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Effect of structure on the electronic density of states of doped lanthanum cuprate

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We present a series of detailed band calculations on the various structural phases of doped lanthanum cuprate: HTT, LTO, and LTT. The LTO distortion is shown to have little effect on the electronic density of states (DOS). A fit to the pressure dependence of the superconducting transition temperature indicates that only 2.5% of the DOS is affected by the HTT→LTO transition. The LTT distortion also has little effect on the DOS for the experimental value of the octahedral tilt angle. Larger tilt angles, though, lead to a dramatic change in the DOS.

Doped lanthanum cuprate, $La_{2-x}M_xCuO_4$, where M is typically Sr or Ba, is the prototype system for the class of copper oxide materials known as high-temperature superconductors. It exhibits a number of structural phases, each of which has different superconducting properties. The HTT (high-temperature body-centered tetragonal) phase occurs for low temperatures only for $x > 0.2$, where superconductivity is suppressed. At lower temperatures for $x < 0.2$, one finds the LTO (low-temperature face-centered orthorhombic) phase, which is superconducting over a range of x values. Near $x = 0.125$, the LTT (low-temperature primitive tetragonal) phase forms for the Ba system with suppressed superconductivity. A small dip in T_c near $x = 0.115$ is found in the Sr system, but no evidence for the LTT phase is found. More information has now been gathered by hydrostatic pressure experiments.[1] For the range of x values where one has a superconducting LTO phase, the HTT phase can be stabilized by pressure and is actually found to have maximal T_c. Near $x = 0.125$ for the Ba system, pressure destroys the LTT phase, yet superconductivity is still strongly suppressed.

Understanding this series of puzzling results may help to unravel the mystery behind high-temperature superconductivity. An obvious first step in this direction is to understand the effect these various structural distortions have on the electronic structure. Of course, many band-structure calculations have been performed on these systems in the past.[2] A recent calculation by Pickett, Cohen, and Krakauer[3] for the LTT phase revealed a strong suppression in the density of states (DOS) near the Fermi energy (E_F), which they then connected to the suppressed superconductivity of this phase. Because of this intriguing result, and the various additional experimental phenomena mentioned above, we decided to perform a series of band calculations for the various phases, accurately calculate the DOS in the vicinity of E_F, and attempt to connect these results to the experimental observations.

We use the linearized muffin-tin orbital method[4] (LMTO) including combined correction terms. Three independent codes were employed as checks, one of which contains nonspherical corrections to the potential inside the muffin tins[5] (all three codes gave comparable results). The calculations presented in this paper are scalar relativistic, employ the Hedin-Lundvist form for the exchange-correlation potential, and use two empty spheres per formula unit [located at the (1/2,0,1/4) points in the HTT notation]. Doping was simulated by reducing the Z value of the La site. Calculations were converged on a 90 k point mesh inside the irreducible wedge of the Brillouin zone. For the final iteration, eigenvalues for 180 k points for the HTT and LTO and 144 k points for the LTT phase were generated and the results were fit using a Fourier series spline analysis. The spline fit was checked by plotting bands along various symmetry directions, and then used to generate a DOS based on a tetrahedral decomposition of the zone (around 1.6×10^6 tetrahedra were used).

The HTT calculation was done using the lattice parameters of Cox *et al.*[6] for $x = 0.1$ Ba at 295 K. Four LTO calculations were carried out, one which used the results[6] for $x = 0.1$ Ba at 91 K, and three which used new results on the Sr system at 10 K for x values of 0.1, 0.15, and 0.2.[7] Two LTT calculations were performed, one which used the results[6] for $x = 0.1$, Ba at 15 K, and another based on theoretical parameters of Pickett, Cohen, and Krakauer[3] obtained by minimization of the total energy.[8] The latter set of parameters has a tilt angle of the copper oxide octahedra about twice that of the former.

Before moving to the main discussion of the DOS, we first comment on the matter of rigid-band behavior. This has been questioned based on the fact that the Cu ion would prefer to be close to a d^9 configuration, and thus rigid-band behavior may not be observed since the states at E_F are a mixture of Cu d and O p states. Our own doping results, based on adjusting the Z value of the La nucleus, exhibit an intriguing behavior. While we indeed

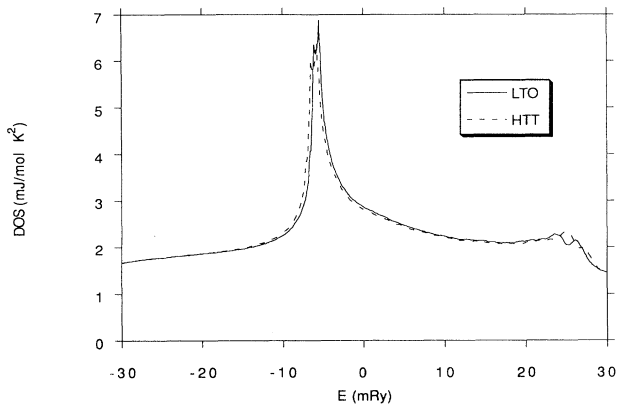

FIG. 1. Density of states (per formula unit) for the HTT and LTO $x=0.1$ Ba cases. The zero of energy is at $x=0.1$.

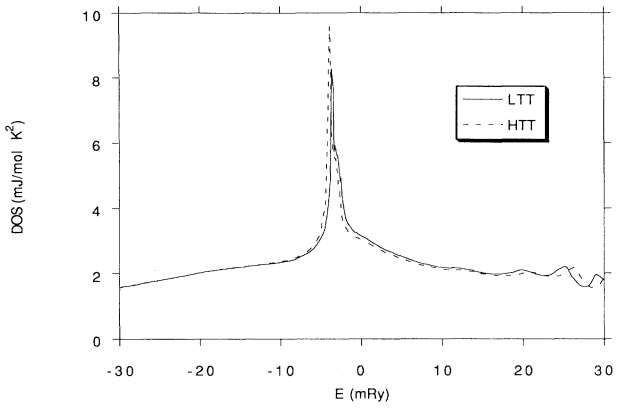

FIG. 3. Density of states (per formula unit) for the HTT and LTT $x=0.1$ Ba cases. The zero of energy is at $x=0.125$.

found rigid-band behavior in the DOS, the charge density did not exhibit such behavior. In particular, the DOS has about 60% Cu d character, with the remainder mostly O p. But comparing charges at 0% doping and 10% doping, only about 20% of the change in charge came from the Cu d orbitals, with the remaining 80% coming from the La site. We should note that the charge on the La site is almost all due to reanalysis of charge from the surrounding O sites since the LMTO method uses overlapping spheres. Our speculation is that the change in potential on the La site due to the reduction of the Z value causes the charge analysis on that site to change in order to compensate for the charge loss due to doping, thus largely preserving the d count on the Cu site. This occurs, however, in such a way that rigid-band behavior is maintained in the DOS.

In Fig. 1, we show plots of the LTO and HTT DOS for the $x=0.1$ Ba calculation. The HTT results were generated assuming LTO symmetry so as to eliminate differences due to using different Brillouin zones. As one can see, there are virtually no differences in the curves. This has been further verified by plots of the Fermi surface which show no detectable differences between HTT and LTO (the "gaps" seen in the LTO Fermi-surface plots in the literature[2] are simply a zone-fold back effect and have nothing to do with the orthorhombic distortion).

We show plots of the LTO DOS for the $x=0.1$, 0.15, and 0.2 Sr calculations in Fig. 2. Again, there are virtually no differences in the curves, indicating again that the orthorhombic distortion has only a weak effect on the DOS (we note that the orthorhombic distortion increases as x decreases).

Plots of the LTT and HTT DOS for the $x=0.1$ Ba calculation are presented in Fig. 3. The HTT results were generated assuming LTT symmetry so as to eliminate differences due to the differing Brillouin zones. The zero of energy was set at 12.5% doping, where the LTT phase is seen experimentally. Again, there are virtually no differences in the DOS. This indicates that the suppression of T_c for the LTT phase is probably not connected with a density of states effect.

In Fig. 4, we show plots of our LTT calculation for $x=0.1$ Ba versus a calculation done using the lattice parameters of the previous work of Pickett, Cohen, and Krakauer.[3] We note that the octahedral tilt angle used in their work is about a factor of two larger than what we used based on the Cox *et al.* parameters.[6] One can see that the van Hove peak is split with the Pickett, Cohen,

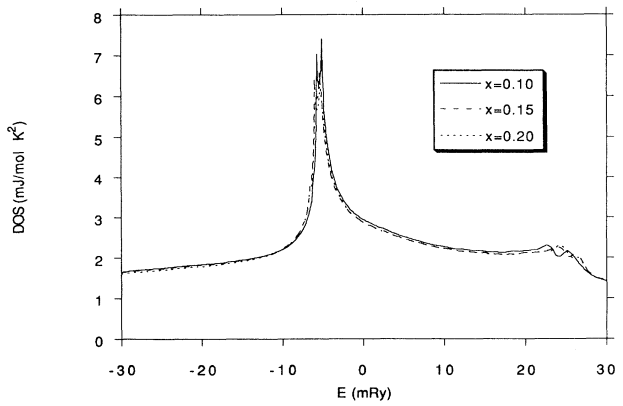

FIG. 2. Density of states (per formula unit) for the LTO $x=0.1$, 0.15, and 0.2 Sr cases. The zero of energy is at $x=0.1$.

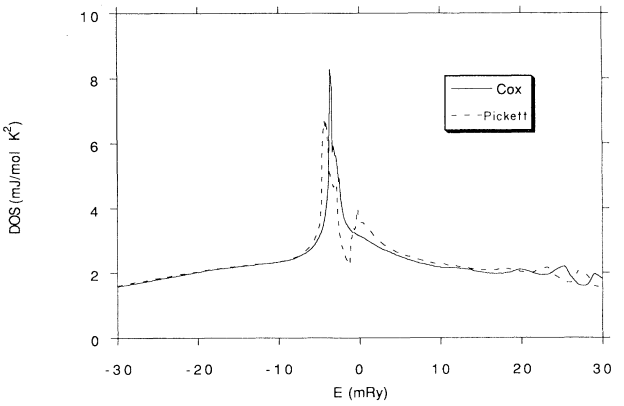

FIG. 4. Density of states (per formula unit) for the LTT $x=0.1$ Ba case (Ref. 6) (Cox) and the LTT case with the Pickett, Cohen, and Krakauer (Ref. 3) lattice parameters (Pickett). The zero of energy is at $x=0.125$.

and Krakauer[3] parameters (our DOS plot is very similar to theirs). The van Hove peak is also split with our choice of parameters, but the effect is too small to be noticeable in the DOS. This difference occurs because the splitting of the van Hove peak depends quadratically on the tilt angle.[8] The large splitting in the Pickett, Cohen, and Krakauer[3] case gives a notch in the DOS close to E_F which led them to suspect that this might be responsible for the suppressed superconductivity. Because of this strong dependence on tilt angle, it is of some importance for experimentalists to attempt to accurately determine the octahedral tilt angle for the LTT structure.

We conclude this part by remarking that the LTO and LTT structural distortions have little effect on the DOS, though large differences are found for the LTT case with increased octahedral tilt angle. We should also remark that the LMTO calculations place the van Hove singularity at about 21–22 % doping, whereas full potential linearized augmented plane-wave (FLAPW) calculations place this peak at about 17% doping.[2] We have found that LMTO calculations which do not include the combined correction terms place the van Hove peak at the same doping as the FLAPW calculations, indicating that the location of the peak is sensitive to details of the electronic-structure calculation.

We now attempt to connect some of these observations with experiment. We start with the LTO→HTT transition induced by pressure.[1] T_c increases linearly with pressure, then saturates at this transition. The pressure dependence of the structural transition can be estimated from anomalies in the thermal expansion. To describe this, we employ a theory due to Bilbro and McMillan.[9] This theory assumes that the superconducting pair potential is independent of pressure, and that the pressure dependence comes from a competition between a DOS change caused by the structural distortion and the formation of a superconducting gap. This involves solving two coupled mean-field equations involving the superconducting gap and the charge-density-wave gap (assumed to only occur over part of the Fermi surface). At a pressure where the two transitions merge, the ratio of dT_s/dp to dT_c/dp (where T_s is the structural transition temperature, T_c the superconducting transition temperature, and p the pressure) is equal to $-(N-N_1)/N_1$ (where N is the total DOS, and N_1 is that part of the DOS removed by the structural distortion). The data for both $x=0.17$ and 0.19 (where some information exists for estimating the pressure dependence of the structural transition) give values of $dT_s/dp \simeq -5.75$ K/kbar and $dT_c/dp \simeq 0.15$ K/kbar. Thus, $N_1/N \simeq 0.025$, i.e., only 2.5% of the $N(E_F)$ value is affected by the structural transition. Such a small number is within the error bars of the band calculations, and thus the data independently support our conclusion that the LTO distortion has a very weak effect on the DOS. Moreover, this theory would also predict that for pressures where the structural transition is near (but larger than) T_c, one should see a saturation of the orthorhombic distortion for $T < T_c$. This effect should be observable by neutron-scattering experiments.

As for the LTO→LTT phase transition and the resultant suppression of superconductivity, our conclusion based on this work is that the density of states does not play an important role. This is consistent with the pressure data, which show that even when the LTT transition is gone, superconductivity is still suppressed. Recent data[10] indicate that magnetic ordering occurs for this concentration range, and thus is the most likely reason for the T_c suppression. Given that band-structure calculations do not give rise to a magnetic transition for stoichiometric La_2CuO_4, we do not expect to be able to describe this magnetism. As has been noted, the magnetism may be due to a commensuration effect at $x=1/8$. More theoretical work is certainly needed to address this interesting effect.

In conclusion, we find little effect of the structural distortions of doped La_2CuO_4 on the electronic density of states. This result is supported by some experimental data on both the HTT→LTO and LTO→LTT transitions.

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