LA-UR-92- 342

LA-UR--92-342

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SUBMITTED TO: Proceedings of "Lattice Effects in High T_c Superconductors"
Santa Fe, New Mexico January 13-15, 1992

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FORM NO. 836 R4
ST. NO. 2629 5/91

INFRARED ABSORPTION SPECTRA OF VARIOUS DOPING STATES IN CUPRATE SUPERCONDUCTORS

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Doping states in a two-dimensional three-band extended Peierls-Hubbard model are investigated within inhomogeneous Hartree-Fock and random phase approximations. They are very sensitive to small changes of interaction parameters and their distinct vibrational and optical absorption spectra can be used to identify different doping states. For electronic parameters relevant to cuprate superconductors, as intersite electron-phonon interaction strength increases, the doping state changes from a Zhang-Rice state to a covalent molecular singlet state accompanied by local quenching of the Cu magnetic moment and large local lattice distortion in an otherwise undistorted antiferromagnetic background. In a region where both intersite electron-phonon interaction and on-site electron-electron repulsion are large, we obtain new stable global phases including a bond-order-wave state and a mixed state of spin-Peierls bonds and antiferromagnetic Cu spins, as well as many metastable states. Doping in the bond-order-wave region induces separation of spin and charge.

1. Introduction

The importance of lattice effects has become increasingly recognized in the investigations of high-temperature superconductivity: We believe that both electron-phonon and electron-electron interactions must be properly considered for an understanding of its nature It is demonstrated here that the nature of doping states and their interactions are indeed extremely sensitive to effects going beyond a pure 2-d, 1-band Hubbard model. In particular we find, within a 2-d, 3-band extended Peierls-Hubbard Hamiltonian, that a moderate intersite electron-lattice coupling triggers a rapid crossover from a small polaron with well formed moment on Cu to a local collapse of the Cu magnetic moment and strong local lattice distortion in the AF background (Fig. 1(a)). This can be viewed as a transition from a Zhang-Rice

singlet[1] to a covalent molecular state. When the intersite electron-phonon interaction is even larger and competing with on-site electron-electron repulsion, we obtain at stoichiometry a global bond-order-wave state, a spin-Peierls state, and a mixed state of spin-Peierls bonds and antiferromagnetic Cu spins as stable states, and also many metastable states. Doping states in the background of the bond-order-wave are characterized by separation of spin and charge. The various doping states produce distinct infrared optical absorption spectra, relevant to chemical[2] and photodoping experiments.[3]

2. Model and Method

We have considered a 2-d 3-band extended Peierls-Hubbard model:

$$\begin{aligned} H &= \sum_{i\neq j,\sigma} t_{ij}(\{u_k\})c^\dagger_{i\sigma}c_{j\sigma} + \sum_{i,\sigma} e_i(\{u_k\})c^\dagger_{i\sigma}c_{i\sigma} \\ &+ \sum_i U_i c^\dagger_{i\uparrow}c^\dagger_{i\downarrow}c_{i\downarrow}c_{i\uparrow} + \sum_{(i\neq j),\sigma,\sigma'} U_{ij}c^\dagger_{i\sigma}c^\dagger_{j\sigma'}c_{j\sigma'}c_{i\sigma} \\ &+ \sum_l \frac{1}{2M_l}p_l^2 + \sum_{k,l}\frac{1}{2}K_{kl}u_k u_l \ . \end{aligned} \tag{1}$$

Here, $c^\dagger_{i\sigma}$ creates a *hole* with spin σ at site i in the Cu $d_{x^2-y^2}$ or the O $p_{x,y}$ orbital. For the lattice part, we study only the motion of O atoms along the Cu-O bonds and assume that only diagonal components of the spring-constant matrix are finite, $K_{kl} = \delta_{k,l}K$, for simplicity. For electron-lattice coupling, we assume that the nearest-neighbor Cu-O hopping is modified by the O-atom displacement u_k as $t_{ij} = t_{pd} \pm \alpha u_k$, where the + (−) applies if the bond shrinks (stretches) with positive u_k. The other electronic matrix elements are: O-O hopping ($-t_{pp}$) for t_{ij}, Cu-site (ϵ_d) and O-site (ϵ_p) energies for e_i, with $\Delta = \epsilon_p - \epsilon_d$, Cu-site ($U_d$) and O-site ($U_p$) repulsions for U_i, and the nearest-neighbor Cu-O repulsion (U_{pd}) for U_{ij}. We have taken $t_{pd} = 1$, $t_{pp} = 0.5$, $U_p = 3$, $U_{pd} = 1$, and changed U_d with $\Delta = \frac{1}{2}U_d - 1$. (When $U_d = 8$, this parameter set is almost in proportion to those derived from constrained LDA calculations for cuprate superconductors.[4]). We introduce the dimensionless electron-phonon coupling strength $\lambda_\alpha = \alpha^2/(Kt_{pd})$ and vary λ_α. Comparison of our results for local lattice distortion and reduced Cu magnetic moments accompanied by added holes[5] with generalized, inhomogeneous LDA calculations for cuprate superconductors[6] is consistent with values of $U_d = 8$, $\lambda_\alpha = 0.28$, and $K = 32t_{pd}/\AA^2$.

We have used a Hartree-Fock (HF) technique, totally unrestricted in both spin *and* direct space, where self-consistency conditions for on-site and nearest-neighbor, charge and spin densities as well as lattice displacements are imposed without assumption on the form of these quantities. Calculations were made on systems of 6×6 unit cells with periodic boundary condition. The undoped system refers to that with one hole per Cu site. To the generally inhomogeneous HF configurations, we have

added a similarly inhomogeneous RPA analysis of linear fluctuations[7,8] to calculate infrared-active (IR) phonon modes.

3. Zhang-Rice vs. Covalent Molecular Singlets

In this section, we take strong on-site repulsion ($U_d = 8, 10$) and vary the strength of the intersite electron-phonon interaction λ_α.

In the LDA parameter set[4] (above) with $\lambda_\alpha = 0$, each added hole is localized primarily on a single Cu site and four surrounding O sites. The spin density at the central Cu site is in the opposite direction to the undoped case, so that it is termed a small ferromagnetic polaron. The spin densities at the four O sites are small and have the opposite direction to that at the central Cu site. As λ_α is turned on, the Cu magnetic moment is reduced and the O atoms displace toward the central Cu, as shown in Fig. 1(a) for $U_d = 10$. Two HF eigenstates per added hole are located deeply inside the charge-transfer gap (Fig. 1(b)) and their associated wavefunctions are spatially well localized: the higher one corresponds to an oxygen state formed by the four O that surround a Cu and has smaller weight on Cu. The lower one corresponds mainly to the central Cu, has opposite spin to the previous one, and has smaller weight on O. In a Zhang-Rice picture this many-body state mixes quantum mechanically with a similar state in which the directions of the spins on Cu and O are reversed.

At the site where a small polaron resides, reduction of the Cu magnetic moment results in strong local mixing of the four surrounding O with the central Cu. When λ_α is finite, it gains energy by the O approaching the Cu, locally increasing the covalency between Cu and O. Covalency and the displacements of the O atoms reinforce each other synergistically. Thus substantially *below* a critical value of λ_α for destruction of the stoichiometric AF state, both localized $\uparrow$ and $\downarrow$ levels become nearly degenerate and the magnetic moment on the central Cu collapses. This quenching with λ_α can be visualized as a rapid crossover from a Heitler-London-like state corresponding to the Zhang-Rice singlet to a highly covalent molecular state. Above a critical value $\lambda_{\alpha c}$ the *undoped* ground state is replaced by a nonmagnetic bond-order-wave state.

It should be added that, if $U_d = 10$ and $\lambda_\alpha < 0.4$, an intermediate-size ferromagnetic polaron has lower energy than the small polaron above. The former extends to about four Cu sites and the spin densities at these sites are almost in the same direction and perpendicular to the background AF Cu spins. Tunneling between the small and intermediate-size polarons can be anticipated beyond our HF level calculations. (For $U_d = 8$, the intermediate-size polaron is unstable for all λ_α.)

Doping states are evidently very sensitive to small changes of the parameters in the Hamiltonian and a purely analytical determination of the true ground state is very difficult. On the other hand an experimental distinction between them is possible through their different spectroscopic signatures. In Fig. 2 we show IR optical absorption spectra obtained from the current-current correlation functions.

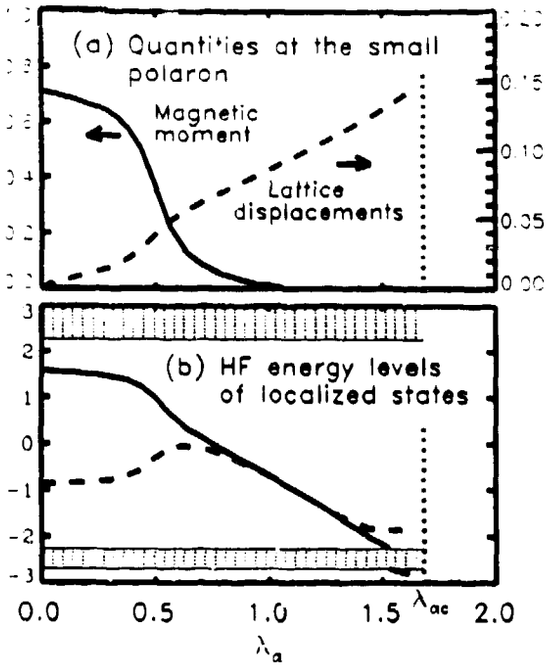

Fig. 1. (a) Magnetic moment on the central Cu site, ratio of lattice displacement of the surrounding O to Cu-O distance (1.89$\AA$) and (b) gap energy levels, for the small polaron state as a function of λ_a. Parameters are $t_{pd} = 1$, $t_{pp} = 0.5$, $\Delta = 4$, $U_d = 10$, $U_p = 3$, $U_{pd} = 1$ and $K = 32t_{pd}/\AA^2$. (Shaded bands are extended states.)

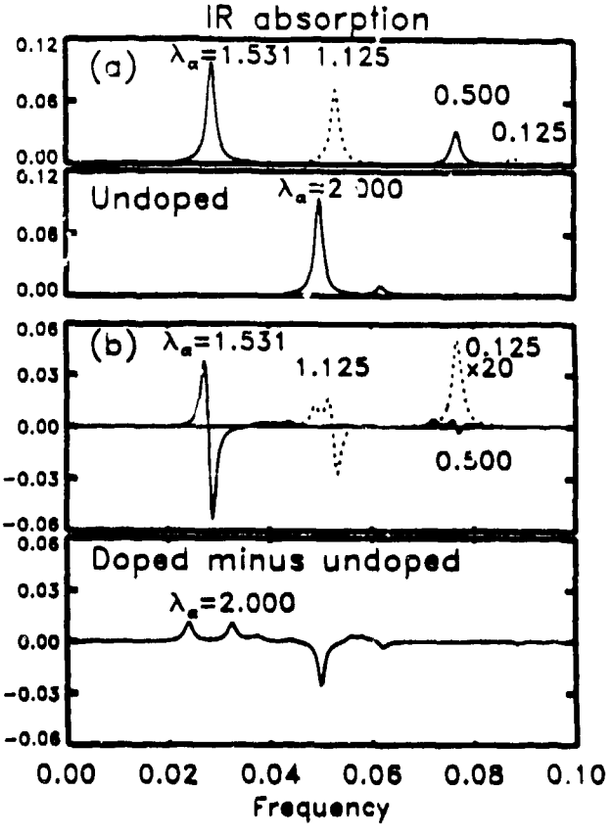

Fig. 2. (a) Infrared absorption spectra in the undoped systems and (b) *difference* spectra for the one-hole doped and the undoped 6 × 6 systems. Same parameters as in Fig. 1.

To evaluate them, we used the adiabatic approximation in the RPA, where quadratic and higher order terms with respect to frequency are neglected in the RPA electronic bubble. In the phonon-frequency range, including the IR range, this approximation is expected to work well. With $K = 32t_{pd}/\AA^2$ and $U_d = 10$, bare phonons ($\lambda_a = 0$) oscillate with $\omega = 0.0914t_{pd} \simeq 840cm^{-1}$ which is comparable with the in-plane stretching IR active mode found in La_2CuO_4 ($706cm^{-1}$).[3] As the electron-lattice coupling λ_a increases, phonons are softened.

In the state with an intermediate-size ferromagnetic polaron ($\lambda_a = 0.125$, $U_d = 10$), IR active phonon modes are induced at $\omega = 0.0768$ (Fig. 2(b)) , which correspond to "shape" oscillations of the polaron. Soft electronic modes mix with the phonon modes giving a very large oscillator strength for the doping peak as compared with the undoped peak at $\omega = 0.0880$ (Fig. 2(a)). In the states with a small polaron ($\lambda_a = 0.500, 1.125$, $U_d = 10$), two local IR active phonon modes appear, which produce structure on the low-energy side of the undoped main peak. The lower-frequency

modes correspond to in-phase oscillations of pairs of opposite O atoms surrounding the central Cu of the small polaron. The higher-frequency modes are localized in one direction and extended in the other direction. When λ_α is close to and smaller than $\lambda_{\alpha c}$ ($\lambda_\alpha = 1.531$), the undoped peak is shifted to lower frequency and the doping modes are localized only in one direction. The undoped phonons have a nonsmooth dispersion relation, which is reminiscent of a transition by breaking of analyticity.[9] Phonons with $\omega \sim 0.04$ have their symmetry broken and develop IR activity. These IR spectra are qualitatively consistent with the experimentally observed[3] bleaching of phonon modes and intensity shift to lower frequencies: Because we are not including all the relevant phonons we postpone a detailed comparison. Also observed in the same experiments[3] is a bleaching of the interband electronic absorption and the corresponding activation of an electronic absorption in the gap, which we can qualitatively associate with the appearance of gap states (Fig. 1(b)).

4. Separation of Spin and Charge

In this section, we study the competition of U_d and λ_α, taking strong intersite electron-phonon interaction ($\lambda_\alpha = 2$) and varying the strength of the on-site repulsion U_d.

The undoped system varies (see Fig. 3) between: a (nonmagnetic) charge-density-wave state (CDW) accompanied by symmetric lattice distortion with respect to a Cu site for $U_d \leq 4.5$; a (nonmagnetic) bond-order-wave state (BOW) with asymmetric lattice distortion for $5 \leq U_d \leq 11$; a mixed state of spin-Peierls bonds and AF Cu spins (SP+AF) for $12 \leq U_d < 13$; a uniform spin-Peierls state (SP) for $U_d \simeq 13$; and the antiferromagnetic state (AF) without lattice distortion, relevant to stoichiometric cuprate oxides, for $14 \leq U_d$. In the crossover region (BOW and SP+AF), there are many metastable states with small energy differences and quantum fluctuation can be expected to destroy some of the mean-field states.

Upon doping, various inhomogeneous mean-field states are found in the respective backgrounds. Doping states in the crossover region are especially interesting: (i) doping states in the BOW are characterized by separation of spin and charge (Fig. 4).

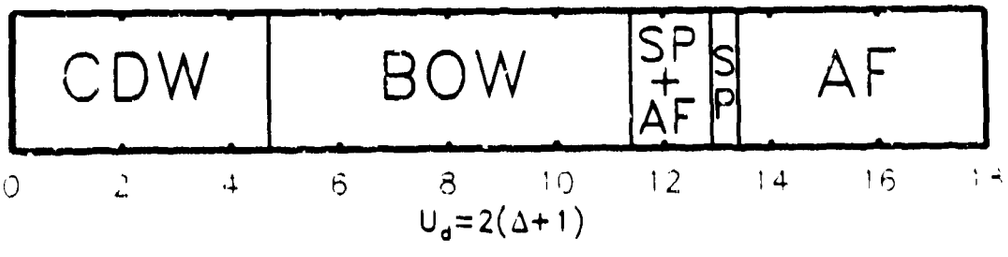

Fig. 3. Phase diagram of global stoichiometric phases for strong intersite electron-phonon interaction ($\lambda_\alpha = 2$). Parameters are $t_{pd} = 1$, $t_{pp} = 0.5$, $U_p = 3$, and $U_{pd} = 1$.

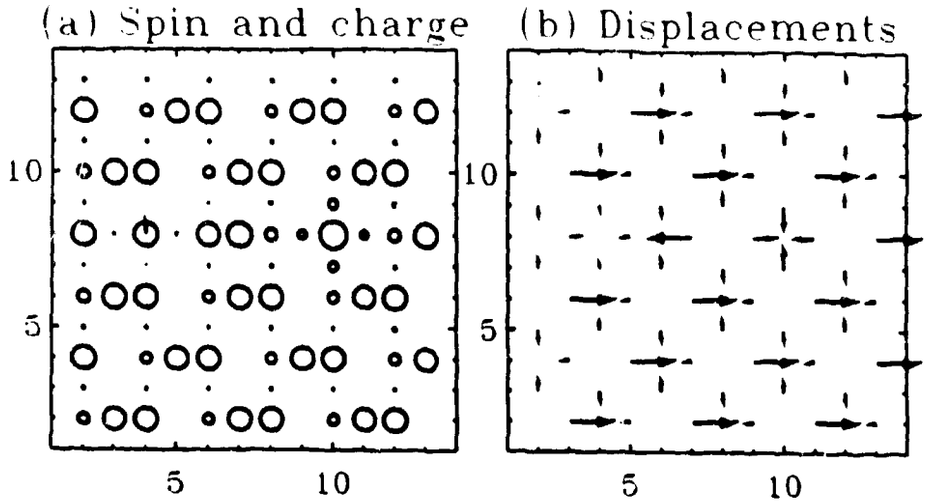

Fig. 4. (a) Spin (arrows) and charge (radii of the circles) densities and (b) lattice displacements of O atoms for the one-hole doped system with separated spin and charge. The BOW background consists of Cu-O-Cu bonds. Here $\lambda_a = 2$, and other parameters are as in Fig. 1.

An unpaired spin is located on a Cu site, disfavors and suppresses lattice distortion around it, and redistributes bond charge densities and lattice displacements. Excess charge is in a covalent molecular singlet described above, which is accompanied by local symmetric lattice distortion with respect to another Cu site separated from the unpaired spin. This separation of spin and charge is a consequence of both large U_d and large λ_a competing with each other. (ii) Doping states in SP+AF accommodate excess charges again in covalent molecules. But the covalent molecules are now formed in AF regions of the undoped case, thus suppressing Cu spins on the molecules. (iii) As doping increases, excess spins, excess charges, and (redistributed) lattice displacements frustrate each other, by breaking delicate energy balances between competing interactions. Effective interactions among quasiparticles are qualitatively different from those in the CDW and AF regimes.

The IR absorption spectra for the BOW state and the state with the separated spin and charge are included in Fig. 2 (a) and (b), respectively ($\lambda_a = 2$). There are four peaks in the undoped case due to lower lattice symmetry. The doped IR modes with $\omega = 0.0240$ and 0.0325 correspond to in-phase oscillations of pairs of opposite O atoms in the covalent molecule, whereas the weaker active modes around the main undoped peak correspond to oscillations in a region between the separated spin and charge, where phonon frequencies are more or less affected.

The states in the crossover region can be viewed in terms of decoration of a bipolaron lattice. In the BOW, each bipolaron consists of two holes on a Cu-O-Cu unit, where one Cu-O bond is strong and the other is weak. All sites in the undoped system are completely covered by them. In the SP+AF, a bipolaron has spin densities on the two Cu sites in a Cu-O-Cu bond. (Thus termed a spin-Peierls bond). They partially cover the system even at stoichiometry and the remaining Cu

sites are occupied by nearly localized spins. The Cu spin densities on spin-Peierls bonds and localized-spin sites are aligned antiferromagnetically. Metastable states are characterized by different configurations of the bipolaron lattice (including the numbers of bipolarons in the case of SP+AF).

5. Summary

The competition of broken-symmetry ground states in the 2-d 3-band extended Peierls-Hubbard model is very sensitive to parameter values. Around doping sites, covalency and displacements of the O atoms reinforce each other through intersite electron-lattice coupling and produce a rapid crossover from a Zhang-Rice regime to a molecular singlet state with local quenching of the Cu moment and large local lattice distortion. This occurs in an electron-lattice coupling strength regime extending substantially *below* the critical value for destruction of the stoichiometric AF state. When electron-electron and electron-phonon interactions are competing, we have observed a novel separation of spin and charge in a BOW background. The various doping states are characterized by distinct high energy (electronic optical absorption) and low energy (IR,Raman) signatures relevant to chemical[2] and photodoping experiments.[3]

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