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

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Abstract

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Reference


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Different doping from apical and planar oxygen vacancies in Ba$_2$CuO$_{4-δ}$ and La$_2$CuO$_{4-δ}$: First-principles band structure calculations

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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 that may promote high-temperature superconductivity. Other studies involving O vacancies in the high-$T_c$ cuprate Sr$_2$CuO$_{2−δ}$ (SCO) have shown that the superconducting $T_c$ may become surprisingly large, reaching 95 K for certain heat treatments. These superconductors have the same 214 structure as La$_2$CuO$_4$ (LCO) and it is believed that the La substitution with Sr is associated with vacancy formation on the oxygen lattice. Interestingly, up to 30% of the oxygen might be missing in the superconducting samples. This finding is at odds with the doping dependence of $T_c$ in La$_{2−x}$Sr$_x$CuO$_4$ (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.

II. METHOD OF CALCULATIONS

We specifically extract position-dependent mechanisms by which the oxygen vacancies in Ba$_2$CuO$_4$ (BCO) and La$_2$CuO$_4$ modify the electronic structure. Since Ba is isoelectronic with Sr, our results for the valence electrons are also applicable to Sr$_2$CuO$_{4−δ}$. Self-consistent first-principles calculations are performed for (4,2,2) extensions of the basic cell 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 and the local density approximation (LDA). While the LDA does not provide a satisfactory description of the electronic structure in underdoped cuprates because of inadequate treatment of correlations, good agreement is found between LDA and various experiments 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).

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-3$d^9$ and O-2$p$ 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 inset to Fig. 1 is shown the total DOS for undoped BCO (for the same supercell as for doped cases), and with nine 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 the Fermi level. A DOS enhancement produced by O vacancies was found in coherent-potential-approximation (CPA) calculations\textsuperscript{18,19} where all the oxygen sites (planar and apical) had equivalent random occupation. Notably, rigid bandlike pictures\textsuperscript{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 CPA-type mean-field approaches\textsuperscript{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 electron less than La, the Fermi level is shifted downward compared to the situation in LSCO. In this case, bands of both $d_{x^2-r^2}$ and $d_{z^2}$ character are present near the Fermi level, with the latter dominating the DOS as shown by the right-hand side inset 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 nine 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\textsuperscript{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\textsuperscript{24} and electron energy-loss spectroscopy on SCO\textsuperscript{25} have determined that such peaks belong to the apical oxygen unoccupied partial DOS. Clearly, changes in these unoccupied DOS peaks\textsuperscript{13} mirror trends shown in Fig. 2 associated with the apical oxygen character in the occupied DOS.

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 vacuum distribution do not seem to be important since results from two different configurations (for eight and ten vacancies) give almost identical results. In BCO with vacancies...
TABLE I. Average valence charge of Cu ($Q_{\text{Cu}}$), within the atom sphere radius of 0.335$a_0$ and its difference relative to the case without vacancy ($\Delta Q_{\text{Cu}}$) for different number of oxygen vacancies $n_V$ within planar and apical positions in Ba$_2$Cu$_2$O$_{6-2n}$, $V_{n_V}$ (BCO) and La$_2$Cu$_{16}$O$_{64-n_V}$, $V_{n_V}$ (LCO). The corresponding average valence charge of the oxygen vacancy ($Q_{\text{V}}$) within atomic sphere radii of 0.317$a_0$ and 0.345$a_0$ 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 eight and ten 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.

<table>
<thead>
<tr>
<th>$n_V$</th>
<th>BCO</th>
<th>BCO</th>
<th>BCO</th>
<th>LCO</th>
<th>LCO</th>
<th>LCO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{\text{Cu}}$</td>
<td>$\Delta Q_{\text{Cu}}$</td>
<td>$Q_{\text{V}}$</td>
<td>$Q_{\text{Cu}}$</td>
<td>$\Delta Q_{\text{Cu}}$</td>
<td>$Q_{\text{V}}$</td>
</tr>
<tr>
<td>9 (plane)</td>
<td>10.054</td>
<td>-0.010</td>
<td>0.662</td>
<td>10.331</td>
<td>-0.063</td>
<td>0.889</td>
</tr>
<tr>
<td>8 (plane)</td>
<td>10.055</td>
<td>-0.009</td>
<td>0.655</td>
<td>10.321</td>
<td>-0.053</td>
<td>0.877</td>
</tr>
<tr>
<td>5 (plane)</td>
<td>10.057</td>
<td>-0.007</td>
<td>0.650</td>
<td>10.368</td>
<td>-0.026</td>
<td>0.877</td>
</tr>
<tr>
<td>1 (plane)</td>
<td>10.062</td>
<td>-0.002</td>
<td>0.640</td>
<td>10.394</td>
<td>0.000</td>
<td>0.892</td>
</tr>
<tr>
<td>0</td>
<td>10.064</td>
<td>0.000</td>
<td>-</td>
<td>10.394</td>
<td>0.000</td>
<td>-</td>
</tr>
<tr>
<td>1 (apical)</td>
<td>10.071</td>
<td>0.007</td>
<td>0.303</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>0.043</td>
<td>0.313</td>
<td>10.450</td>
<td>0.056</td>
<td>0.623</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>0.081</td>
<td>0.308</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>9 (apical)</td>
<td>10.164</td>
<td>0.100</td>
<td>0.327</td>
<td>10.456</td>
<td>0.062</td>
<td>0.662</td>
</tr>
<tr>
<td>10 (apical)</td>
<td>10.179</td>
<td>0.115</td>
<td>0.326</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11 (apical)</td>
<td>10.200</td>
<td>0.137</td>
<td>0.336</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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 $Q_{\text{V}}$ in Table I yields a simple physical picture of the difference 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., $Q_{\text{V}}$ 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 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 0.03$a_0$ 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. 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 e electrons. However, the Cu atom next to the vacancy gains 0.05 e electrons compared to Cu in ideal BCO, and this is independent of relaxation. The Ba atom loses 0.08 e electrons and the vacancy (with the same volume as the O atom) gains 0.10 e electrons. Other sites typically change their charge by ±0.01 e 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$_2$CuO$_3$ (BCO-3) where one layer of apicals is missing. Figure 3 compares the DOS of BCO-3 to stoichiometric Ba$_2$CuO$_4$ (BCO-4) and La$_2$CuO$_4$ (LCO-4), demonstrating that the DOS of BCO-3 and LCO-4 are almost identical near $E_F$ (i.e., for the $d_{xz},-yz$ 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
high-$T_c$s 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,\textsuperscript{34} although the reason for this is not clear. In the case of BCO, the possibility of altered $d_{x^2-y^2}$ orbital character near $E_F$ due to vacancy ordering could also modify the superconducting properties.

\section*{IV. Conclusion}

Our study shows that properties of copper oxide 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$_2$CuO$_4$-$\delta$ 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.

\section*{Acknowledgments}

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\begin{thebibliography}{99}
\bibitem{6} The advantage with BCO compared to SCO is that the simple virtual crystal approximation scheme can be used to capture aspects of the electronic structure changes induced by Ba/La substitutions as an alternative to the more complicated supercell calculations.\textsuperscript{7}
\bibitem{8} Atomic positions (in units of the lattice constant $a_0 = 3.787$ Å) within the basic cell are (0,0,±1.265) for Ba/La, ($\frac{1}{2}$,0,0) and (0, $\frac{1}{2}$,0) for planar O, (0,0,±0.641) for apicals and (0,0,0) for Cu. The ratio $c/a_0$ is 1.754.
\end{thebibliography}
Calculations for three different configurations of two apical vacancies in the double cell (Ba$_4$Cu$_2$O$_6$, assuming the same unit cell volume and no distortions) show that the configuration with one layer of missing oxygens has a lower total energy than the other two possible configurations. The differences are 1 to 2 eV per cell with the least stable configuration when two apical vacancies surround one of the Cu atoms. The DOS for the checkerboard configuration of missing O above or below Cu is not too different from the DOS shown in Fig. 3, while there is a pseudogap at $E_F$ if the two vacancies surround both sides of one Cu. Spin-polarized calculations for the double cells (Ba$_4$Cu$_2$O$_6$ and La$_4$Cu$_2$O$_8$) with imposed antiferromagnetic order on Cu give a smaller exchange enhancement in the former case by factors of 0.6 to 0.8 relative to LCO, depending on how the two apical vacancies are distributed.