered on the square lattice ["antiferro-orbital" (AFO)]. The possible deformations of the spin system under doping are the uniform canting and spiral states. In the canted state (CS) the spins on the A (B) sublattice deviate by an angle $\delta\theta/2$ from their orientations in the Néel state, while in the spiral state (SS) the spins are rotated by an angle $\delta\theta$ when we move along the spiral. Thus, both states are characterized by a single parameter $\delta\theta$. In order to diagonalize the hopping Hamiltonian H_t^h, one has to rewrite it for the two sublattices corresponding to the Néel state and express the hopping amplitudes by the characteristic angle, $\delta\theta$. Due to the antiferromagnetic orientation of spins one finds that

$$\sin(\Delta\theta_{i\delta}/2)=\pm\cos(\delta\theta/2)\ ,$$

and

$$\cos(\Delta\theta_{i\delta}/2)=\pm\sin(\delta\theta/2)\ ,$$

where $\delta\theta$ is the canting/spiral angle. The signs $\pm$ depend whether one moves from A to B sublattice, or from B to A and on the chosen convention concerning the spin deviations defined by the angle $\delta\theta$. After making this step one may use the usual Fourier transformation of the hole operators for a two-sublattice system,

$$h^\dagger_{m\mathbf{k}\pm}=\frac{1}{\sqrt{N}}\left[\sum_{\mathbf{R}_i\in A}e^{i\mathbf{R}_i\cdot\mathbf{k}}h^\dagger_{mi}\pm\sum_{\mathbf{R}_i\in B}e^{i\mathbf{R}_i\cdot\mathbf{k}}h^\dagger_{mi}\right]\ , \tag{41}$$

where N is the number of lattice sites (in both sublattices) and the $\mathbf{k}$ vectors are defined in the antiferromagnetic (folded) Brillouin zone. $+$ and $-$ quasiparticles correspond to the wave vectors $\mathbf{k}$ and $\mathbf{k}+\mathbf{Q}$, where $\mathbf{Q}=(\pi,\pi)$ is the nesting vector, of the original (unfolded) Brillouin zone. The dispersion is defined, as usual, by the structure factors, being

$$\begin{aligned}\gamma_{c\mathbf{k}\pm}&=(2/z)(\cos k_x\pm\cos k_y)\ ,\\ \gamma_{s\mathbf{k}\pm}&=(2/z)(\sin k_x\pm\sin k_y)\ .\end{aligned} \tag{42}$$

The dispersion of a uniform square lattice is of course given by $\gamma_{c\mathbf{k}+}$. The opposite signs of $\cos(k_x)$ and $\cos(k_y)$ in $\gamma_{c\mathbf{k}-}$ result from the opposite phases of the effective hopping term which involves the hole transfer between the $d_{x^2-y^2}$ and $d_{3x^2-r^2}$ orbitals in the x and y direction, expressed by the term $(-1)^{\delta y}$ in Eq. (40). These two functions suffice to describe the hole motion in the CS. In the SS one finds that, depending on whether the hole moves along or against the spiral, the signs of the hopping amplitudes alternate in the real space. This gives after Fourier transformation the two other functions, $\gamma_{s\mathbf{k}+}$ and $\gamma_{s\mathbf{k}-}$. As above, they correspond to the *intraorbital* and *interorbital* hoppings, which do not mix and do mix the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals, respectively.

The resulting form of the hopping Hamiltonian, H_t^h, in $\mathbf{k}$ space depends on the chosen orbital order. Assuming FO, one finds 4×4 matrices of the form,

$$\begin{bmatrix}-A_{\mathbf{k}} & C_{\mathbf{k}} & 0 & D_{\mathbf{k}}\\ C_{\mathbf{k}} & -B_{\mathbf{k}} & -D_{\mathbf{k}} & 0\\ 0 & -D_{\mathbf{k}} & A_{\mathbf{k}} & -C_{\mathbf{k}}\\ D_{\mathbf{k}} & 0 & -C_{\mathbf{k}} & B_{\mathbf{k}}\end{bmatrix}\begin{bmatrix}|1\mathbf{k}+\rangle\\ |2\mathbf{k}+\rangle\\ |1\mathbf{k}-\rangle\\ |2\mathbf{k}-\rangle\end{bmatrix}=\frac{\omega(\mathbf{k})}{t}\begin{bmatrix}|1\mathbf{k}+\rangle\\ |2\mathbf{k}+\rangle\\ |1\mathbf{k}-\rangle\\ |2\mathbf{k}-\rangle\end{bmatrix}\ , \tag{43}$$

yielding after diagonalization

$$\omega_{1,2,3,4}(\mathbf{k})=\pm t(1/\sqrt{2})[A_{\mathbf{k}}^2+B_{\mathbf{k}}^2+2(C_{\mathbf{k}}^2+2D_{\mathbf{k}}^2)\pm\sqrt{(A_{\mathbf{k}}^2-B_{\mathbf{k}}^2)^2+4(A_{\mathbf{k}}+B_{\mathbf{k}})^2C_{\mathbf{k}}^2+4(A_{\mathbf{k}}-B_{\mathbf{k}})^2D_{\mathbf{k}}^2+16C_{\mathbf{k}}^2D_{\mathbf{k}}^2}\,]^{1/2}\ . \tag{44}$$

The quantities $A_{\mathbf{k}}$, $B_{\mathbf{k}}$, $C_{\mathbf{k}}$, and $D_{\mathbf{k}}$ give the quasiparticle dispersions and depend on the chosen state, CS or SS. For the SS,

$$A_{\mathbf{k}}=\left[b^2+\frac{a^2}{\alpha_0}\right]\sin\left[\frac{\delta\theta}{2}\right]z\gamma_{s\mathbf{k}+}\ ,$$
$$B_{\mathbf{k}}=\frac{a^2}{\alpha_0}\sin\left[\frac{\delta\theta}{2}\right]z\gamma_{s\mathbf{k}+}\ ,$$
$$C_{\mathbf{k}}=\frac{a}{\sqrt{\alpha_0}}b\sin\left[\frac{\delta\theta}{2}\right]z\gamma_{s\mathbf{k}-}\ , \tag{45}$$
$$D_{\mathbf{k}}=\frac{a^2}{\alpha_0}\cos\left[\frac{\delta\theta}{2}\right]z\gamma_{c\mathbf{k}+}\ .$$

For CS one finds similar expressions, with $\gamma_{s\mathbf{k}\pm}\rightarrow\gamma_{c\mathbf{k}\pm}$. The free energy of the doped system is defined as $\mathcal{F}_{tJ}=\langle H_{tJ}\rangle$, where H_{tJ} is given by Eq. (38) and the average stands for the classical approximation. For the hole-doped system $\mathcal{F}^h_{tJ}$ is approximately given in the limit of low hole concentration ($\delta\ll 1$) by

$$\mathcal{F}^h_{tJ}(\mathrm{FO})=-zJb^2(b^2+2\alpha_1a^2)\cos(\delta\theta)+zJ\alpha_2a^4 +E_Sa^2+\delta\omega_1\ . \tag{46}$$

Here ω_1 stands for the minimum over $\mathbf{k}$ of the lowest eigenvalue as defined by Eq. (44).

If AFO orbital ordering is assumed, the structure of the Hamiltonian in $\mathbf{k}$ space is somewhat simplified since the orbital ordering does not lead to a doubling of the matrix size, as in the FO case. The quasiparticle states are found from

$$\begin{bmatrix}A_{\mathbf{k}}-C_{\mathbf{k}}\\ -C_{\mathbf{k}}B_{\mathbf{k}}\end{bmatrix}\begin{bmatrix}|1\mathbf{k}-\rangle\\ |2\mathbf{k}+\rangle\end{bmatrix}=\frac{\omega(\mathbf{k})}{t}\begin{bmatrix}|1\mathbf{k}-\rangle\\ |2\mathbf{k}+\rangle\end{bmatrix}\ , \tag{47}$$

and from a similar equation for $|1\mathbf{k}+\rangle$ and $|2\mathbf{k}-\rangle$ states, with the opposite sign of the diagonal elements. We find the eigenenergies,

$$\omega_{1,2,3,4}(\mathbf{k})=\pm(t/2)[\,A_{\mathbf{k}}+B_{\mathbf{k}}\pm\sqrt{(A_{\mathbf{k}}-B_{\mathbf{k}})^2+4C^2_{\mathbf{k}}}\,]\ . \tag{48}$$

For the SS we obtain,

$$A_{\mathbf{k}}=\left[b^2-\frac{a^2}{\alpha_0}\right]\sin\left[\frac{\delta\theta}{2}\right]z\gamma_{s\mathbf{k}+} -2\frac{a}{\sqrt{\alpha_0}}b\cos\left[\frac{\delta\theta}{2}\right]z\gamma_{c\mathbf{k}-}\ ,$$
$$B_{\mathbf{k}}=\frac{a^2}{\alpha_0}\sin\left[\frac{\delta\theta}{2}\right]z\gamma_{s\mathbf{k}+}\ , \tag{49}$$
$$C_{\mathbf{k}}=\frac{a}{\sqrt{\alpha_0}}b\sin\left[\frac{\delta\theta}{2}\right]z\gamma_{s\mathbf{k}-}-\frac{a^2}{\alpha_0}\cos\left[\frac{\delta\theta}{2}\right]z\gamma_{c\mathbf{k}+}\ .$$

The expressions for the CS are given again by the replacement $\gamma_{s\mathbf{k}\pm}\rightarrow\gamma_{c\mathbf{k}\pm}$. The free energy found in the classical approximation for the AFO case is

$$\mathcal{F}^h_{tJ}(\mathrm{AFO})=-zJb^2(b^2-2\alpha_1a^2)\cos(\delta\theta) +zJ\alpha_2a^4+E_Sa^2+\delta\omega_1\ , \tag{50}$$

where ω_1 is again the minimum over $\mathbf{k}$ of the lowest eigenvalue in Eq. (48). We have studied Eqs. (46) and (50) numerically and our findings are summarized in Figs. 11 and 12. For positive low-spin exciton energies (E_S) we find the conventional high-spin phase to be stable. It develops a spiral or canting structure (both structures are degenerate in this simple classical picture) under hole doping. For strongly negative E_S, the low-spin phase is stable in which the holes move freely. The novelty occurs in the vicinity of what otherwise would be the high-spin–low-spin transition line (dashed line, Fig. 12). We find a mixed phase, separated by first-order boundaries from the other phases, characterized by the ordering presented in a schematic way in Fig. 9(d): (i) a coexistence of spin and pseudospin ordering, (ii) no tendency to spiral or cant the spins, and (iii) an AFO ordering in both the spin and the orbital (a,b) channel, resulting in a net ferromagnetic ordering of the pseudospins [Eq. (29)].

The phase boundary between the high-spin and low-spin states of the hole-doped system (dashed line, Fig. 12) may be easily found analytically. In the high-spin phase $a=0$, $b=1$, and the lowest eigenvalue of H_t is

$$\omega_1(\mathbf{k})=-t\sin\left[\frac{\delta\theta}{2}\right]z\gamma_{s\mathbf{k}+}\ .$$

Assuming spirals, the minimum of $\omega_1(\mathbf{k})$ is found at $\mathbf{k}=(\pi/2,\pi/2)$, i.e., the high-spin phase is doped in the pockets at the edge of the antiferromagnetic Brillouin zone, in the same way as the standard t-J model with singlet holes.[41] By the minimization over the spiral an-

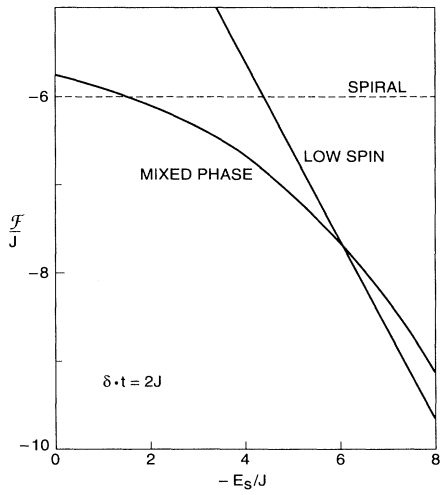

FIG. 11. Semiclassical zero-temperature free energies, $\mathcal{F}/J$ for the hole-doped low-spin–high-spin d^8 problem as a function of the negative of the low-spin exciton energy, $-E_S/J$. The phase transitions are first order as in the case of the d^9 problem, but there is no indication of phase separation.

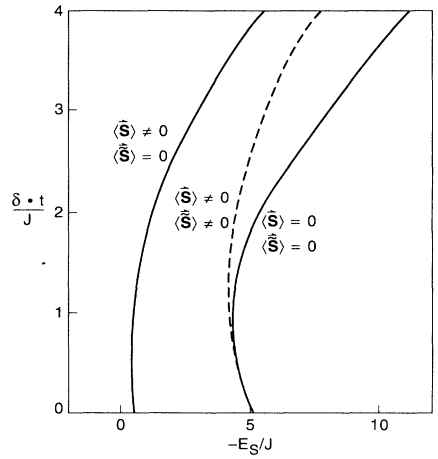

FIG. 12. Semiclassical phase diagram for the hole-doped low-spin–high-spin d^8 problem as a function of the negative of the low-spin exciton energy, $-E_S/J$, and the hole kinetic energy, $t\delta/J$. Around the low-spin–high-spin transition (dashed line) the hole-stabilized mixed phase [Fig. 9(d)] is found.

gle, $\delta\theta$, one finds for small doping ($t\delta \ll zJ$) that $\delta\theta = t\delta/2J$ and the free energy takes the form,

$$\mathcal{F}^h_{tJ}(\mathrm{HS}) = -zJ - z\frac{(t\delta)^2}{8J} . \tag{51}$$

Thus, the spiral angle increases gradually with increasing doping and the period of the spiral becomes equal to that of the antiferromagnetic lattice at a doping of $t\delta = zJ$, where the system orders ferromagnetically. On the contrary, in the low-spin phase the hole motion does not cause any change in the singlet (A_i) background and one may choose $\cos(\delta\theta/2)=1$. [Another choice of $\sin(\delta\theta/2)=1$ gives the same free energy in the limit of ferromagnetically ordered spins in the mixed phase decreasing to zero.] The minimum of $\omega_1(\mathbf{k})$ is found now at $\mathbf{k}=(0,0)$ [if one starts from the ferromagnetic system, the minimum is again at $\mathbf{k}=(\pi/2,\pi/2)$], and the free energy reads,

$$\mathcal{F}^h_{tJ}(\mathrm{LS}) = zJ\alpha_2 + E_S - (z/\alpha_0)t\delta . \tag{52}$$

Consequently, the transition between the low- and high-spin phase occurs when

$$\frac{E_S}{zJ} = -(1+\alpha_2) + \frac{1}{\alpha_0}\left[\frac{t\delta}{J}\right] - \frac{1}{8}\left[\frac{t\delta}{J}\right]^2 . \tag{53}$$

For standard parameters and at a moderate doping of $t\delta = 2J$, one finds this transition at $E_S/J = -4.33$ (see Figs. 11 and 12).

This does not complete the phase diagram, since a mixed phase with AFO orbital order occurs near the above transition. One finds the lowest energy for AFO ordering, while the doped holes have momenta near $\mathbf{k}=(0,\pi)$. The net $\mathbf{S}_i$ is staggering with reduced magnitude with no tendency to spiral, while the pseudospins $\mathbf{S}_i$ orient ferromagnetically because the spin and orbital staggerings cancel each other [Fig. 9(d)]. It follows from Eq. (50) that the free energy of the mixed phase (MP) at low doping in the vicinity of momentum $\mathbf{k}=(0,\pi)$ is

$$\mathcal{F}^h_{tJ}(\mathrm{MP}) = -zJb^2(b^2-2\alpha_1 a^2) + zJ\alpha_2 a^4 + E_S a^2 - (2z/\alpha_0)abt\delta . \tag{54}$$

Unfortunately, this free energy cannot be solved analytically as the minimization over a ($b=\sqrt{1-a^2}$) gives a polynomial equation of higher order. However, as can be checked *a posteriori*, the singlet component, $\langle n(A)\rangle$, is relatively small and thus an expansion in small a makes sense. Expanding around the high-spin phase ($a^2 \ll 1$) yields

$$\mathcal{F}^h_{tJ}(\mathrm{MP}) \simeq -zJ + 2zJ(1+\alpha_1+E_S/2zJ)a^2 - (2z/\alpha_0)at\delta , \tag{55}$$

and we find at the saddle point

$$\mathcal{F}^h_{tJ}(\mathrm{MP}) \simeq -zJ - z\frac{(t\delta)^2}{2J\alpha_0(1+\alpha_1+E_s/2zJ)} . \tag{56}$$

The transition from the high-spin spiral phase to the mixed phase can be approximately determined by comparing the free energies obtained in Eqs. (51) and (56). We find that this transition is initially independent of doping (see also Fig. 12), and occurs at

$$E_S^{(1)} = 2zJ[4-\alpha_0(1+\alpha_1)]/\alpha_0 . \tag{57}$$

For the standard parameters one finds a transition at $E_S^{(1)} = -0.333J$. This approximate result is consistent with the numerically determined transition line at low dopings which is found at $E_S \simeq -1.4J$ (Fig. 11). The discrepancy comes from the neglect of higher-order terms which are already playing some role, since $a^2 \simeq 0.23$ at the transition point in Fig. 11. By decreasing the value of the singlet energy, E_S/J, the low-spin component in the mixed phase increases. In the neighborhood of the low-spin phase it is therefore more appropriate to expand instead around large a^2. We find

$$E_S^{(2)} = -2zJ(t\delta/2J - \alpha_1 + \alpha_2) . \tag{58}$$

For the usual parameters and taking $\delta t = 2J$, the transition would occur at $E_S^{(2)} = -7J$, somewhat larger than the numerical result $E_S^{(2)} \simeq -6.0J$ in Fig. 11. Unlike the transition between the high spin and the mixed phase (57), the transition from the mixed to the low-spin phase depends on the doping level. For larger doping the mixed phase expands at the expense of the low-spin phase.

Both transitions to the high- and low-spin phases are first order. The origin of this first-order behavior is similar to what we found in the previous section. The doped holes occupy different regions in $\mathbf{k}$ space: the hole has a momentum close to $(\pi/2,\pi/2)$ in the spiral phase and (0,0) in the low-spin phase, while in the mixed phase it has a momentum close to $(0,\pi)$. As in the d^9 case, the flip of the hole in momentum space determines the order of the transition. In spite of the first-order nature of the phase transitions, we do not find a tendency for phase separation in the present case.

Obviously, this classical phase diagram (Fig. 12) is merely suggestive. The largest corrections are expected for the transition line between the high-spin spiral phase and the mixed phase, since the energy of the former phase is severely underestimated in the classical theory. The importance of quantum corrections to the mixed state is less clear. Although the excitations are massive, we already notice in the previous subsection that this classical approximation is possibly not very accurate at the smallest length scales.[36]

C. Electron doping

Let us now turn to electron doped systems. The propagation of electrons (n-type doping) is quite similar to that of the holes, except that the carriers ($\sim|x\sigma\rangle$) propagate now better in the low-spin than in the high-spin background because of the orbital channel. Instead of Eq. (35) one finds

$$\begin{aligned}
&(A_i,\uparrow_j)\xrightarrow{t}(\uparrow_i,A_j)\ ,\\
&(A_i,\uparrow_j)\xrightarrow{-t/\sqrt{\alpha_0}}(\downarrow_i,B_{j,1})\ ,\\
&(A_i,\downarrow_j)\xrightarrow{t/\sqrt{\alpha_0}}(\uparrow,B_{j,-1})\ ,\\
&(B_{i,m},\sigma_j)\xrightarrow{Ot/\alpha_0}(\sigma_i,B_{j,m})\ ,
\end{aligned}\tag{59}$$

where O is a spin-overlap factor as in Eq. (6). The hopping Hamiltonian for electrons is obtained by replacing $X_{i,\pm}$ in Eq. (36) with

$$X^{\dagger}_{i,\pm}=B^{\dagger}_{i,0}/\sqrt{2\alpha_0}\pm(-1)^{\delta\cdot y}A^{\dagger}_i\ ,\tag{60}$$

and by weighting the last two terms in Eq. (36) by $1/\alpha_0$. Therefore, for the n-type doping one finds again a similar form of the classical kinetic energy (40), but the factors $\sim\sqrt{\alpha_0}$ are now in front of b_i instead of a_i,

$$\begin{aligned}
H^e_t=t\sum_{i\delta}\Bigg[&\cos\left[\frac{\Delta\theta_{i\delta}}{2}\right]\left[\frac{b^{\dagger}_{i+\delta}b_i}{\alpha_0}h^{\dagger}_{i,1}h_{i+\delta,1}+a^{\dagger}_{i+\delta}a_i(h^{\dagger}_{i,1}h_{i+\delta,1}+h^{\dagger}_{i,2}h_{i+\delta,2})\right.\\
&\left.-\frac{(-1)^{\delta\cdot y}}{\sqrt{\alpha_0}}(a^{\dagger}_{i+\delta}b_ih^{\dagger}_{i,1}h_{i+\delta,2}+b^{\dagger}_{i+\delta}a_ih^{\dagger}_{i,2}h_{i+\delta,1})\right]\\
&-\sin\left[\frac{\Delta\theta_{i\delta}}{2}\right]\left[\frac{(-1)^{\delta\cdot y}}{\sqrt{\alpha_0}}(a^{\dagger}_{i+\delta}b_i-b^{\dagger}_{i+\delta}a_i)h^{\dagger}_{i,1}h_{i+\delta,1}+a^{\dagger}_{i+\delta}a_i(h^{\dagger}_{i,1}h_{i+\delta,2}-h^{\dagger}_{i,2}h_{i+\delta,1})\right]\Bigg]\ .
\end{aligned}\tag{61}$$

This rescaling of parameters compared to the hole doped case does not change the phase diagram in Fig. 12 qualitatively. The same phases occur but the reparametrization reshuffles the phase boundaries. We proceed in the same way as for hole doping and we find for the free energy of the high-spin SS at low dopings,

$$\mathcal{F}^e_{tJ}(\mathrm{HS})=-zJ-\frac{z}{\alpha_0^2}\frac{(t\delta)^2}{8J}\ .\tag{62}$$

Compared to the hole-doped case, the hopping of the electron in the high-spin phase is further frustrated by the fact that the Hund's-rule coupling has forced the carrier in the "wrong" orbital channel. The low-spin phase profits, not only because the electrons do not have to fight the exchange interactions in order to delocalize, but also because they can hop in the "right" orbital channel. The low-spin free energy is

$$\mathcal{F}^e_{tJ}(\mathrm{LS})=zJ\alpha_2+E_S-zt\delta\ .\tag{63}$$

The transition between the low- and high-spin phase happens now much earlier, if E_S decreases, and is given by the condition

$$\frac{E_S}{zJ}=-(1+\alpha_2)+\left[\frac{t\delta}{J}\right]-\frac{1}{\alpha_0^2 8}\left[\frac{t\delta}{J}\right]^2\ .\tag{64}$$

For the standard parameters and at the $t\delta=2J$, the transition occurs at $E_S/J=2.77$ (see Fig. 13). Again a mixed phase with AFO orbital order is found in the vicinity of this transition, which is of the same sort as the hole stabilized one [electrons doped at momentum $\mathbf{k}=(0,\pi)$, ferromagnetic-ordered $\tilde{\mathbf{S}}_i$ and staggered normal spin components]. In contrast to the hole-doped case, the singlet component is small in the whole region of stability of the mixed phase and one can therefore expand around

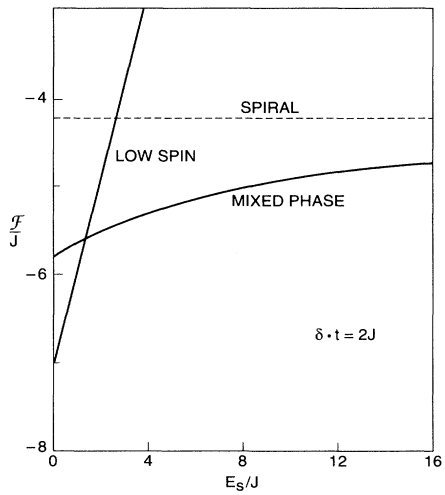

FIG. 13. Semiclassical free energies, $\mathcal{F}/J$, like in Fig. 11, but now for the electron doped problem (note the positive sign of E_S/J). In this case the mixed phase is more stable than a high-spin spiral phase up to very large values of the low-spin exciton energy, ($E_S\simeq 80J$).

a high-spin phase ($a^2=0$) everywhere. The transition between the high-spin and mixed phase is approximately given by the simple condition,

$$E_S^{(1)}=2z^2J\alpha_0 , \tag{65}$$

independently of the doping. For the standard parameters one finds this transition at a very high value of $E_S^{(1)}=96J$ (while numerical analysis gives $E_S^{(1)}\simeq 80J$). The analytic condition for the transition from the mixed to the low-spin phase is more complex and we do not reproduce it here. One finds this transition at $E_S^{(2)}\simeq 2.19J$ from the expansion and at $E_S^{(2)}\simeq 1.40J$ from the numerical analysis (see Fig. 13). Both transitions in Fig. 13 are first order which reflects again the fact that the doping of the distinct phases occurs in quite different regions of the Brillouin zone.

Compared to the hole-doped case, the stability of the mixed phase is a less problematic affair for electron doping. In the former case, we have implicitly assumed that the propagation of the holes is severely hindered by the antiferromagnetic order of the spins in the high-spin phase, although the high-spin phase is optimal in this respect in sofar orbital dynamics is involved. Although the situation is not as catastrophic as for $S=\frac{1}{2}$, this classical feature is also suspicious for holes hopping in a $S=1$ system. On the other hand, in the electron doped system, "true" kinetic energy is paid in the high-spin phase because the holes hop in an unfavorable orbital channel. Therefore, electron doping of nickelates will tend to help the low-spin state and it is not unlikely that in some doping regime the mixed phase might be realized. Unfortunately, it turns out to be extremely hard to make n-type nickelates.[42]

Finally, compared to the d^9 case, phonons are expected to play a less important role. Because a coupling between the local singlet and triplet states at half-filling involves a change in total spin, it follows directly that the Jahn-Teller–like terms giving rise to the quadrupolar distortions in the d^9 case are inoperable and we are left only with the less important "diagonal" electron-phonon terms.

V. CONCLUSIONS

In this paper, we have explored possible ramifications of orbital degeneracy in the context of strongly coupled doped Mott-Hubbard insulators. We have found a rather interesting physical landscape. We arrived at the basically trivial conclusion that binding of excitons to carriers happens nearly always. The hard part is to find out whether these "three-particle bound states" have significant consequences on macroscopic scales. They clearly do if the mass of the relevant exciton is of the order of the hopping energy and/or superexchange. By its very nature, the subject then turns into a rather nonuniversal affair. The first question to ask is if the relevant crystal-field exciton does or does not change the local total spin state of the ions. If the holes and excitations involved are all in their maximum local spin states, the problem is a somewhat exotic mixture of t-J–like complications and simple single-particle motives. If the carriers and/or the spins do not have total maximum spin, one is forced to consider rather unconventional possibilities, like the ordering of the pseudospins presented in Sec. IV. The picture is then complicated further by the many ways that orbital-angular momentum symmetry is broken by the lattice structure, while this "orbital" dynamics itself feed backs on the lattice via the electron-phonon coupling.

Admittedly, we cannot point at a single example where this kind of physics is realized in nature (except, of course, for the "Kugel-Khomskii" instabilities). The first problem is that the experimental study of doped Mott-Hubbard insulators is still in its infancy. Even in the thoroughly studied high-T_c cuprates, effects of this sort cannot yet be completely disregarded, as we argued. The second problem is the theoretical complexity of this subject matter. The models we have derived are more complex than the usual t-J model. We have limited ourselves to semiclassical considerations, which might be misleading as is well known from the study of the t-J model. Finally, as already stated, the physics we have described relies on some fine tuning. Nevertheless, with these new findings in mind it is hard to believe that the last word has been spoken about doped Mott-Hubbard insulators.

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[1]N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. B **36**, 2036 (1987); O. Gunnarsson and K. Schönhammer, *ibid.* **28**, 4315 (1983).

[2]D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).

[3]M. Cyrot and C. Lyon-Caen, J. Phys. (Paris) **36**, 253 (1975); C. Lacroix, *ibid.* **13**, 5125 (1980).

[4]P. W. Anderson, Science **256**, 1526 (1992).

[5]S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition Metal Ions in Crystals* (Academic, New York, 1970).

[6]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[7]J. van Elp, J. L. Wieland, H. Eskes, P. Kuiper, G. A. Sawatzky, F. M. F. de Groot, and T. S. Turner, Phys. Rev. B **44**, 6090 (1991).

[8]A. E. Ruckenstein and C. M. Varma, Physica C **185-189**, 134 (1991).

[9]C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. **62**, 681 (1987); P. B. Littlewood, C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Phys. Rev. B **39**, 12 371 (1989); Phys. Rev. Lett. **63**, 2602 (1989).

[10]J. Zaanen, A. M. Oleś, and P. Horsch, Phys. Rev. B **46**, 5798 (1992).

[11]J. Zaanen, in *Unoccupied Electronic States,* Vol. 69 of Topics

of Applied Physics, edited by J. C. Fuggle and J. E. Inglesfield (Springer, Berlin, 1992).
[12]P. Fulde and I. Peschel, Adv. Phys. **21**, 1 (1972); Y. Y. Hsieh and M. Blume, Phys. Rev. B **6**, 2684 (1972).
[13]K. I. Kugel and D. I. Khomskii, Usp. Fiz. Nauk **136**, 621 (1982) [Sov. Phys. Usp. **25**, 231 (1982)].
[14]A. M. Oleś, Phys. Rev. B **28**, 327 (1983).
[15]J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954); A. K. McMahan, J. F. Annett, and R. M. Martin, Phys. Rev. B **42**, 6268 (1990).
[16]M. S. Hybertsen, E. B. Stechel, W. M. C. Foulkes, and M. Schlüter, Phys. Rev. B **45**, 10 032 (1992).
[17]H. Eskes, M. B. J. Meinders, and G. A. Sawatzky, Phys. Rev. Lett. **67**, 1035 (1991).
[18]C. T. Chen, L. H. Tjeng, J. Kwo, H. L. Kao, P. Rudolf, F. Sette, and R. M. Fleming, Phys. Rev. Lett. **68**, 2543 (1992); E. Pellegrin, N. Nücker, J. Fink, S. L. Molodtsov, A. Gutierrez, E. Navas, O. Strebel, Z. Hu, M. Domke, G. Kaindl, S. Uchida, Y. Nakamura, J. Markl, M. Klauda, G. Saemann-Ischenko, A. Krol, J. L. Peng, Z. Y. Li, and R. L. Greene, Phys. Rev. B **47**, 3354 (1993).
[19]H. Eskes and G. A. Sawatzky, Phys. Rev. Lett. **61**, 1415 (1988); H. Kamimura and M. Eto, J. Phys. Soc. Jpn. **59**, 3053 (1990); V. I. Anisimov, M. A. Korotin, J. Zaanen, and O. K. Andersen, Phys. Rev. Lett. **68**, 345 (1992).
[20]J. Zaanen and G. A. Sawatzky, J. Solid State Chem. **88**, 8 (1990).
[21]P. Kuiper, G. Kruizinga, J. Ghijsen, G. A. Sawatzky, and H. Verweij, Phys. Rev. Lett. **62**, 221 (1989).
[22]A. Fujimori and F. Minami, Phys. Rev. B **30**, 957 (1984).
[23]J. Zaanen and G. A. Sawatzky, Prog. Theor. Phys. Suppl. **101**, 231 (1990).
[24]J. van Elp, H. Eskes, P. Kuiper, and G. A. Sawatzky, Phys. Rev. B **45**, 1612 (1992).
[25]A. Ramšak, P. Horsch, and P. Fulde, Phys. Rev. B **46**, 14 305 (1992).
[26]J. Zaanen, A. M. Oleś, and L. F. Feiner, in *Dynamics of Magnetic Fluctuations in High Temperature Superconductors,* edited by G. Reiter, P. Horsch, and G. Psaltakis (Plenum, New York, 1991), p. 241.
[27]S. Schmitt-Rink, C. M. Varma, and A. E. Ruckenstein, Phys. Rev. Lett. **60**, 2793 (1988); C. L. Kane, P. A. Lee, and N. Read, Phys. Rev. B **39**, 6880 (1989).
[28]D. M. Newns and N. Read, Adv. Phys. **36**, 799 (1987).
[29]L. F. Feiner and J. Zaanen, in *Electronic Properties of High-T_c Superconductors and Related Compounds,* edited by H. Kuzmany, M. Mehring, and J. Fink (Springer Verlag, Berlin, 1990).
[30]J. Zaanen and P. B. Littlwood (unpublished).
[31]W. Weber, Z. Phys. B **70**, 323 (1988).
[32]D. I. Khomskii, Physica B **171**, 44 (1991).
[33]T. Krekels, T. S. Shi, J. Reyes-asga, G. van Tendeloo, J. van Landyut, and S. Amelinckx, Physica C **167**, 677 (1990).
[34]A. R. Bishop, J. Röhler, and A. Larisch, in *Electronic Properties of High-T_c Superconductors and Related Compounds,* edited by H. Kuzmany, M. Mehring, and J. Fink (Springer Verlag, Berlin, 1990).
[35]T. Egami *et al.*, in *Electronic Structure and Mechanisms of High T_c Superconductivity,* edited by J. Ashkenazi and G. Vezzoli (Plenum, New York, 1991).
[36]L. F. Feiner, A. M. Oleś, and J. Zaanen (unpublished).
[37]L. N. Bulaevskii, E. L. Nagaev, and D. L. Khomskii, Zh. Eksp. Teor. Fiz. **54**, 1562 (1968) [Sov. Phys. JETP **27**, 836 (1968)]; B. I. Shraiman and E. D. Siggia, Phys. Rev. Lett. **60**, 740 (1988); S. A. Trugman, Phys. Rev. B **37**, 1597 (1988).
[38]A. M. Oleś, J. Zaanen, P. Horsch, and V. Drchal (unpublished).
[39]P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955); P.-G. de Gennes, *ibid.* **118**, 141 (1960).
[40]B. I. Shraiman and E. D. Siggia, Phys. Rev. Lett. **61**, 467 (1988); Phys. Rev. B **42**, 2485 (1990).
[41]W. Stephan and P. Horsch, Phys. Rev. Lett. **66**, 2258 (1991).
[42]R. J. Cava (unpublished).