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Freezing electronic correlations by polaronic instabilities in doped La_2NiO_4

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In doped Mott-Hubbard insulators, the electron-phonon interaction and strong Coulomb repulsion can reinforce each other to stabilize small polarons, domain walls, and charge-density waves. We discuss how the electron-phonon coupling stabilizes domain-wall states in an antiferromagnetic spin background for small doping, and promotes coupled spin- and charge-density wave transitions at larger doping, and we explain why this coupling is more important in the nickelate than in the cuprate. We discuss our results in the light of recent experiments on $La_{2-x}Sr_xNiO_{4+y}$.

The problem of doped Mott-Hubbard insulators has attracted much attention recently because of its relevance to the cuprate superconductors. The cuprates are in fact rather exceptional as most Mott-Hubbard insulators cannot be made metallic by doping. Already long ago it was recognized that electron-phonon (EP) interactions are critical for the persistent insulating character of the Mott insulators.[1]

Doped La_2NiO_4 is a close structural relative of the cuprate superconductors, but remains insulating,[2] and it has become clear that the difference with the cuprates is the larger effect of the EP coupling.[3–5] Obviously, in the light of the anomalies of the high-T_c cuprates it would be desirable to know what happens in the strongly coupled, localized limit realized in the nickelates. Very recent structural investigations have revealed a complex variety of charge and spin ordering phenomena. At high doping levels ($x=1/3,1/2$) in $La_{2-x}Sr_xNiO_4$ commensurate polaron lattices have been found,[6] while in La_2NiO_{4+y} at lower doping levels ($y=0.125$) a simultaneous incommensurate charge and spin ordering occurs: the polarons bind to and thereby stabilize domain walls in the Néel background and these domain walls order into a striped phase.[7] $La_{2-x}Sr_xNiO_4$ at low doping ($x=0.2$) shows incommensurate diffuse peaks in both neutron[8] and x-ray[9] scattering which are consistent with a disordered arrangement of domain walls, although the evidence here is less clear and other interpretations of the data may be possible.

In this paper we will show that these findings are consistent with the outcomes of simple mean-field theory (Hartree-Fock, classical phonons) applied to a three-band Hubbard model augmented with Peierls-type EP couplings. The $x=0.5$ (Fig. 2) polaron lattice, as well as the low doping charged diagonal domain wall (DDW) lattice (Fig. 3) turn out to correspond to the ground states of this theory. Our calculations indicate that these ordering phenomena principally reflect the dominant role of the electron-electron interactions. Already in the absence of EP couplings, instabilities such as charged domain walls are stable solutions of semiclassical[10,11] (and better[12]) theory. Although quantum and thermal fluctuations may destroy the ordering, strong dynamical correlations of this sort do exist on relatively long time scales. We show here that there is a synergy by which EP couplings further stabilize the ordering tendencies of electronic origin. The disproportionately large effect of the rather small elemental EP couplings in the nickelates is explained in terms of a positive feedback[3,13] between EP and Zhang-Rice[14] localization, as tuned by the splitting between the oxygen $2p$ and the lower Hubbard (LH) band (Fig. 1). At large dopings, the residual interactions between these polarons leads to ordering into polaron lattices (Fig. 2),[6] but at low dopings the electronic localization proceeds better in domain wall textures (Fig. 3).[7]

We now turn to the calculations (a more extensive account will be published elsewhere[15]). The dominant source of EP coupling is expected to come from the modulation of the electronic transfer integrals and the simplest models are then of the Hubbard-Peierls variety. Neglecting the lattice kinetic energy [$m,n,(\sigma)$ are orbital (spin) labels],

$$H=\sum_{im\sigma} E_m c^\dagger_{im\sigma}c_{im\sigma}+\sum_{\langle i,j\rangle,m,n,\sigma} t_{im,jn}(u_{ij})(c^\dagger_{im}c_{jn}+\text{H.c.})+\frac{1}{2}\sum_{\langle i,j\rangle} K_{ij}u^2_{ij}$$
$$+\sum_{i,m\sigma,n\sigma_1,m'\sigma',n'\sigma'_1} U(m\sigma,n\sigma_1,m'\sigma',n'\sigma'_1)c^\dagger_{im\sigma}c_{in\sigma_1}c^\dagger_{im'\sigma'}c_{in'\sigma'_1}. \quad (1)$$

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The electron-phonon coupling enters through the bond-length dependence of the transfer integrals $t_{ij} \sim 1/d^{\alpha_{ij}}$, so that for small displacements (u_{ij}): $t_{im,jn}(u_{ij}) = t_{im,jn}(1+\alpha_{ij}u_{ij})$. (We scale the displacements u by the Ni-O bond length.) The classical saddle point equations for the displacements are

$$u_{ij} = -\frac{\alpha_{ij}}{K_{ij}} \sum_{nm\sigma} t_{im,jn} \langle c^{\dagger}_{in\sigma} c_{jm\sigma} + \text{H.c.} \rangle . \qquad (2)$$

The displacements are given by the weighted sum of bond kinetic energies of the bare electrons, to be determined self-consistently from the Hamiltonian. In Hartree-Fock, the effects of the electron-electron interactions are cast in a form similar to Eq. (2) but now involving the onsite Hubbard-Stratonovich fields $\Delta_{inm} = \langle c^{\dagger}_{in} c_{im} \rangle$, which are treated as classical variables. The interplay of electronic and EP interactions leads to a set of coupled nonlinear integral equations.

We consider the usual three-band model, treating both planar σ bonding O $2p$ orbitals as well as the $3d$ orbitals,[16] with the EP coupling originating in the p-d hybridization.[13] Besides the usual $d_{x^2-y^2} \sim d_x$ orbital, the $d_{3z^2-1} \sim d_z$ Ni d orbital has to be included in order to describe the high-spin state at half-filling $\sim d_{x\sigma} d_{z\sigma}$, as well as the low-spin hole states $\sim d_{x\uparrow} d_{x\downarrow} d_{z\sigma}$. The charge-transfer energy Δ [splitting between upper Hubbard (UH) and p-band], U_{eff} (splitting between the lowest lying subbands of the multiplet-split UH and lower Hubbard bands), the Hund's rule coupling J_H, and the x-z crystal-field splitting E_z (Ref. 17) are needed as parameters.

For parameters appropriate to the nickelate, the single hole solutions are a breathing-mode polaron, with the hole centered on a Ni site (e.g., Fig. 2). In Fig. 1 we show the total relaxation energies per carrier (the energy gained by allowing for nonuniform solutions) of the single hole[18] and diagonal wall solutions, as a function of Δ and realistic values[19] for the other parameters, both in the absence and the presence[20] of the EP coupling. The most striking feature is the peak in both the pure electronic and the electron-phonon relaxation energy if $\Delta \simeq U_{\text{eff}}$. This explains the much bigger effect of the electron-phonon coupling in La-Sr-Ni-O compared to the cuprates:[3] for the cuprates $\Delta \ll U_{\text{eff}} = U$ while for the nickelate $\Delta \simeq U_{\text{eff}}$, close to the maximum in the lattice-polaronic binding energy (δE_{ph}). We find $\delta E_{\text{ph}} \sim 0.2 t_{pd}$, estimating the EP coupling constant $\lambda_{pd} = t_{pd}\alpha^2_{pd}/K_{pd} \sim 0.5$ [$t_{pd} \simeq 1$ eV, $\alpha_{pd} \simeq 4$, and $K_{pd} \simeq 32$ eV (Ref. 13)]. This compares favorably with the lattice polaronic binding energy estimated from transport measurements.[21] As is well known, the characteristic scale for phonon-assisted small polaron hopping seen at intermediate temperatures in the dc resistivity is $\delta E_{\text{ph}}/2$, while the polaronic resonance in $\sigma(\omega)$ peaks near $2\,\delta E_{\text{ph}}$, because of Franck-Condon overlap factors.[1] Experimentally these quantities are of order 0.1 (Ref. 4) and 0.5 eV,[5] respectively, in the doped nickelate.[22] In contrast, for the cuprates at low doping, lattice polarons lead to an absorption at 0.1–0.2 eV, consistent with a smaller electron-phonon coupling.[23]

The first effect of the local p-d hybrization is to bind the (p-like) hole to the spin on a particular Ni site and this composite hole then moves as a whole through the lattice with a bandwidth much smaller than its binding energy.[14]

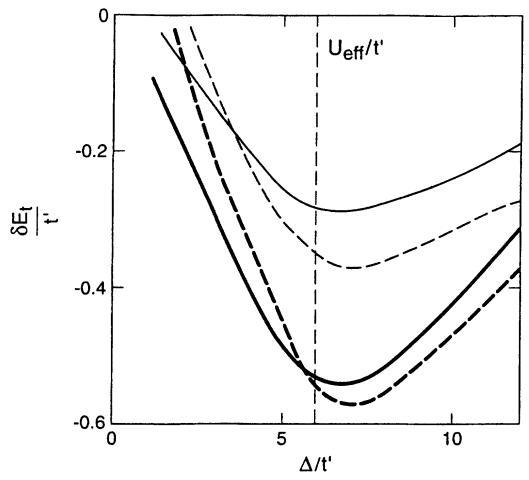

FIG. 1. The total relaxation energies per carrier δE_t in units of t' (Ref. 20), defined as the difference between the energy of the fully self-consistent nonuniform Hartree-Fock state and the energy of the state where the additional hole(s) are added to the rigid bands at half-filling. These are obtained from the nickelate model described in the text, both in the presence (bold lines, $\lambda_{pd} = 0.5$) and absence (thin lines) of the electron-phonon coupling, as a function of the charge transfer energy for fixed U_{eff} (Ref. 17). The lattice-polaronic binding energy, given by the energy difference between bold and thin lines, peaks at $\Delta \simeq U_{\text{eff}}$, as is the case in the nickelates. The dashed and full lines indicate isolated $S = 3/2$ polarons and diagonal domain walls, respectively. The latter are stabilized by smaller Δ as well as by the electron-phonon coupling. Other parameters are $J_H = t'$ and $E_z = 0$.

The bond kinetic energy is already to a large extent "prelocalized" on the bonds surrounding a particular Ni and the EP coupling becomes more efficient in causing a small polaron. In the unrestricted Hartree-Fock (HF) approximation this effect shows up via a positive feedback involving spin-bag-like[24] and EP driven localization:[3,13] the moment decreases at a particular Ni site, increasing the bond-kinetic energy locally, increasing the transfer integrals because of Eq. (2), which in its turn decreases the moment further, etc. This effect is largest when the LH and p band are degenerate, causing the maxima in the relaxation energies in Fig. 1.

At a doping-level with one hole per two unit cells ($x = 0.5$), the best solution is the simple staggered polaron lattice as shown in Fig. 2. The above mechanism strongly favors the Ni centered polarons over all other (bond, O-centered, bipolarons, etc.) possibilities, in agreement with experiment.[6] The spin ordering is a more subtle affair. We find a ferrimagnetic ordering to be most stable, where the spins of the polarons ($S = 1/2$) and unoccupied sites ($S = 1$) are antiparallel. However, the (double) exchange between the Ni(II) and Ni(III) states is quite weak and therefore the calculations indicate a much smaller scale for magnetic interactions than in the undoped insulator.

In Fig. 3 we show a diagonal domain wall in real space. One important aspect (in comparison to previous work on the Hubbard and three-band models[10,11]) is the larger spin; in the nickelate the hole itself carries spin-1/2 and a DDW has a ferromagnetic moment. We find that the DW is dimerized, which is readily understood because the parallel spins on the wall give rise to a one-dimensional (1D) band. This band is

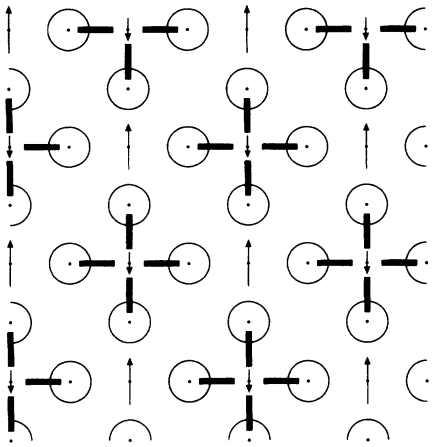

FIG. 2. The polaron lattice obtained at a doping concentration of 1/2 hole/unit cell from our model calculations, to be compared with the data of Chen *et al.* (Ref. 6). The circles indicate the excess charge density on O due to doping, the arrows spins on the Ni (maximally $\sim 1.6\mu_b$), and the bars indicate bond deformations (maximally $\sim 5\%$). Parameters are $\Delta=6$, $U_{\text{eff}}=7$, $E_z=-1$, $J_H=1$ (all in units of t), and $\lambda_{pd}=0.5$.

half-filled if there is one carrier per DW unit cell and a Peierls instability follows, causing a gap in the DW band and special stability at this filling. In most cases, this centers the charge predominantly around one of the Ni atoms in the DW unit cell, although a bond-order wave is found on the DW if the holes have substantial planar $3z^2-1$ character.[15]

Note that the polaron lattice of Fig. 2 can be conceptually viewed as a striped phase of DDW at the maximum density. At different densities of holes, one may expect commensurate phases; for example, the structure at $x=1/3$ proposed by Chen *et al.*[6] corresponds to the removal of every third DDW from the polaron lattice.

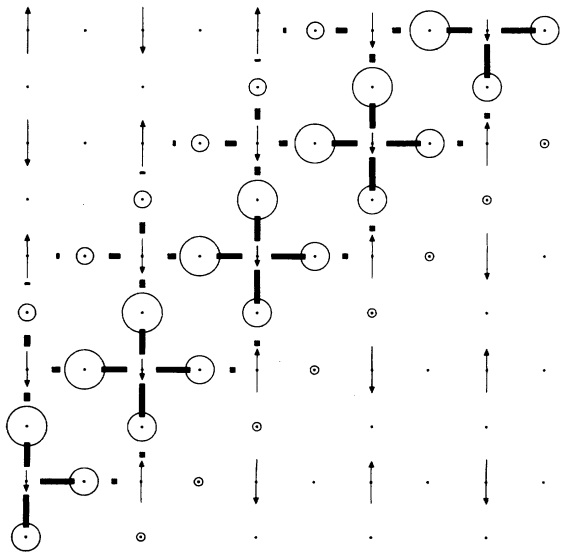

FIG. 3. Fragment of a diagonal domain wall according to our model calculations. These walls line up to form a striped phase as in $La_2NiO_{4+\delta}$ (Ref. 7). Parameters as in Fig. 2.

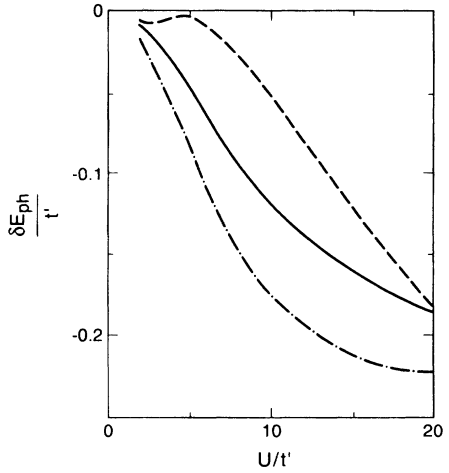

FIG. 4. The lattice polaronic binding energy per carrier $\delta E_{\text{ph}}=\delta E_t(\lambda=1)-\delta E_t(\lambda=0)$, derived from the single band spin-degenerate Hubbard model, as a function of U. Full, dashed-dotted, and dashed lines correspond with diagonal and vertical domain walls, and isolated polarons, respectively. Domain walls are stable for $U<10t'$. The total relaxation energy $\sim -t$ for large U.

HF studies on the single band Hubbard model indicated that domain walls are favored at intermediate couplings, with vertical domain walls most stable for small U/t, and polarons for $U>8t$.[11] Independent of the size of the spins, we find in three-band models the same trend as a function of Δ which now controls the degree of localization. More interestingly, the synergy of electronic and EP localization favors domain walls over isolated polarons or bipolarons. Most of the lattice polaronic energy comes from nearest neighbor Ni—O bonds, while the minimum length scale distinguishing the domain walls from other solutions is set by the Ni—Ni separation. Accordingly, the stabilization of DW relative to polarons is much more evident in single band models. In Fig. 4 we show the lattice-polaronic contribution to the stabilization energy of the domain wall and polaron solution, obtained from the usual (d^9) single band Hubbard model augmented by strong EP coupling, now referring to the d-d hybridization. In the intermediate coupling regime where domain walls are stable for $\lambda=0$ ($U/t<10$), the lattice-polaronic stabilization of the domain-wall states is larger than that of isolated polarons. The holes self-localize to a larger extent in domain-wall spin textures than in polarons[25] and this enhances the effect of EP couplings.[15] Of course, this mechanism will break down if the EP couplings get too strong. Should the polaron shrink to within a unit cell, other mechanisms (e.g., impurity pinning) will take over. While the trends with increasing U and λ are clear, the difference in energy between the possible ordered phases are small, and our calculations are not reliable for the absolute stability of any of the phases.

In our HF theory, we of course observe spin ordering concomitant with the lattice distortion, but this need not be the case at the finite-temperature transition. Neither DW nor the polaron lattice formations lead to frustration in the spin system, and the absence of magnetic ordering at the charge ordering transition of the latter indicates that the Ni(II)-Ni(III) exchange is quite small. One expects the ex-

change interactions between spins separated by a DW to be of the same order, but the difference is now these small interactions mediate between large domains of already strongly antiferromagnetically correlated spins. Analogous to the situation in quasi-1D spin systems it is not surprising to find a spin freezing at the DW freezing transition in $La_2NiO_{4.125}$. In the presence of quenched disorder this might be different, since ruptures in domain walls cause spin frustration.

In conclusion, a simple model theory is able to reproduce some of the ordering phenomena observed in doped La_2NiO_4.[6–9] The Hubbard-Peierls model catches the essence of the physics although further refinements of the theory might appear to be necessary in order to give a full account of the experiments. The important lesson learned from the nickelates is about the complexity of the electron-correlation problem. We argued here that the electron-phonon coupling acts in first instance to make this aspect more accessible experimentally, without changing its essence. These findings suggest ways to think about the complex electron fluids as realized in the closely related cuprate superconductors.

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[21] It is sometimes asserted that the larger spin in the nickelate is responsible for the localization. Using Zaanen *et al.* [Phys. Rev. B **46**, 5798 (1992)] one finds a coherent hole bandwidth $\sim zJ/\sqrt{2}$ in the $S=1$ spin system and together with the smaller exchange [Sugai *et al.*, Phys. Rev. B **42**, 1045 (1990)] we find the electronic mass to be enhanced by only a factor of 6 compared to the cuprates.

[22] In fact, the diminishing dynamical spectral weight transfer (DSWT) as found by Ido *et al.* [Phys. Rev. B **44**, 12 094 (1991)] from optical conductivity measurements of $La_{2-x}Sr_xNiO_4$ yields in fact unambiguous evidence for strong lattice polaronic effects. DSWT [e.g., Eskes *et al.*, Phys. Rev. Lett. **67**, 1035 (1991)] has to vanish when the polaron wave functions are entirely localized within a unit cell.

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