Different doping from apical and planar oxygen vacancies in $Ba_{2}CuO_{4-\delta}$ and $La_{2}CuO_{4-\delta}$: First-principles band structure calculations

T. Jarlborg, B. Barbiellini, R. S. Markiewicz, and A. Bansil

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Different doping from apical and planar oxygen vacancies in $Ba_2CuO_{4-\delta}$ and $La_2CuO_{4-\delta}$

T. Jarlborg[1], B. Barbiellini[2], R.S. Markiewicz[2], A. Bansil[2].
[1]*DPMC, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland*
[2]*Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA*

First principles band-structure calculations for large supercells of $Ba_2CuO_{4-\delta}$ and $La_2CuO_{4-\delta}$ with different distributions and concentrations of oxygen vacancies show that the effective doping on copper sites strongly depends on where the vacancy is located. A vacancy within the Cu layer produces a weak doping effect while a vacancy located at an apical oxygen site acts as a stronger electron dopant on the copper layers and gradually brings the electronic structure close to that of $La_{2-x}Sr_xCuO_4$. These effects are robust and only depend marginally on lattice distortions. Our results show that deoxygenation can reduce the effect of traditional La/Sr or La/Nd substitutions. Our study clearly identifies location of the dopant in the crystal structure as an important factor in doping of the cuprate planes.

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I. INTRODUCTION

Recent work on high-T_c cuprates has explored the role of oxygen defects and ordering of oxygen into superstructures. For instance, x-ray diffraction measurements on small patches of copper oxide superconductors reveal structures which may promote high temperature superconductivity[1]. Other studies involving O vacancies in the high-T_c cuprate $Sr_2CuO_{4-\delta}$ (SCO) have shown that the superconducting T_c may become surprisingly large, reaching 95 K for certain heat treatments[2,3]. These superconductors have the same 214 structure as La_2CuO_4 (LCO) and it is believed that the La substitution with Sr is associated with vacancy formation on the oxygen lattice. Interestingly, up to 30 percent of the oxygen might be missing in the superconducting samples[2]. This finding is at odds with the doping dependence of T_c in $La_{2-x}Sr_xCuO_4$ (LSCO), since the maximum T_c is found for a moderate hole doping x of about 0.15 holes per Cu. It is clear thus that it is important to understand the role of oxygen vacancies in doping the Cu-O planes, which are widely believed to be the seat of superconductivity. So motivated, we examine in this article how location of the oxygen vacancies can affect the doping of cuprate planes[4,5]. An outline of this paper is as follows. In Sec. II, we present the details of the electronic structure computations in large supercells. The theoretical results are presented and discussed in Sec. III, and the conclusions are summarized in Sec. IV.

II. METHOD OF CALCULATIONS

We specifically extract position dependent mechanisms by which the oxygen vacancies in Ba_2CuO_4 (BCO) and La_2CuO_4 modify the electronic structure. Since Ba is isoelectronic with Sr, our results for the valence electrons are also applicable to $Sr_2CuO_{4-\delta}$.[6,7] Self-consistent first principles calculations are performed for (4,2,2) extensions of the basic cell[8] into supercells containing 16 formula units with 112 atomic sites in total, as well as for smaller cells with 7 and 14 sites, by using the Linear Muffin-Tin Orbital (LMTO) method[9] and the Local Density Approximation (LDA)[10]. While the LDA does not provide a satisfactory description of the electronic structure in underdoped cuprates because of inadequate treatment of correlations[11], good agreement is found between LDA and various experiments[12–14] for optimally and overdoped cuprates. The present calculations consider mostly the metallic regime where LDA is expected to be a reasonable approximation. The converged self-consistent results are obtained using a mesh of 125 k-points within the irreducible Brillouin zone. A precise tetrahedron method is used to determine the density-of-states (DOS)[15]. All sites in the cell are considered as non-equivalent throughout the self-consistency cycle. We have previously used supercell computations along these lines to search for weak ferromagnetism around Ba-clusters in $La_{2-x}Ba_xCuO_4$ (LBCO)[7]. However, the present calculations are mostly non spin-polarized, since magnetism is not an issue here. In fact, earlier self-consistent spin-polarized band-structure calculations with 28-atom unit cells have revealed that oxygen vacancies strongly reduce the tendency toward antiferromagnetism in LCO[16]. The LMTO results for non-magnetic La_2CuO_4 are in excellent agreement with full potential calculations[17] demonstrating the high quality of our basis set.

Vacancies (V) on oxygen sites are introduced in such a way as to avoid clustering of vacancies. We consider configurations with number of vacancies n_V equal to 1, 5, 8, 9, 10 or 11. The corresponding oxygen deficiencies for $Ba_2CuO_{4-\delta}$ are given by $\delta = n_V/16$. Thus δ ranges between 0.06 and 0.69. The maximum T_c in the SCO system is reported to occur for $\delta \approx 0.6$, and another dome of high T_c in an uninvestigated region of the phase diagram has been proposed[2]. The same type of supercells with n_V equal to 5 and 9 are used in calculations with La replacing Ba in order to compare the trends for Cu-d

band filling in BCO and LCO. The lattice constant is kept fixed in all calculations. The present computations are performed with the oxygen vacancies either in the planes or in apical sites.

III. RESULTS AND DISCUSSION

The Cu-d band filling can be monitored through inspection of the DOS or the effective charge within the Cu muffin-tin spheres. The DOS at the Fermi energy, $N(E_F)$, is dominated by Cu-d electrons in all high-T_c cuprates, and the mechanism of superconductivity likely involves the Cu-$3d$ and O-$2p$ character on the Fermi surface (FS). Therefore, it is important to see to what extent the d-band filling is affected by oxygen vacancies or other dopants. In the left insert to Fig. 1 is shown the total DOS for undoped BCO (for the same supercell as for doped cases), and with 9 vacancies either in the planes or at the apical positions. Despite the unavoidable noise in the DOS, there is a clear d-band shift to lower energy (with respect the Fermi level) for vacancies on apical sites compared to the pure case (BCO), while the shift for vacancies in the planes is much smaller with even some small enhancement of the DOS above E_F. A DOS enhancement produced by O vacancies was found in coherent-potential-approximation (CPA) calculations[18,19] where all the oxygen sites (planar and apical) had equivalent random occupation. Notably, rigid band like pictures[20,21] have often been invoked in describing the doping evolution of the overdoped and optimally doped cuprates. Our large supercell treatment here goes beyond the simple rigid band models or the CPA-type mean-field approaches[22] to elucidate the local electronic and magnetic properties of the system.

Insight into the underlying physics is provided by the main frame of Fig. 1, which compares the partial DOS of planar and apical oxygen in the undoped parent compound. Note that since Ba donates one less electron than La, the Fermi level is shifted downward compared to the situation in LSCO. In this case, bands of both $d_{x^2-y^2}$ and d_{z^2} character are present near the Fermi level, with the latter dominating the DOS as shown by right hand side insert in Fig. 1. Consequently, the partial DOS of the apical O near the Fermi level is larger, since the electrons of these O atoms hybridize with the Cu d_{z^2} electrons.

Figure 2 shows the total DOS for pristine BCO (for the same supercell as for doped cases), and with up to 9 vacancies in the planes or up to 11 vacancies in the apical positions. Apical site deoxygenation shows a clear trend, shifting the d-band to lower energy. The effect is also consistent with the change of the number of valence electrons within the Cu muffin-tin spheres for different vacancy configurations, shown in Table I. The strikingly different DOS shapes of apical and planar O-p bands in BCO suggest that x-ray emission spectroscopy (XES) would be a good experimental method for detection of doping dependencies. Furthermore, the d band shift below E_F seen in Fig. 2 for the apical but not for planar O vacancies would be a key signature to look for with XPS. Notably, recent O K-edge x-ray absorption (XAS) experiments on SCO/LCO superlattices[23] have shown that the reduction of the second hole peak in the unoccupied DOS of SCO provides a signature of apical oxygen vacancies in SCO. In fact, earlier XAS measurements on overdoped LSCO[24] and electron energy-loss spectroscopy on SCO[25] have determined that such peaks belong to the apical oxygen unoccupied partial DOS. Clearly, changes in these unoccupied DOS peaks[13] mirror trends shown in Fig. 2 associated with the apical oxygen character in the occupied DOS.

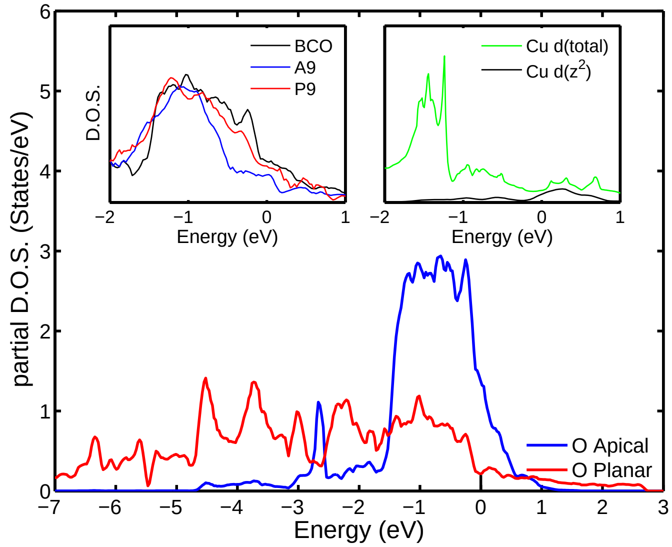

FIG. 1: (Color online) Local oxygen-p part of the DOS on one apical and one planar oxygen site in pristine $Ba_{32}Cu_{16}O_{64}$. Left insert: DOS near the Fermi energy for 3 configurations, $Ba_{32}Cu_{16}O_{64}$ (BCO) and vacancy doped $Ba_{32}Cu_{16}O_{55}V_9$, with the 9 oxygen vacancies in plane (P9) and apical (A9) positions, respectively, all calculated from 125 k-points. Right insert: Local copper-d part of the DOS (total and $d(z^2)$ contributions) near the Fermi energy. All the DOS plots include a small broadening of 5 meV.

The Cu muffin-tin spheres have the same radius in all cases. For an increased number of apical vacancies in BCO there is a monotonic increase of the Cu charge so that about 0.1 electrons are added to the sphere for $\delta \approx 0.56$. The fine details of the vacancy distribution do not seem to be important since results from two different configurations (for 8 and 10 vacancies) give almost identical results. In BCO with vacancies within the CuO_2 planes, there is little modification of the Cu charge, about 1/10 of the change due to apical vacancies. These small changes shown in Table I indicate less Cu charge for O vacancies within the CuO_2 plane, i.e. there is an effective hole doping within the Cu band.

The average valence charge of the oxygen vacancy Q_V in Table I yields a simple physical picture of the differ-

TABLE I: Average valence charge of Cu (Q_{Cu}, within the atom sphere radius of $0.335a_0$) and its difference relative to the case without vacancy (ΔQ_{Cu}) for different number of oxygen vacancies n_V within planar and apical positions in $Ba_{32}Cu_{16}O_{64-n_V}V_{n_V}$ (BCO) and $La_{32}Cu_{16}O_{64-n_V}V_{n_V}$ (LCO). The corresponding average valence charge of the oxygen vacancy (Q_V within atomic sphere radii of $0.317a_0$ and $0.345a_0$ for planar and apical sites, respectively) is also reported. Since there are in total 64 oxygen sites in the 112 atom cell, the effective doping is $\delta = n_V/16$. Different distributions of 8 and 10 vacancies on apical sites for BCO show very little difference in the charge transfer. The cases $n_V = 1$ with or without lattice distortion are almost identical, see text.

n_V	BCO Q_{Cu}	BCO ΔQ_{Cu}	BCO Q_V	LCO Q_{Cu}	LCO ΔQ_{Cu}	LCO Q_V
9 (plane)	10.054	-0.010	0.662	10.331	-0.063	0.889
8 (plane)	10.055	-0.009	0.655	-	-	-
5 (plane)	10.057	-0.007	0.650	10.368	-0.026	0.877
1 (plane)	10.062	-0.002	0.640	-	-	-
0	10.064	0.000	-	10.394	0.000	-
1 (apical)	10.071	0.007	0.303	-	-	-
5 (apical)	10.107	0.043	0.313	10.450	0.056	0.623
8 (apical)	10.142	0.078	0.320	-	-	-
8 (apical)	10.145	0.081	0.308	-	-	
9 (apical)	10.164	0.100	0.327	10.456	0.062	0.662
10 (apical)	10.179	0.115	0.326	-	-	-
10 (apical)	10.180	0.116	0.329	-	-	-
11 (apical)	10.200	0.137	0.336	-	-	-

ence between vacancies in planar and apical O-positions. When the oxygen vacancy is located in the Cu-O planes, it acts as an electron trap (i.e. Q_V is large), while when the vacancy is in the charge reservoir, the electrons are more attracted by the Cu-O planes than by the vacancy. Hence, apical vacancies behave as expected from simple valence arguments: $O^{2-} \rightarrow V + 2e$, which dopes the planes with two electrons per vacancy. On the other hand, planar vacancies are anomalously charged, so : $O^{2-} \rightarrow V^{-} + e$, resulting in a weaker electron doping. Note that in both cases, electrons are doped into the planes, but for planar O vacancies, they are more localized on the vacancy. Apical oxygen vacancies will thus mainly remove O-p bands in the interval where the apical O-DOS is high ranging from E_F down to 1.5 eV below E_F. In contrast, the DOS reduction due to planar oxygen vacancies will be spread over a wider energy range because of the wider partial DOS for planar oxygen sites shown by Fig. 1.

We also carried out computations on LCO to further demonstrate the robustness of our results. In particular as illustrated in Table I, the electron doping from apical O-vacancies in LCO is comparable to that of BCO. Moreover, to estimate the effect of lattice relaxation around vacancies, calculations were made with a vacancy on one apical oxygen position for BCO, where a large lattice relaxation is imposed. The two atoms surrounding the

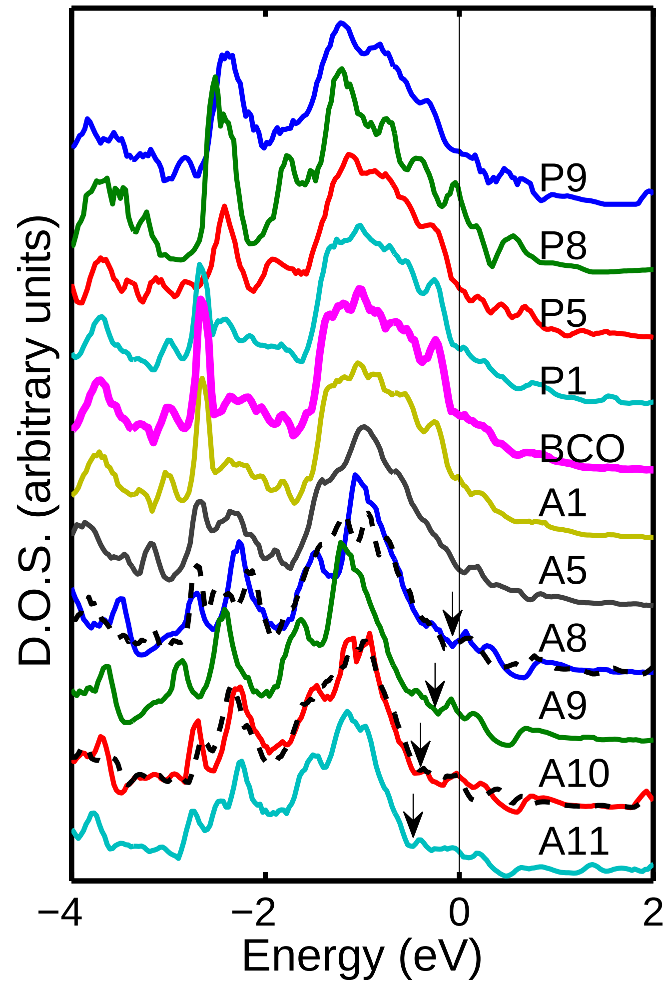

FIG. 2: (Color online) DOS near the Fermi energy for various vacancy configurations in $Ba_{32}Cu_{16}O_{64-n}$. BCO is the undoped case, "Pn" refers to n vacancies in the plane and "An" refers to n apical vacancies. The DOS plots include a small broadening of 5 meV. The Fermi energy is taken as zero in all cases. Black dashed lines show the DOS for different arrangements of the same number and type of O vacancies. This illustrates the robustness of the main trends. When $n \geq 8$ for the apical vacancies, the arrows indicate the onset of the sharp rise associated with the d_{z^2} band below the Fermi level.

missing O site, namely the Ba above (along the c axis) and the Cu below were allowed to fill in the empty space by moving $0.03a_0$ towards the center of the missing O. The amplitude of these distortions is rather large, corresponding to a thermal distortion amplitude for a temperature of several hundred degrees Kelvin[26]. This distortion is found to make very little change in the number of electrons on the Cu sites. No Cu atom changes its charge more than 0.005 electrons. However, the Cu atom next to the vacancy gains 0.05 electrons compared to Cu in ideal BCO, and this is independent of relaxation. The Ba atom looses 0.08 electrons and the vacancy (with the same volume as the O atom) gains 0.10 electrons. Other sites typically change their charge by ±0.01 electrons or less. Therefore, our finding of net charge transfer due to high vacancy concentration is essentially independent of lattice relaxations.

To better understand the role of apical vacancies in doping the planes, we also present some calculations for a related compound with even more apical O vacancies: Ba_2CuO_3 (BCO-3) where one layer of apicals is missing[27]. Figure 3 compares the DOS of BCO-3 to stoichiometric Ba_2CuO_4 (BCO-4) and La_2CuO_4 (LCO-4), demonstrating that the DOS of BCO-3 and LCO-4 are almost identical near E_F – i.e., for the $d_{x^2-y^2}$ band. At lower energies, from 1 eV below E_F, there are differences because of the removal of three hybridized O-p bands. In contrast, the DOS of BCO-4 is very different even near E_F. These DOS functions are consistent with the trend shown in Fig. 2, despite the different compositions and orderings. Disorder has some effect on the details but not on the main features of the DOS. The Cu valence charge in BCO-3, 10.25 electrons, is consistent with the results in Table I for an extrapolated concentration of 16 apical vacancies. Thus, the DOS and FS of the relevant Cu-O single band of BCO-3 and LCO-4 behave in the same way, but for an effective Cu charge that is slightly smaller in BCO-3: about 10.25 vs. 10.39 in LCO-4, see Table I. There is a striking similarity of the FS of BCO-3 (shown in the upper inset of Fig. 3) and the well-known FS of LCO-4 (see ref.[28]). Furthermore, it can be verified that the FS's of the two systems have an almost identical evolution with the number of holes p in the single band at E_F as shown in the insert of Fig. 3 for BCO-3.

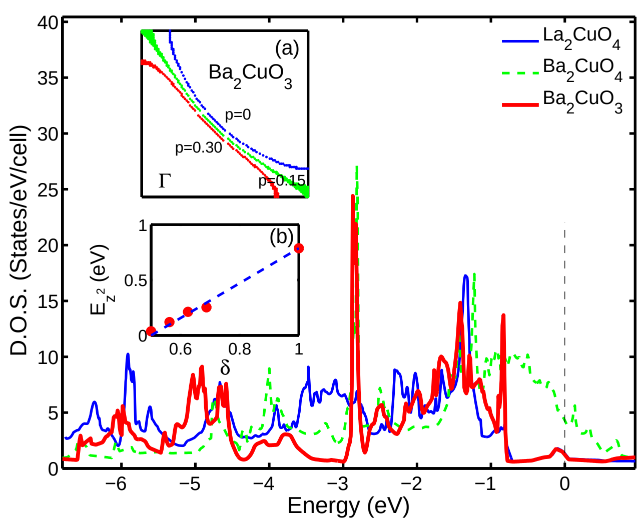

FIG. 3: (Color online) DOS near the Fermi energy for Ba_2CuO_3, Ba_2CuO_4 and La_2CuO_4. Insert (a) shows the evolution of the Fermi surface in the $k_z = 0$-plane in Ba_2CuO_3 as a function of the rigid-band doping for 0, 0.15 and 0.30 holes per unit cell, while insert (b) shows how the Fermi level shifts above the d_{z^2} band onset as vacancies are added.

We can now understand that the role of apical vacancy doping is to push the Fermi level from the middle of the d_{z^2} band for $n_V = 0$ to the middle of the $d_{x^2-y^2}$ band for $n_V = 16$. For $n_V \geq 8$, the sharp rise associated with the d_{z^2} band is located below the Fermi level as shown by the arrows in Fig. 2. We plot the energy shift between the d_{z^2} onset and E_F as a function of $\delta = n_V/16$ in insert (b) of Fig. 3. Remarkably, the shift for BCO-3 also fits on the same line. A linear shift is expected if the DOS is approximately constant, as in Fig. 3. Hence, we find that in BCO for δ between 0.5 and 1, the vacancies dope electrons into an essentially empty $d_{x^2-y^2}$ band, and the physics should be similar to that of strongly hole-overdoped LCO.

In comparing our results to experiments on the $Sr_2CuO_{4-\delta}$ system, we note that Gao *et al.*[3] conclude that the missing oxygens are outside the CuO plane and that the structure remains stable even at this high doping[29]. These conclusion are also corroborated by our calculated total energies for having 1 apical or 1 planar vacancy in the undistorted 112 site supercell, since the total energy is considerably lower for the apical position, of the order of 1.5 eV. Vacancy ordering leading to long range periodicity is suspected to be important for boosting T_c to high values[1,30–32]. Orderings of apicals or other defects, leading to long-range periodicity, are expected to induce a lowering of the total energy because of the appearance of a partial gap at E_F[26].

Since each apical vacancy contributes two electrons to the CuO_2 plane, the addition of apical vacancies could lead to a new route for electron-doping LCO. We note that O vacancies in the reservoir layers also provide electron doping in $YBa_2Cu_3O_{7-y}$ (YBCO)[33], even though YBCO is structurally very different from both LCO and BCO. The doping for high-T_cs in BCO cuprates corresponds to a nearly empty $d_{x^2-y^2}$ band, consistent with the suggestion of a second superconducting dome. It is interesting to note that dopings for high-T_c in pnictides often seem to be associated with the Van Hove singularity at a band onset[34], although the reason for this is not clear. In the case of BCO, the possibility of altered d_{z^2}-$d_{x^2-y^2}$-orbital character near E_F due to vacancy ordering could also modify the superconducting properties.

IV. CONCLUSION

Our study shows that properties of copper oxides high temperature superconductors depend dramatically on the concentration and position of oxygen vacancies. Our results indicate that manipulation of apical oxygen vacancies is an effective pathway for optimizing the electronic structure for higher T_c. The similarity between the band structure for apical vacancy doped BCO and the commonly doped LCO system is striking, but consistent with the notion that the high T_c in $Sr_2CuO_{4-\delta}$ is due to another "dome" of superconductivity with a different hole doping on Cu-sites. The slight difference in Cu valence charge between the two systems can affect the magnetic response despite a very similar Fermi surface. Another implication of our study is that O vacancy formation can compensate the doping resulting through conventional La substitutions.

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