Interface Controlled Electronic Charge Inhomogeneities in Correlated Heterostructures

Natalia Pavlenko[*] and Thilo Kopp

*EP VI and Center for Electronic Correlations and Magnetism, Universität Augsburg,
Universitätsstrasse 1, D-86135 Augsburg, Germany*
(Received 24 March 2006; published 30 October 2006)

For heterostructures of ultrathin, strongly correlated copper-oxide films and dielectric perovskite layers, we predict inhomogeneous electronic interface states. Our study is based on an extended Hubbard model for the cuprate film. The interface is implemented by a coupling to the electron and phonon degrees of freedom of the dielectric oxide layer. We find that electronic ordering in the film is associated with a strongly inhomogeneous polaron effect. We propose to consider the interfacial tuning as a powerful mechanism to control the charge ordering in correlated electronic systems.

The surfaces and interfaces in strongly correlated transition metal oxides are of fundamental importance for complex oxide superlattices and oxide electronic devices. Moreover they open a new field to study correlation effects not observed in the bulk. In correlated oxides, the doped carriers, which give rise to superconductivity and colossal magnetoresistance, also lead to charge-ordered states [1]. In manganites like $La_{1.2}Sr_{1.8}Mn_2O_7$, ARPES measurements suggest polaronic metallic properties with anisotropic band structure [2]. The observed anisotropy can be possibly related to the local charge order near the ferromagnetic Curie temperature where the CMR effect is observed. On the other hand, in cuprates, recent STM studies indicate hidden electronic ordered states like checkerboard four CuO_2 unit cell patterns or stripes [3]. The checkerboard states [3–5] coexist with the superconducting state and can play an important role in the appearance of superconductivity.

As compared to surface-related states, the physics is even more complex and less understood at interfaces between correlated oxides and structurally compatible perovskites. If the heterostructure is formed by an oxide film grown on an insulating layer with high dielectric constant like $SrTiO_3$ or $BaTiO_3$, the correlated charge carriers of the film are coupled at the interface to the charge and lattice degrees of freedom of the dielectric layer. Recent studies of complex oxide interfaces show that not only chemical or electrostatic doping, but also the microscopic electronic structure of the interface perovskite titanate layer can lead to a metal-insulator transition with a mixed valence charge modulation in $LaTiO_3/SrTiO_3$ superlattices [6,7] or to a suppression of the superconducting state in $YBCO/SrTiO_3$ heterostructures [8,9]. In the perovskite titanate layers, the nonzero dielectric polarization is stabilized due to the hybridization between Ti^{4+} d orbitals and $O^{2−}$ p orbitals in the TiO_6 octahedra [10]. The TiO covalent hybridization is strongly modulated by the dynamical polar lattice displacements [11] which is essential for ferroelectricity in perovskite titanates. Consequently, if the strongly correlated oxide film of a few nm thickness is grown on a dielectric layer, the new interface states caused by the

TiO dynamical covalent charge are not shunted by "bulk behavior" and dramatically affect the properties of the entire system.

In this work, we consider a basic model which allows us to investigate how the dynamical covalency and the phonons of the perovskite titanate can act on the correlated states of the oxide film. For the oxide films, formed by weakly coupled transition metal oxide planes, we focus on the first plane at the interface without detailed analysis of the interplanar charge redistribution. With regard to recent experiments [3,4], we allow for electronic states with a checkerboard ordering. We consider an extended Hubbard-type model on a N-site square lattice with tight-binding dispersion $\varepsilon_k = -2t\eta_k^+$, $\eta_k^+ = \cos k_x + \cos k_y$:

$$H_{\text{film}} = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{\langle ij\rangle} n_i n_j. \quad (1)$$

Here $c_{k\sigma}^\dagger$ are electron creation operators, $n_i = \sum_\sigma n_{i\sigma}$ and V is the nearest-neighbor Coulomb repulsion. Furthermore, to study the charge ordering in the film we introduce the index α for two sublattices I and II and the order parameter $\delta = n_I - n_{II} = x_{II} - x_I$ where $n_{I/II}$ are the sublattice electron concentrations and $n = (n_I + n_{II})/2$. To specify the interface microstructure, we consider a high-T_c cuprate film where the superconductivity can be tuned by electrostatic interface doping [12]. For such films with CuO_2 planes between BaO layers, recent TEM studies show the most probable interface arrangement to be of a stacking sequence TiO_2-BaO-CuO_2 [13]. In the emerging Ti-O-Cu interface chemical bonding, the Coulomb interaction of the hybridized $3d − 2p$ TiO electrons with the charge carriers of the CuO_2 planes remains almost unscreened (about 1–2 eV) and can strongly affect the planar electron transfer [9]. In the context of the interface physics related to the Ti-O-Cu bonding, we focus on two aspects.

The first (*electronic*) aspect concerns the modulation of the $p − d$ hybridization in TiO through doped holes in the CuO_2 planes, represented by a term

$$H_{\text{pd−hole}} = V_{pd}\sum_i (1 - n_i)(p_i^\dagger d_i + d_i^\dagger p_i). \quad (2)$$

The $3d$ and $2p$ states in each interface TiO group with $H_{gap} = (\Delta_{pd}/2)\sum_i(d_i^\dagger d_i - p_i^\dagger p_i)$ are separated by the gap $\Delta_{pd} \approx 3$ eV. As the effective charge of Ti (about 2.2–2.89 $|e|$ [10,14]) arises predominantly from the TiO hybridization and provides up to 0.76 hybridized electrons per TiO bond, we assume the one-electron constraint $p_i^\dagger p_i + d_i^\dagger d_i = 1$ to hold for the TiO hybridization. This constraint allows us to introduce a pseudospin formalism through $d_i^\dagger d_i - p_i^\dagger p_i = -2s_i^z$; $d_i^\dagger p_i + p_i^\dagger d_i = s_i^x$. Consequently, the coupling (2) can be rewritten in terms of a pseudospin flipping $H_{pd-hole} = V_{pd}\sum_i(1 - n_i)s_i^x$ and the gap-term by $H_{gap} = -\Delta_{pd}\sum_i s_i^z$.

As the second (*lattice*) aspect of the interface coupling, we analyze the interaction of polar TiO-phonon modes with the doped CuO$_2$ holes, which is accounted for by a Holstein approach

$$H_{pol} = \hbar\omega_{TiO}\sum_i b_i^\dagger b_i - \eta_0\sum_i(1 - n_i)(b_i^\dagger + b_i) \quad (3)$$

The phonon operators $b_i^\dagger(b_i)$ refer to a particular TiO-mode of frequency ω_{TiO} [$\hbar\omega_{TiO}/t = 0.1$]; $\eta_0 = \sqrt{\hbar\omega_{TiO}E_p}$ is the hole-phonon coupling, and E_p is the polaron binding energy. Applying a combined two-step unitary transformation $U_{pol}U_{pd}$ to (2) and (3) (U_{pol} is the variational Lang-Firsov transformation and $U_{pd} = \exp[(iV_{pd}/\Delta_{pd})\sum_i s_i^y(1 - n_i)]$) [9,15], we can eliminate the first-order coupling terms (2) in V_{pd} and (3) in η_0. Averaging over the TiO-pseudospin states and phonon bath, we find a renormalization of the parameters of the extended Hubbard model of the film including the electron chemical potential μ, Hubbard repulsion and electron hopping. The Hubbard coupling $U_{eff} = U - \Delta U$ is renormalized by the attractive contribution $\Delta U = E_p\gamma_\alpha(2 - \gamma_\alpha) + V_{pd}^2/4\Delta_{pd}$ [9] where the adiabatic parameters γ_α for each sublattice should be found by minimization of the film free energy. The first term in ΔU contains a polaronic energy gain whereas the second term comes from the flipping of the TiO pseudospins, induced when a neighboring interface hole approaches the TiO group. On the other hand, the renormalization leads to a reduction of the effective intersublattice hopping $t_{eff} \sim \xi t$ in the CuO$_2$ plane by the electron-lattice interface factor $\xi = \xi_{pd}\xi_{pol}$. The factor ξ contains the TiO-hybridization contribution $\xi_{pd} = \cos^2 V_{pd}/2\Delta_{pd}$ and the polaron band narrowing factor $\xi_{pol} = \exp(-\sum_\alpha \gamma_\alpha^2 E_p/2\hbar\omega_{TiO}\coth\frac{1}{2}\beta\hbar\omega_{TiO})$ where $\beta = 1/kT$. We investigate the thermodynamical stability of the effective model of the film for varying hole doping $x = 1 - n$ within the Kotliar-Ruckenstein (KR) approach [16]. In such a model, the interface parameters V_{pd} and E_p modulate the relation between the electron kinetic and potential energy V. Consequently, they are responsible for a transition between the electronic disordered and ordered states of the film. From the point of view of high-T_c theory, this transition is of fundamental impor-

tance for the film superconducting properties which are locally suppressed in regions with charge ordering, for example, by a magnetic field [3]. In the present approach tuning by interfacial parameters is considered as a new mechanism to modulate the disorder-order transition associated with the suppression of superconductivity. In the superconducting dome the film is nonmagnetic. As the interface coupling with CuO$_2$ holes (electrostatic coupling with TiO-pseudospins ["dipoles"] and electron-phonon) cannot induce magnetic moments, we focus on the effect of interface on the (nonmagnetic) electron ordering.

Strong evidence for the feasibility of such an interface-driven tuning is presented in Fig. 1 with a sequence of phase diagrams $E_p - x$ for different values of the coupling V_{pd}. In our analysis we choose a weak Coulomb coupling V ($V/t = 1 - 1.5$) which by itself is not sufficiently strong to stabilize the ordered state in the film as is seen in Fig. 1(a): here the film remains disordered in the entire range of $x < 0.5$ and one needs a strong coupling to phonons $E_p/t > 0.8 - 1.4$ to stabilize the ordering. The role of the interface becomes even more crucial for large $V_{pd}/4t > 1.7$ [Fig. 1(b)]. Here the curves, corresponding to a transition between the charge-ordered (CO) and charge-disordered (CD) states, cross approximately in a point which is indicative of a crossover between two qualitatively different regimes. In the first, polaron-driven regime, which persists for lower doping x, the physics in the film is dominated by the electronic kinetic energy. The latter is suppressed by the factor ξ which is reduced when the coupling to phonons or TiO electrons increases. It is essential that such a suppression of the kinetic energy not only leads to the localization of holes but is also accompanied by their ordering. These results can be understood from the analysis of the free energy density
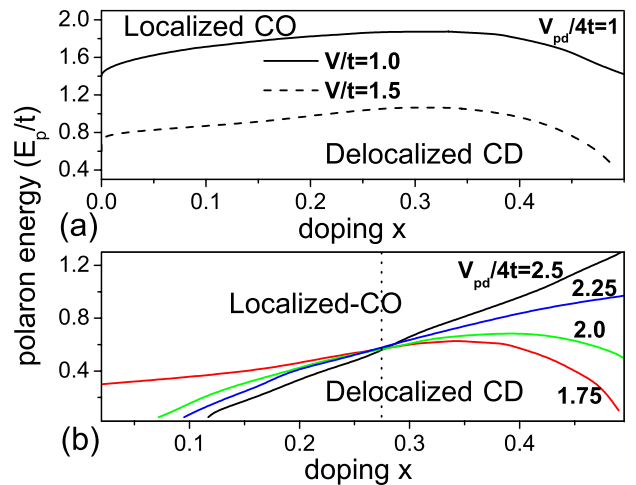

FIG. 1 (color online). Phase diagrams $E_p - x$ for localized CO and delocalized CD states with different coupling V_{pd}. Here $kT/t = 0.05$, $U = 8t$, $\Delta_{pd}/4t = 3$, and $V = 1.5t$. In panel (b) the dotted line indicates the crossover between polaron-driven and flipping-driven regimes.

$$F = -V(4n^2 - \delta^2) + \sum_{\alpha=I,II} [Ud_\alpha^2 - 2\lambda_\alpha^\sigma(p_\alpha^2 + d_\alpha^2)]$$
$$- (4/N)kT\sum_{\boldsymbol{k},\alpha} \log[1 + \exp(-\beta\varepsilon_{\boldsymbol{k}}^\alpha)] + 2\mu n + \Delta E_{\text{IFC}},$$

$$(4)$$

where the quasiparticle energies $\varepsilon_{\boldsymbol{k}}^\alpha$ form two subbands, split by the intersublattice transfer t_{eff} with gap $\Delta\varepsilon_{I,II} = \sqrt{(\Delta\xi_{I,II}^0)^2 + (4t_{\text{eff}})^2}$. Here $\Delta\xi_{I,II}^0 = -4V\delta + \lambda_I^\sigma - \lambda_{II}^\sigma$ and the Lagrange multipliers λ_α^σ constrain the fermion sublattice occupancies in the KR approach. The parameters d_α^2 (p_α^2) are the auxiliary boson fields on doubly (singly) occupied sites. At low $kT/\Delta\varepsilon_{I,II} \ll 1$, a numerical analysis shows that because of the weak renormalization of t_{eff} by $\xi \approx 1$ in the disordered state and because $(\Delta\xi_{I,II}^0/t_{\text{eff}})^2 \gg 1$ holds in the ordered state, the direct influence of the interface coupling (IFC) on the gap $\Delta\varepsilon_{I,II}$ and on all related terms in F is insignificant. Instead, we find that the low-T interface physics is contained in ΔE_{IFC}. The term $\Delta E_{\text{IFC}} = -\sum_\alpha(\Delta E_{\text{pol}} + \Delta E_{pd})$ originates from the effective interaction ΔU and adiabatic interface TiO distortions [15] and consists of the two (polaron and pseudospin) parts

$$\Delta E_{\text{pol}} = -E_p\{\gamma_\alpha(2 - \gamma_\alpha)y_\alpha^2 + (1 - \gamma_\alpha)^2 x_\alpha^2\},$$
$$\Delta E_{pd} = -\{V_{pd}^2/4\Delta_{pd}\}y_\alpha^2. \tag{5}$$

Each part in (5) depends on the spatial hole inhomogeneity, expressed by δ, through the coefficients $y_\alpha^2 = e_\alpha^2 + d_\alpha^2$ $(e_\alpha^2 = d_\alpha^2 + x_\alpha)$ and the polaron adiabatic factors γ_α; both are different in the ordered and disordered states. In the CO state with one of the sublattices preferably occupied by charge, so that $n_I \sim 2n \gg n_{II}$, the number of doubly occupied and empty sites at low x is larger than in the disordered state which implies $(y_\alpha^{\text{CO}})^2 > (y_\alpha^{\text{CD}})^2$. The polaron part ΔE_{pol} in (5) has two competing contributions. The first is proportional to y_α^2 and is significant for $\gamma_\alpha \to 1$ (small-polaron regime). Conversely, the second term in ΔE_{pol} is proportional to x_α^2 and contributes mostly for weak polaron coupling $\gamma_\alpha \ll 1$. If the charge order (CO state) stabilizes for low x, the first, "small-polaron" localizing term prevails, which immediately leads to a strong polaron localization with $\gamma_\alpha^{\text{CO}} > \gamma_\alpha^{\text{CD}}$. Moreover, in the CO state with $n_I \gg n_{II}$, we find a stronger polaron effect for sublattice I: $\gamma_I^{\text{CO}} \gg \gamma_{II}^{\text{CO}}$.

In distinction to the CO state, in the disordered state with the dominant second term in ΔE_{pol}, $\gamma_I^{\text{CD}} = \gamma_{II}^{\text{CD}} \ll 1$, the polaron effect is weak and the holes are delocalized on the lattice. As the strong polaron effect is associated with charge ordering, the suppression of the kinetic energy by increasing E_p or V_{pd} in the polaron-driven regime leads to an extension of the stability of the CO state (Fig. 1, $x < 0.27$) [17]. We note that for the range of the parameters considered in this work, the CO state is found to be stable against the charge separation.

By contrast, in the flipping-driven regime, which prevails for higher doping, $x > 0.27$, the dominant contribution to ΔE_{IFC} (5) comes from the term $\Delta E_{pd} \sim -(V_{pd}y_\alpha)^2$ originating from the effective hole attraction due to the interface hole-pseudospin coupling. Here the numerical studies show that $(y_\alpha^{\text{CO}})^2 < (y_\alpha^{\text{CD}})^2$ and therefore the effective potential energy gain ΔE_{pd} is larger in the disordered state where the pseudospin flipping is caused by weakly dressed ($\gamma_\alpha \ll 1$) holes. This flipping-induced gain leads to a principally new effect when the CD state extends towards larger E_p with an increase of V_{pd} [Fig. 1(b)].

The direct consequence of the competition between the polaron- and flipping-driven regimes is clearly seen in Fig. 2. For lower x, the monotonic decrease with V_{pd} of the CO/CD-transition curve is caused by the interface-induced hole localization. Conversely, for larger x, the nontrivial behavior with a minimum at $V_{pd}/4t \approx 1.75$ originates from the competition between the two different types of the interface coupling [phonon-induced hole localization versus flipping-driven delocalization]. For the considered range of coupling energies, we obtain significant corrections $-\Delta U$ and a strong reduction of the Hubbard repulsion to $U_{\text{eff}} \approx 4t$ at the interface. Such a weak U_{eff} is well below the Mott transition and is not sufficient to prevent high sublattice densities $n_I > 1$ in the CO state in Fig. 2.

For weaker interface coupling, $V_{pd}/4t < 1.5$, as we approach the range $x \approx 0.5$, the region of the CO state extends again (Fig. 1) which leads to the checkerboard ordering at substantially smaller $E_p/t \ll 1$. Although the order in the vicinity of quarter-filling is widely discussed in the literature where it appears due to the nearest-neighbor Coulomb interactions [18], we should stress that in our studies, it is the interface coupling, which plays a key role in the charge ordering of correlated films.

The main interface factor, which drives the transition for weak Coulomb interaction V, is the coupling to phonons which is clear from Fig. 1 where the CO state stabilizes with increasing E_p. Moreover, the phase diagrams $T - E_p$ in the polaron-driven regime (Fig. 3) show some analogy with the $T - V$ diagrams [18]. The reentrant temperature
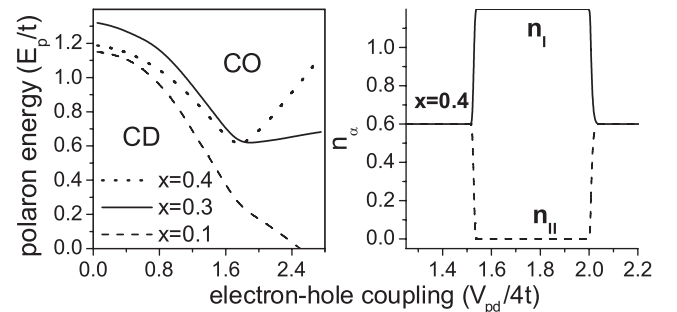

FIG. 2. Phase diagrams $V_{pd} - E_p$ for $kT/t = 0.05$ in polaron-driven $(x = 0.1)$ and flipping-driven $(x = 0.3;\ 0.4)$ regimes. Right panel: the reentrant CD/CO/CD transition for $x = 0.4$.
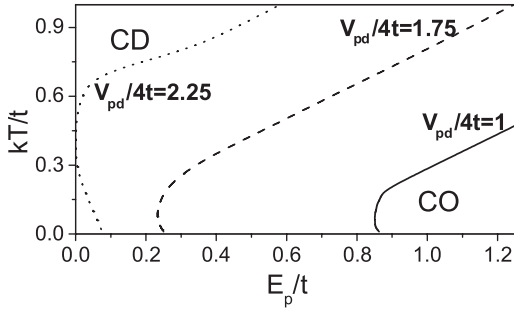
FIG. 3. Phase diagrams $T - E_p$ in the polaron-driven regime at lower doping $x = 0.1$ for different V_{pd}.

behavior for $kT/t < 0.1$ with the negative slope of $T_c(E_p)$ can be understood from the analysis of the entropy contribution $S \sim \sum_{k,\alpha} \log[1 + \exp(-\beta \varepsilon_k^\alpha)]$ to the free energy F. In the CO state, where the charge is localized and $t_{eff}/t \ll 1$, the two energy subbands ε_k^α degenerate into two energy levels $\varepsilon^\alpha = -\mu + 4V n_\alpha + \lambda_\alpha^\sigma$. At low T, the entropy S for such $(N/2)$-degenerated two-level systems grows stronger than the entropy in the disordered state with ε_k^α split by $t_{eff} \sim t$. With a further increase of T, the increasing charge entropy of the homogeneous state dominates and we have a standard melting behavior. As V_{pd} increases, the entire curve $T_c(E_p)$ in Fig. 3 is shifted to smaller E_p due to the V_{pd}-induced suppression of the disorder in the polaron-driven regime.

There is, however, a crucial difference between the reentrant behavior in the polaron-driven and the flipping-driven regime, demonstrated for $x = 0.3$ in Fig. 4. Here, in the reentrant area, we find a new, intermediate-ordered (IO) state (indicated by dashed curves in the $T - E_p$ phase diagrams). In distinction to the disordered phase, the I/II-concentration difference δ in the IO state is less than in the CO state (Fig. 4, inset). Moreover, contrary to
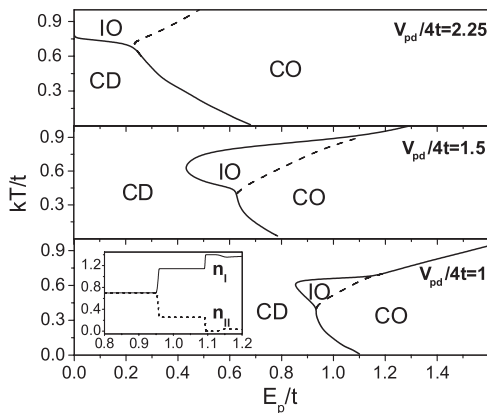

FIG. 4. Phase diagrams $T - E_p$ in the flipping-driven regime for $x = 0.3$. The panels show the appearance of the intermediate IO phase and the expansion of CO and IO states upon an increase of V_{pd}. Inset: evolution of n_α through the phase transitions CD-IO-CO with E_p.

the CO state where the charge in the sublattice I is strongly localized, in the IO state we find a rather weak polaron effect with $\gamma_\alpha^{CD} < \gamma_\alpha^{IO} < \gamma_\alpha^{CO}$. Because of $\delta^{IO} < \delta^{CO}$, the stability of this intermediate state can be explained by the smaller gap $\Delta \varepsilon_{I,II}$ and consequently larger S contribution in expression (4) for F.

In conclusion, we have studied the interface tuning of electronic states in a correlated cuprate film through degrees of freedom which originate from an interface dielectric layer. Even for a weak nearest-neighbor Coulomb coupling, the doped charge in the film can be ordered and localized by the interface coupling. We identified a competition between two types of coupling (to phonons and to hybridized electrons). It becomes manifest in a crossover between the underdoped regime with a dominating charge-ordered (localized) state, and the high doping regime, where a state of almost free mobile holes stabilizes. With the emerging possibilities for electrostatic and chemical control of interfaces, the considered interface tuning of the order-disorder transition can be essential for controlling superconductivity in the film.

*Also at the Institute for Condensed Matter Physics, 79011 Lviv, Ukraine.
[1] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000); E. Dagotto, Science **309**, 257 (2005).
[2] N. Mannella *et al.*, Nature (London) **438**, 474 (2005).
[3] J. E. Hoffman *et al.*, Science **295**, 466 (2002).
[4] T. Hanaguri *et al.*, Nature (London) **430**, 1001 (2004).
[5] M. Vershinin *et al.*, Science **303**, 1995 (2004).
[6] A. Ohtomo *et al.*, Nature (London) **419**, 378 (2002).
[7] S. Okamoto and A. J. Millis, Nature (London) **428**, 630 (2004).
[8] S. Oh *et al.*, Phys. Rev. B **70**, 064509 (2004); J. N. Eckstein and I. Bozovic, Annu. Rev. Mater. Sci. **25**, 679 (1995).
[9] N. Pavlenko and T. Kopp, Phys. Rev. B **72**, 174516 (2005).
[10] R. E. Cohen, Nature (London) **358**, 136 (1992).
[11] R. Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. **37**, 1155 (1976); H. Bilz *et al.*, Phys. Rev. B **35**, 4840 (1987).
[12] J. Mannhart, Supercond. Sci. Technol. **9**, 49 (1996).
[13] S. Bals *et al.*, Physica (Amsterdam) **C355**, 225 (2001).
[14] E. Heifets *et al.*, Phys. Rev. B **64**, 235417 (2001).
[15] H. Fehske *et al.*, Phys. Rev. B **51**, 16 582 (1995).
[16] G. Kotliar and A. E. Ruckenstein, Phys. Rev. Lett. **57**, 1362 (1986).
[17] The mean-field analysis of a simplified extended Hubbard model with a similar interface hole-phonon coupling leads to a suppression of the CD state and to a polaron-driven charge localization, in agreement with the present studies. More careful studies would require an extensive analysis of the charge fluctuations and disorder which can affect the interface coupling to phonons and excitons.
[18] R. Pietig, R. Bulla, and S. Blawid, Phys. Rev. Lett. **82**, 4046 (1999).