Polaronic Anharmonicity in the Holstein-Hubbard Model

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We demonstrate for the nearly half-filled Holstein-Hubbard model that the presence of antiferromagnetic spin correlations can cause polaronic carrier self-localization, and hence a strongly anharmonic lattice potential, already at moderate electron-phonon coupling strengths $\lambda \sim 0.2$–0.4, up to substantial hole dopant concentrations $c_h \sim (20$–$30)\%$. The results are compared to recent observations of anharmonicity in the apical oxygen c-axis motion of cuprate superconductors.

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The cuprate superconductors are strongly correlated electron systems [1] which exhibit antiferromagnetic (AF) spin correlations well into the superconducting doping regime [2]. More recently, it was discovered that several cuprate systems also show large-amplitude anharmonic lattice displacement fluctuations, involving primarily the apical oxygen c-axis motions [3]. These "breathing" modes couple directly, to linear order in the displacement, to the planar CuO_2 conduction electron system [4,5] and should be clearly distinguished from the planar oxygen "buckling" and octahedral "tilting" modes which, by symmetry, to linear order, couple only very weakly (or not at all) to the conduction electrons, but may develop anharmonicity due to *ionically* driven [5] incipient structural instabilities [6].

In the present paper, we propose that the observed anharmonic breathing fluctuations may be intimately related to, in fact caused by, the presence of strong Coulomb interactions and AF spin correlations. Based on a Hubbard model [7] with a linear, Holstein-type [8] electron-phonon (EP) coupling, we show that the presence of AF spin correlations causes polaronic carrier self-localization, and hence strong lattice anharmonicity, already at rather weak EP coupling strengths, e.g., for a *bare* $\lambda \gtrsim 0.2$–0.4, even up to substantial dopant concentrations $c_h \sim (20$–$30)\%$. In contrast to proposed anharmonic phonon models [9], this type of anharmonicity does not require close proximity to any global structural instabilities and persists over a wide range of parameter values. The anharmonic displacement fluctuations have low excitation energies, $\hbar\Omega_{\rm anh} \lesssim 10$ meV, and large renormalized coupling strengths to the conduction electrons, $\lambda_{\rm anh} \gtrsim 20$–$30$ for $\lambda \sim 0.2$–0.4. In effect, Coulomb interactions and AF spin fluctuations are thus causing a substantial enhancement of the EP coupling strength. These results are of fundamental theoretical importance since they suggest the possibility that the low-energy charge, spin, and superconducting pairing response of the CuO_2 conduction electron system are strongly affected by the anharmonic lattice fluctuations and that the low-energy physics of the doped cuprates may not be adequately described, even qualitatively, in terms of a purely electronic model. This is very much in contrast to the underdoped systems where, due to the presence of the Mott-Hubbard gap, even rather strong EP couplings ($\lambda \sim 1$) have very little effect on the observable low-energy electronic and lattice excitations [10].

Our model consists of a single dispersionless (Einstein) optical phonon branch, with bare phonon frequency $\Omega \equiv (K/M)^{1/2}$, restoring force constant K and oxygen atomic mass M, which is coupled to a single-band extended Hubbard [7] electron system, with on-site and nearest-neighbor (nn) repulsions, U and V, respectively, and nn hopping t. The Holstein EP coupling [8] is $H_{ep} = \sum_j C u_j (n_j - 1)$, where u_j denotes the oxygen c-axis displacement and $n_j = n_{j\uparrow} + n_{j\downarrow}$ is the electron occupation number at site j. C is the deformation potential constant, corresponding to a bare phonon-mediated on-site interaction $U_B = -C^2/K < 0$ and a bandwidth-averaged bare coupling constant $\lambda \equiv \bar{\rho}|U_B| = |U_B|/8t$ for an averaged density of states $\bar{\rho} = 1/8t$. Because of particle-hole symmetry, only the hole-doped case $N_h \equiv N - N_e \geq 0$ needs to be considered where $N_e = \sum_j n_j$ and N is the number of Cu sites.

In the zero-bandwidth limit, $t \equiv 0$, the model can be solved exactly [10] and exhibits two competing ground states, referred to below as the polaronic or "P" state and the bipolaronic or "B" state, respectively. At half filling, the P state favors single occupancy, i.e., $n_j = 1$ at all sites, whereas the B state favors $n_j = 2$ and $n_j = 0$ in the two respective sublattices. For small $t \neq 0$, the half-filled P state develops antiferromagnetic spin-density-wave order whereas the B state has charge-density-wave order. Dopant-induced holes in the P state form empty-site small polarons [8] with a local lattice distortion $\Delta u_m = u_P \equiv C/K$ at a polaron "centroid site" m where $n_m = 0$. The $t = 0$ phase boundary separating the P from the B state is at $U = |U_B| + 4V$, independent of the dopant concentration $c_h \equiv N_h/N$, up to $c_h = \frac{1}{2}$. In the EP weak-coupling limit $|U_B| \ll 8|t|$, we expect an additional competing ground state where dopant-induced carriers remain delocalized, referred to as the "D state" below. The observation of AF spin- (rather than charge) density-wave correlations in the CuO_2 planes [2] suggests that the cuprates correspond to the D or P state, whereas, in the $BaBiO_3$ system [11], the three-dimensional analog

of the B state may be realized.

To explore how these competing ground states evolve as a function of U/t and $|U_B|/t$ for finite bandwidth $8t>0$, we take the Born-Oppenheimer limit, $M\to\infty$, and consider the effective lattice potential energy $W(\hat{u})=\sum_j \frac{1}{2}Ku_j^2+E_e(\hat{u})$, where $E_e(\hat{u})$ is the ground-state energy of the Hubbard electron system, including H_{ep}, for an arbitrary displacement configuration $\hat{u}\equiv\{\ldots u_j\ldots\}$. On a finite model cluster, we obtain $E_e(\hat{u})$ by Lanczos exact diagonalization methods and then minimize $W(\hat{u})$ by steepest descent, starting from the known (P,B,D) solutions for $t=0$ or $U_B=0$. In Fig. 1(a), we show the U vs $|U_B|$ ground-state "phase" diagrams of a square-shaped $N=\sqrt{8}\times\sqrt{8}$ lattice with periodic boundary conditions, $V=0$, for $N_h=0$, 1, and 2 dopant-induced holes. Both the D-P and P-B boundaries are "first order" in the sense that each phase continues to exist as a local (but not global) minimum of $W(\hat{u})$ in some finite (U,U_B) region beyond its phase boundaries. The P-B boundary is very close to the zero-bandwidth result, $|U_B|=U$, and essentially independent of N_h even for rather weak couplings $\lambda=|U_B|/8t\ll 1$. Most importantly, we find that the hole-doped D ground state is unstable towards polaron formation already at rather weak EP couplings, i.e., typically for $\lambda\equiv U_B/8t\lesssim 0.2$–$0.4$ for $U/t\sim 8$–12. The enhanced tendency towards polaron formation can be understood physically as a consequence of the preexisting self-localization of dopant-induced carriers relative to their local distortion of the AF spin background and resulting band narrowing [12] which facilitates phonon-induced self-localization. This picture is supported by comparing to the corresponding spin-polarized hole-doped system where AF spin correlations are eliminated and the D-P phase boundary is shifted to a much larger $\lambda\cong 0.96$ for a $N=\sqrt{8}\times\sqrt{8}$ cluster with $N_h=1$. The hole density, e.g., in the single-polaron ($N_h=1$) P state, is mostly localized at the centroid site m with a hole occupancy of at least $\langle 1-n_m\rangle\gtrsim 0.7$, for $\lambda\sim 0.2$–0.4. This indicates a somewhat extended, but still well-localized small polaron. Therefore, we expect that finite-size effects do not qualitatively alter our results. We have verified this in the Holstein-Hubbard model with up to $N=\sqrt{10}\times\sqrt{10}$ and in the Holstein-t-J model with up to $N=4\times 4$ sites.

The presence of self-localization in the P state implies that $W(\hat{u})$ exhibits many energetically degenerate or nearly degenerate minima and hence strong anharmonicity. In Fig. 1(b), we show rough estimates for the nn tunneling barrier height Δ_B for a single dopant-induced polaron ($N_h=1$) in the P state. Δ_B is obtained by evaluating $W(\hat{u})$ along a linear tunneling path in $\hat{u}$ space which connects two minimum-W polaronic displacement configurations, $\hat{u}^{(m)}$ and $\hat{u}^{(l)}$, say, corresponding to nn polaron centroid sites, m and l, respectively. If the path is parametrized, e.g., by $\hat{u}(s)\equiv(1-s)\hat{u}^{(m)}+s\hat{u}^{(l)}$, then $W(\hat{u}(s))$ has local minima at $s=0$ and $s=1$ and the in-

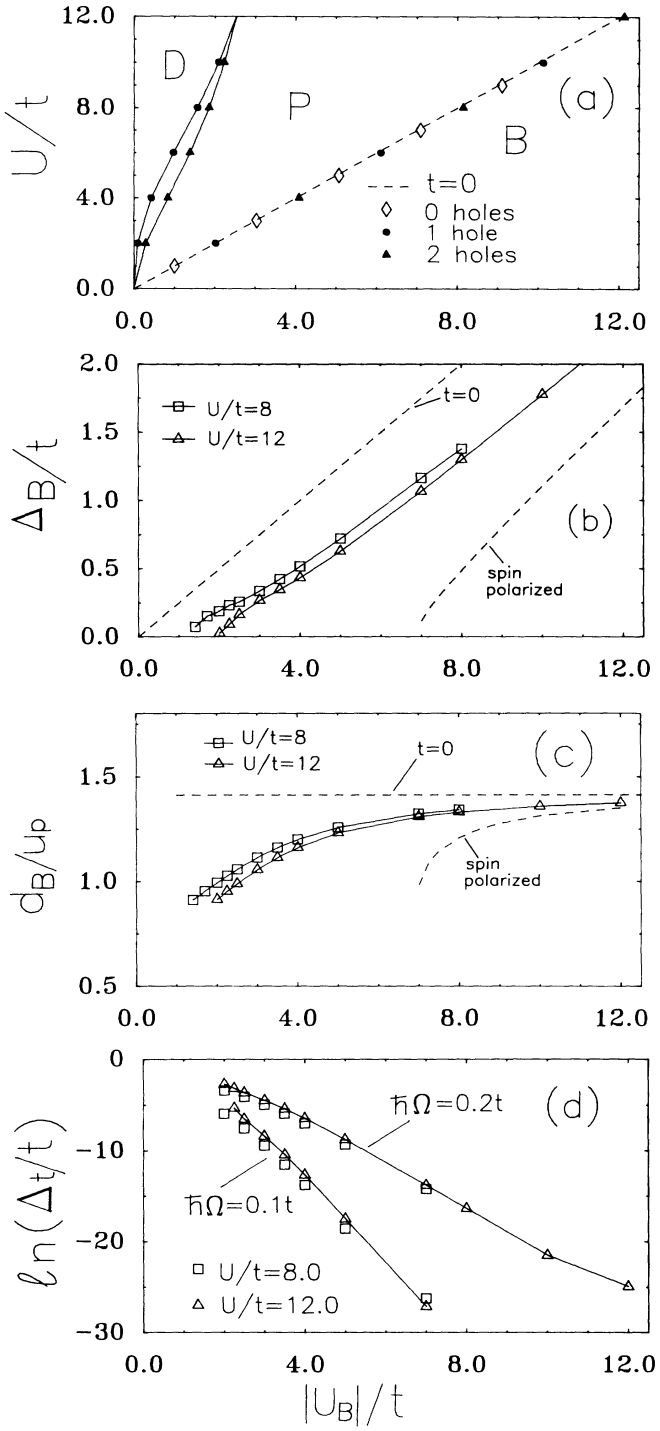

FIG. 1. (a) U/t vs $|U_B|/t$ ($\equiv 8\lambda$) ground-state phase diagram of a $N=\sqrt{8}\times\sqrt{8}$ lattice with periodic boundary conditions, $V=0$, and $N_h=0$, 1, and 2 dopant-induced holes. Also shown vs $|U_B|/t\equiv 8\lambda$ are (b) the $N_h=1$ nn tunneling barrier height, Δ_B/t; (c) the corresponding barrier width, d_B/u_P (in units of $u_P\equiv C/K$); and (d) the logarithm of the tunneling splitting, $\ln(\Delta_t/t)$, for $U/t=8$ and 12 and, in (d), for $\hbar\Omega/t=0.1$ and 0.2. Dashed lines indicate corresponding results for the $t\to 0$ limit and/or the spin-polarized system. Solid lines are a guide to the eye.

tervening barrier maximum is at $s_{max}=\frac{1}{2}$. In Fig. 1(c), we also show the corresponding barrier widths d_B, estimated as the minimum-to-minimum distance in $\hat{u}$ space. Both Δ_B and d_B are substantially reduced by the delocalization term $t\neq 0$ from their respective values $\Delta_B=|U_B|/4$ and $d_B=\sqrt{2}u_P$ in the $t=0$ limit. The second nn tunneling barrier heights (not shown) have qualitatively the same U_B/t and U/t dependence, but, remarkably, are about (30–40)% lower than the nn heights in Fig. 1(b). The second nn barrier widths are about the same as in Fig. 1(c). Thus, longer-range tunneling processes may contribute substantially (if not dominantly) to the anharmonic dynamics.

Clearly, the polaronic anharmonicity described here is a nonlocal, collective phenomenon which cannot be adequately represented by a system of local anharmonic oscillators [9]. Nevertheless, to obtain at least a rough order-of-magnitude estimate for the energy scale of the anharmonic fluctuations, we have calculated the nn tunneling splitting $\Delta_t\equiv 2t_t$ between the ground and first excited state in the double-well potential $W(\hat{u}(s))$, describing the constrained collective 1D lattice motion along the linear nn tunneling path $\hat{u}(s)$ with $-\infty<s<\infty$. As shown in Fig. 1(d), Δ_t decreases very rapidly with $|U_B|$, but increases with U and $\hbar\Omega$. By contrast, the small-amplitude harmonic excitation energy $\hbar\Omega_{har}$, i.e., roughly the ground to second excited state splitting (not shown), is within 10% of the respective bare $\hbar\Omega$, suggesting a weak dopant-induced renormalization of the breathing mode phonons, consistent with the experiments [13].

In multiply doped Holstein-Hubbard and Holstein-t-J clusters (with $N_h\geq 2$), we find that $W(\hat{u})$ has additional local minima where, e.g., for $N_h=2$, only one of the dopant-induced holes is self-localized while the other remains delocalized. Near the D-P boundary, such "mixed" states are almost degenerate with the competing D and P states, to within $\lesssim\hbar\Omega$. It is then possible to have polaron-to-delocalized (PD) processes whereby the $\hat{u}$ field, near a dopant-induced hole, tunnels locally from a self-localized to a delocalized configuration. In such a process, an initially self-localized carrier is released from its trap and becomes essentially delocalized whereas, in the reverse process, an initially delocalized carrier will be captured by a spontaneously generated polaronic local distortion. PD processes and the ensuing partial carrier delocalization will greatly enhance the effective carrier mobility and may well be necessary for obtaining "metallic" conductivity in this model.

To compare to experiments, we assume $t=0.35$ (± 0.05) eV, $U=3.5(\pm 0.5)$ eV [7(b)], and $K=M\Omega^2=9.6$ eV/Å^2, obtained from $\hbar\Omega=50(\pm 10)$ meV, and $M\cong 16$ amu for the oxygen c-axis mode [5,13]. If we roughly identify the observed apical oxygen anharmonic fluctuation energy scale in Tl(2212) [3(b),3(c)], $\hbar\Omega_{anh}^{(exp)}\sim 10$ meV, with the nn polaron tunneling bandwidth $8t_t\equiv 4\Delta_t$, i.e., $4\Delta_t/t\sim 0.029$, we can estimate the required EP coupling strength as $\lambda\equiv|U_B|/8t\cong 0.30$. Thus, $C=(|U_B|K)^{1/2}\sim 2.8$ eV/Å. Since $\lambda\cong 0.30$ is quite close to the D-P phase boundary, $\lambda\cong 0.25$ for $U/t=10$, the mixed state, e.g., for $N_h=2$ and $N=\sqrt{8}\times\sqrt{8}$, is only $\sim 0.36\hbar\Omega$ above the P state. Thus, PD processes may contribute substantially to the anharmonic dynamics. From λ, U/t, and $u_P=C/K\sim 0.30$ Å we can predict the barrier heights $\Delta_B\sim 70$ meV and $\Delta_B'\sim 50$ meV for nn and second nn tunneling, respectively, and the magnitude of single-site fluctuations in the apical oxygen equilibrium position due to intersite and PD tunneling, $\Delta u_j\cong 0.22$ Å, in rough agreement with the observed double peak in the apical oxygen pair distribution function of Tl(2212) with $\Delta u_j^{(exp)}\cong 0.3$ Å [3(b),3(c)]. A nn Coulomb repulsion with $V/t\cong 1.0$, say, changes these results by no more than 5%.

In light of recent theoretical proposals [9], it is of some interest to estimate from the foregoing values the possible superconducting T_c due to anharmonic fluctuation exchange in our model. The effective anharmonic pairing strength from [9] $\lambda_{anh}\sim 2\rho(0)C^2\langle\Delta u^2\rangle_{anh}/\hbar\Omega_{anh}$ is about $\lambda_{anh}\sim 25\gg 1$, using $\rho(0)\sim 2\times(8t)^{-1}\cong 0.7$ eV^{-1}, say, and a fluctuation amplitude $\langle\Delta u^2\rangle_{anh}\sim\frac{1}{4}d_B^2\sim 0.023$ Å^2 from the nn tunneling double well $W(\hat{u}(s))$. Hence, from [9,14] $k_BT_c\cong 0.18\hbar(\langle\omega^2\rangle_{anh}\lambda_{anh})^{1/2}$ and the f-sum rule [9], we get $k_BT_c\cong 0.18\hbar C[\rho(0)/M]^{1/2}\sim 7$ meV, to be compared to the experimental $k_BT_c^{(exp)}\cong 10$ meV. As in other anharmonic models [9], this calculation implies a large isotope effect $\alpha\equiv -d\ln T_c/d\ln M=\frac{1}{2}$ for $\lambda_{anh}\gg 1$. However, it also neglects Coulomb correlations and AF spin fluctuations, which could suppress both T_c and α, as well as couplings to other lattice modes which could increase T_c. It thus remains to be established to what extent anharmonic fluctuations contribute to pairing in the cuprates.

To summarize, we have developed the first general microscopic model of oxygen breathing mode anharmonicity in cuprate superconductors. Based on a Holstein-Hubbard model, we have shown that, in the presence of strong Coulomb repulsions and AF spin correlations, a moderate bare EP coupling strength, $\lambda\sim 0.2$–0.4 can cause self-localization, and hence strong lattice anharmonicity, at substantial dopant densities. The resulting low-energy ($\hbar\Omega_{anh}\lesssim 10$ meV) anharmonic lattice modes have very strong effective coupling, $\lambda_{anh}\gtrsim 20$–30, to the conduction electrons. From more detailed systematic studies, we find qualitatively and quantitatively very similar results in the Holstein-t-J model on lattices with up to $N=4\times 4$ sites and for other types of EP coupling involving, e.g., planar oxygen breathing modes [4] or out-of-plane oxygens in the electron-doped T'-phase cuprates [3(d)]. We are thus confident that the existence of Coulomb or spin-fluctuation-induced polaronic anharmonicity at weak EP coupling strengths is a generic feature of the local charge response in Hubbard- and t-J-type electron systems near half filling. Our basic physical picture is qualitatively

consistent with the observed anharmonic lattice fluctutations [3] and also with other experimental evidence suggesting possible polaronic effects in doped cuprates well into the superconducting regime [15].

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