Optical Conductivity of $La_{2-x}Sr_xCuO_4$ and Soft Electronic Modes

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We calculate the optical conductivity of $La_{2-x}Sr_xCuO_4$ in the inhomogeneous Hartree-Fock plus random phase approximation using the p-d model with parameters taken from first-principles calculations. The ground state evolves from a polaron state for small and moderate doping to a conventional metal for $x \gtrsim \frac{1}{4}$ in consistency with transport and optical experiments. The calculated optical conductivity shows good agreement with experiments regarding the peak positions and relative intensities for zero and small dopings. The precursor of the midinfrared band is identified with transitions from the localized states on Cu to the extended states above the Fermi level.

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One of the striking normal state properties of the high-temperature superconductors is the optical conductivity which has recently received theoretical [1–3] and experimental [4–7] attention. At half filling the system is a charge transfer (CT) insulator with an onset of in-plane optical absorption [6, 8] at ~ 2 eV for $La_2Sr_xCuO_4$ corresponding to Cu-O CT transitions. As the system is doped, spectral weight from the CT band is transferred to a midinfrared (MIR) band initially at ~ 0.5 eV. As doping increases the spectral weight transfer proceeds further and at the same time the MIR band merges with the Drude component. For doping $x > x_c \sim 1/4$ the electronic ground state seems to change as well as the optical conductivity and other normal state properties like the sign of the Hall constant. In this Letter we calculate the optical conductivity in the inhomogeneous Hartree-Fock (HF) plus random phase approximation (RPA) approach applied to the p-d model [9–11]. Positions of the bands and relative intensities are obtained *without free parameters* in our calculations, since the Hamiltonian is completely determined by first principles calculations [12]. For the sake of simplicity we associate x, the concentration of Sr, with the number of added holes in the Cu-O planes. The following picture emerges: At half filling we obtain an onset of in-plane absorption in close agreement with experiments (Fig. 1) due to in-plane Cu-O CT transitions. When a particle is added to our 6×6 unit cell system (extreme dilute limit) a polaron forms. Hybridization effects and the on-site Coulomb repulsion on Cu (U_d) locally renormalize the levels for $\uparrow$ and $\downarrow$ spins. As a consequence, the corresponding Cu-O CT transition becomes a transition from a localized level in the gap to an extended state above the gap, and correspondingly an absorption band grows in the infrared as the CT band is eroded (Fig. 1). Its shape and position are quite similar to what is observed in photoinduced infrared absorption (inset of Fig. 1). As the number of particles increases ($x > 0.1$) the polarons began to feel each other and the system reaches a strongly fluctuating region. When the concentration of particles approaches $x_c \sim 1/4$ the polarons overlap and the system metallizes. Then we expect the MIR precursor mode, which is connected with the delocalization of the Cu holes, to become a soft electronic mode and to merge with the Drude peak as in experiments [6].

The method has already been described [13]. Here we take advantage of the fact that in the small doping regime the HF Hamiltonian conserves the z component of the spin to reduce the large RPA matrix. In the heav-

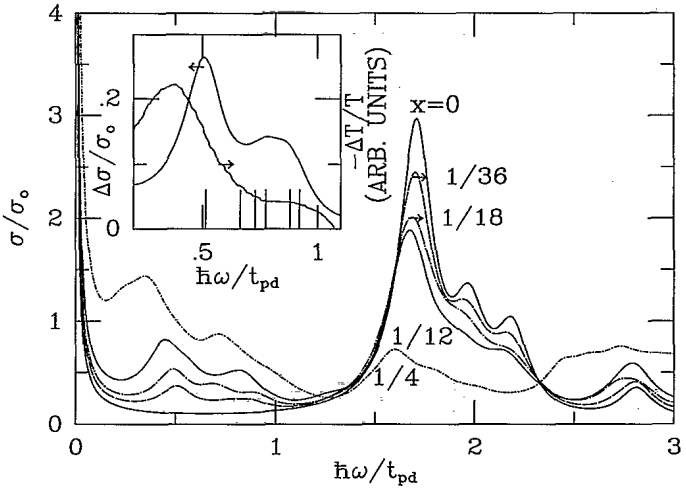

FIG. 1. Optical conductivity of $La_{2-x}Sr_xCuO_4$ for different values of x. A Lorenzian broadening (0.1) has been introduced. For $x = 1/4$ we show the curve corresponding to the "disordered" state mentioned in the text. The upturn at zero energy is due to the broadening. The actual position of the states can be deduced from Fig. 2. The inset shows the difference in the optical conductivity between the $x = 0$ case and the $x = 1/36$ case and the observed photoinduced change in transmission (T) (adapted from Ref. [5]). The long bars indicate the actual positions of the RPA eigenvalues.

ily doped region where our results are more qualitative than quantitative, we restrict ourselves to the configurations that satisfy the above condition. We use the same parameters as Ref. [12] and we only keep the O in-plane p_x, p_y orbitals pointing toward Cu and the $d_{x^2-y^2}$ orbital. Since we are calculating the *in-plane* optical conductivity, we do not expect that out-of-plane orbitals will change our results significantly.

Our units of conductivity and spectral weight are determined by $\sigma_0 = e^2/4d_\perp\hbar\epsilon_b$, $N_0 = 2t_{pd}m_0a_{pd}/\hbar^2\epsilon_b$, where $d_\perp$ is the distance between adjacent Cu-O planes, and a_{pd} and t_{pd} are the in-plane Cu-O distance and hopping integral, respectively. A screening constant (ϵ_b) related to all bound electrons not included in the Hamiltonian is introduced. It is the only unknown parameter and it only affects the overall intensity. We fix it by matching the experimental crossing point of the integrated optical conductivity [6] with our calculated result (Fig. 2). We get $\epsilon_b = 1.3$. With this value and $d_\perp = 12.465$ bohrs, $a_{pd} = 3.606$ bohrs, we get $\sigma_0 = 7.13 \times 10^2\ (\Omega\,\mathrm{cm})^{-1}$, $N_0 = 1.08$. For the rest of the paper we set $\hbar = c = e = a_{pd} = t_{pd} = 1$. Our approximate expression for the optical conductivity is given by the standard Kubo [1, 14] formula with replacement of current matrix elements and excitation energies by the corresponding values in RPA and the Drude weight by the HF value, given by the quadratic change in the HF total energy due to a twist in the boundary conditions parametrized by a vector potential A [1, 14], i.e, $D_{\mathrm{HF}} = (N_0/2N)\partial^2 E_{\mathrm{HF}}/\partial A^2$, with N the number of unit cells. Within the present approximation the f-sum rule [1, 14] is exactly satisfied if kinetic energy expectation values are taken in the HF ground state [15]. Details will be presented elsewhere [16].

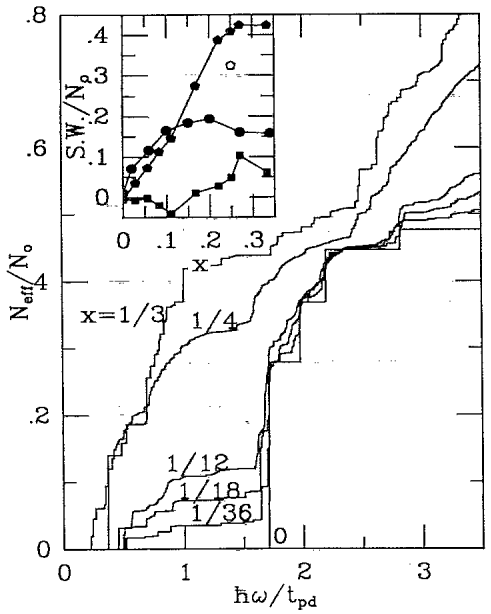

FIG. 2. Integrated optical conductivity of $La_{2-x}Sr_xCuO_4$ for different values of x. For $x = 1/4$ we show the case corresponding to the "disordered" state (see text). The inset shows the experimental [6] (circles) and theoretical (pentagons) integrated conductivity up to the isosbestic point [$N_{\mathrm{eff}}(\omega_{\mathrm{iso}})$] and D_{HF} (squares) as a function of x. The open symbol corresponds to the "disordered" state.

The polaron charge is distributed between a Cu and the four surrounding O. The central spin is reversed with respect to the background [17]. The formation of the polaron can be thought of as a two step process. At the first step a spin is reversed without doping. A metastable HF state realizing such a state shows two gap levels. One coming from the lower Hubbard band is occupied, and corresponds to the flipped spin. The level shift can be understood as an increase of magnetic energy in the HF eigenvalue of the order $8J$, with respect to the more favorable antiparallel orientation. Here J is the effective Cu-Cu superexchange interaction. The other gap level is unoccupied and is due to the fact that to add a particle on O in between two parallel Cu (without any further relaxation) is more favorable in energy by twice the CuO superexchange (J_{CuO}), provided the spin is antiparallel to the one on Cu. At the second step a particle is added to this level. If no further relaxation of charges were to occur, this would be a conventional small ferromagnetic polaron. However, when the strong mixing between Cu and O is taken into account, a different effect takes place. Assuming the central Cu has spin $\downarrow$, the first available level due to the strong mixing has weight on the Cu spin $\uparrow$ state. Part of the added charge goes to the Cu spin $\uparrow$ state and this (via the renormalization of the Cu spin $\downarrow$ level $U_d\langle n_{d\uparrow}\rangle$) pushes up the corresponding $\downarrow$ state from the lower Hubbard band which becomes more mixed with O. As a result the charge on the Cu spin $\downarrow$ state decreases, and the Cu spin $\uparrow$ level decreases due to the $U_d\langle n_{d\downarrow}\rangle$ term and the added particle actually sits in the gap state resulting in the enhanced hybridization of the Cu $\uparrow$ spin and a linear combination of the O states that surround the Cu. The magnetic and covalent effects combine and consequently the distance between the localized Cu level and the O band renormalizes from 1.57 in the undoped case (HF CT gap) to 0.66 in the polaron case. It was recently shown [11] that this enhanced covalency couples strongly with the Cu-O phonon stretching mode (among others) and gives rise to doping induced side phonon bands in infrared spectra (IR) as in experiments [4, 7]. Here for simplicity we do not include such lattice effects. The IR absorption due to phonons is not expected at the energies in which we are interested; however, small changes in the electronic bands can be found due to the relaxation of the lattice.

Figure 1 shows the optical conductivity in RPA. At half filling the CT band peaks at 1.7 (2.5 eV), whereas recent measurements [8] show a peak at 2.25 eV. The sharp decrease at higher energy is also in agreement with the lower temperature measurements of Ref. [8]. They observed a small shoulder at lower energies. We also have

some modes in that energy region but they are not IR active. As the system is doped the optical conductivity for small doping evolves in accordance with experiments. All the curves cross at $\omega_{\rm iso} = 1.25$ (1.8 eV) and the integrated conductivity curves cross at ~ 2.3 (3.4 eV) (Fig. 2) in agreement with the analogous experimental points [6]. Because of the depletion of the optical conductivity at $\omega_{\rm iso}$ the integrated optical conductivity (Fig. 2) for theory and experiment shows a plateau in that region.

In the inset of Fig. 1 we show the difference between the optical conductivity at half filling and for the one-polaron case in the MIR region. For comparison we also show the experimental photoinduced optical absorption [5] spectra. Given the uncertainty in the Hamiltonian parameters, the agreement with shape and position is quite good. The main peak is due to the transition from the $\downarrow$ level in the gap to the first available level with the same spin (extended state) above the Fermi level. The tail, also observed in experiments, is due to transitions to higher excited levels, all renormalized by RPA.

We have studied the two-polaron configuration. The lowest IR mode depends on the distance in between them. For the case of one polaron sitting on the second nearest neighbor Cu of the other we find the lowest IR mode at $\omega = 0.31$, whereas for the slightly more stable case of one polaron sitting on the fourth neighbor Cu of the other we found the lowest IR mode is at $\omega = 0.49$. Since the total energy depends only weakly on the distance, the mixing between different HF configurations will lead to broadening. However, in the dilute regime ($x < 0.1$) such broadening effects occur below the characteristic energy $\omega_{\rm iso}$. Then the integrated conductivity up to that energy $[N_{\rm eff}(\omega_{\rm iso})]$ depends weakly on the particular configuration and we obtain very good agreement with experiments (inset of Fig. 2). At $x = 0$ the experiments extrapolate to a nonzero value probably due to disorder. If the experimental curve is shifted down by that amount, the two curves lay practically on top of each other for small x.

As the number of particles increases, the number of metastable HF configurations increases as well. In such conditions our approach is not expected to work well since RPA is a theory of small amplitude oscillations around some HF state, but the metastable states are indicative of the presence of many Slater determinants in the ground states that cannot be connected by small modifications. Furthermore, the HF ground state for each filling tends to be a polaron lattice commensurate with our system size [17]. This makes the HF state for one particular configuration (the commensurate one) to be pinned more than the others and hence lower in energy, but this is clearly a finite size effect since different sizes have different periodic configurations and all of them should be important in the true ground state (except, perhaps, for the mysterious $x = 1/8$ T_c dip [18]). We believe this effect underestimates the softening of the mode and makes the lower RPA modes produce a narrow peak and lay at a higher energy than what we expect on physical grounds. Instead, if quantum fluctuations were fully taken into account, we expect that the above discussed "configurational" broadening will distribute that intensity over a much wider range of frequency. The experimental results can be interpreted if one assumes that for $x > 0.1$ such broadening effects distribute the intensity beyond $\omega_{\rm iso}$. This explains the deviation from linearity and saturation of the experimental curve as opposed to the theoretical one which instead, due to the pinning of the HF ground state, overestimates the weight below $\omega_{\rm iso}$. If the calculation is done with a metastable "disordered" configuration (Figs. 1 and 2 for $x = 1/4$), it has softer energy modes in the MIR and at the same time a much broader spectra and lower $N_{\rm eff}(\omega_{\rm iso})$ (open pentagon in the inset of Fig. 2).

When the concentration of particles is larger than x_c, there is a plateau of the $N_{\rm eff}(\omega_{\rm iso})$ theoretical curve qualitatively consistent with experiments. For $x > x_c$ the integrated conductivity curves pass above the crossing point instead of below as in experiments. This is probably because the spectral weight transferred to the MIR becomes so broad in the experiment that the range of frequencies over which it is distributed reaches the crossing point frequency (~ 3 eV), and it does not make any more sense to distinguish low energy and high energy features. Our overestimation of the weight at low frequencies gives an integrated spectral weight too large at the crossing point.

We also show in the inset of Fig. 2 $D_{\rm HF}$ as a function of x. For $x = 0$ the value is very small. It should go to zero as $\sim \exp(-\sqrt{N}/\xi_{\rm HF})$ in the thermodynamic limit in analogy with the discussion of Ref. [2]. $\xi_{\rm HF}$ is a localization length in the HF approximation. When a particle is added $\xi_{\rm HF}$ remains finite since the added particle is self-trapped and due to that $D_{\rm HF}$ is still expected to be zero in the thermodynamic limit. The nonzero values of $D_{\rm HF}$ for small x are clearly a finite size effect. The fact that $\xi_{\rm HF}$ remains finite does not mean that the system is really an insulator since there exist many HF solutions with polarons sitting in different cells with the same HF energy. Tunneling between different solutions should recover translational invariance in the ground state. Unfortunately, such processes are beyond RPA since this approximation can only explore the immediate positive curved vicinity of one solution and not the barrier between them. Such tunneling processes should give a small Drude weight in the thermodynamic limit as seen in experiments.

Near x_c the Fermi level reaches a more extended state and $D_{\rm HF}$ increases. At the same time the HF solutions tend to show collapsed magnetic moments. (However, magnetic spatial "fluctuations" are found well above x_c, and mobile holes are expected to screen them at low energies.) Qualitatively we associate that with a metallization of the system and a rapid increase of the effective number of charge carriers consistent with the Hall effect

measurements [19]. This indicates that the Cu holes delocalize and begin to participate in the transport. Since the frequency of the MIR precursor in the dilute limit is determined by the excitation energy to delocalize the original Cu hole, we expect it to become a soft electronic mode near x_c and merge with the Drude component. Such low energy excitations are completely unconventional in a Fermi liquid and we speculate that they are responsible for the possible non-Fermi-liquid behavior. How in detail our MIR band precursor evolves into the corresponding object in the marginal-Fermi-liquid phenomenology [20] deserves more theoretical study. However, we expect that the configurational broadening effects discussed here will give some clues.

It is interesting to compare our results with what was found in a simplified model [13] showing self-trapping. There, as one parameter was varied it was possible to continuously reach a pseudo phase transition at the HF level in which a polaronic solution becomes uniform. The transition was signaled by a RPA mode going to zero frequency.

Our results are restricted to the in-plane conductivity. However, we speculate that the out-of-plane dc conductivity should be strongly suppressed by large Huang-Rhys factors [21] for $x < x_c$. This will result in a partial "confinement" for $x < x_c$ disappearing for $x > x_c$, where the polaronic character is lost.

Another interesting possibility is that these soft electronic modes are the ghost bosons that particles interchange to produce Cooper pairs. We expect that as x_c is approached, fluctuations to the metallic state make the number of effective carriers increase and at the same time the characteristic frequency of the boson decrease. This is what one needs to get a strong dependence of T_c on x.

To conclude, we have calculated the optical conductivity of $La_{2-x}Sr_xCuO_4$ for different values of x. For zero and low x we found good agreement with experiments for band positions and relative intensities *without* free parameters. We identified the precursor of the MIR band with transitions from the localized state to continuum and found a crossover from a polaronic state to a metallic state near the point where a sudden change in transport and optical properties is observed. We argue that near the transition the MIR precursor modes should become soft electronic modes and can probably be related to the breakdown of Fermi-liquid behavior. Our results also show that the method, at least in the small doping regime, is an appropriate bridge between first principles calculations and experiments.

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