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Citation: [Applied Physics Letters](#) **100**, 253111 (2012); doi: 10.1063/1.4729892

View online: <http://dx.doi.org/10.1063/1.4729892>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/100/25?ver=pdfcov>

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Doping and defects in $\text{YBa}_2\text{Cu}_3\text{O}_7$: Results from hybrid density functional theory

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(Received 18 April 2012; accepted 5 June 2012; published online 21 June 2012)

Modified orbital occupation and inhomogeneous charge distribution in high- T_c oxide compounds due to doping and/or defects play a huge role for the material properties. To establish insight into the charge redistribution, we address metallic $\text{YBa}_2\text{Cu}_3\text{O}_7$ in two prototypical configurations: Ca doped (hole doping) and O deficient (electron doping). By means of first principles calculations for fully relaxed structures, we evaluate the orbital occupations. We find that the change of the charge density, in particular in the CuO_2 planes, shows a complex spatial pattern instead of the expected uniform (de-)population of the valence states. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4729892>]

The technical optimization of high- T_c oxide superconductors calls for a detailed knowledge about the effects of manipulations of the materials on the electronic states. In particular, the states in the CuO_2 planes are of interest, as they carry the superconductivity. Experimentally, the electronic structure can be influenced by both doping and incorporation of defects. In this context, it is usually assumed that doping and defects simply modify the population of the valence orbitals.¹ However, the high- T_c oxide superconductors are characterized by a remarkable delocalization of the hybridized Cu-O states in the CuO_2 planes. For this reason, it is well possible that injection or removal of charge carriers will not only result in modified occupation numbers of the valence states, but rather comes along with a spatial redistribution of the valence charge. It is the aim of the present work to shed light on this charge redistribution.

Formation energies for substituting dopants on different $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) lattice sites and O vacancy formation energies have been obtained by Klie and coworkers by means of a theoretical approach.² For Ca doping of YBCO, the average Cu valences in the CuO_2 planes and CuO chains have been measured by means of the idiometric titration method, indicating a transfer of holes from the chains to the planes.³ Because the O content of the samples decreased simultaneously in these experiments, the total Cu valence did not alter. Details of the electronic structure of O deficient (i.e., hole underdoped) YBCO are still a matter of dispute,⁴ where the shape of the Fermi surface is of particular interest. Stripe order and charge anisotropy, remarkably, appear even at an O content of ~ 6.7 .⁵ Understanding this strong interplay between the structure and electronic properties calls for insight into the electronic states of YBCO locally around the impurities.

We present results of first principles calculations based on density functional theory, employing the hybrid PBE0 functional.⁶ Since the electronic states in the vicinity of dopants and defects in YBCO depend remarkably on the local structure, it is necessary to fully relax the crystal structure in

order to obtain a meaningful result. We employ the WIEN2k code, which is a full-potential linearized augmented plane-wave implementation.⁷ It is convenient for analyzing the charge density distribution near spatial inhomogeneities.^{8,9} Effects of doping and defects are fully accessible to the supercell approach with periodic boundary conditions when the supercell is chosen sufficiently large. In all our calculations, we employ a 2×2 supercell, with respect to the ab -plane of the YBCO unit cell.¹⁰ In order to minimize the forces, the atomic coordinates of the experimental structure of YBCO are optimized in a first step. The relaxation of the supercells then starts from these data.

From the electronic point of view, YBCO becomes insulating with a Cu^{2+} (d^9) state in the CuO_2 planes if we lower the O content to 6. The $d_{x^2-y^2}$ orbitals are singly occupied due to strong electron-electron interaction, and the developing magnetic moments are aligned antiferromagnetically. In the remaining Cu chains, the Cu^{1+} ion has a closed shell and, therefore, is electronically inert. On the other hand, fully oxidized YBCO has a nominal Cu valence of $2.5+$ in the CuO_2 planes and of $2+$ in the CuO chains. Due to a coupling between the planes and the chains, holes can be transferred between them. The hole content in the CuO_2 planes thus is a bit lower than the nominal value, and the CuO chains become metallic.¹¹ The charge transfer into the CuO_2 planes is amplified close to grain boundaries¹² as well as interfaces to metals.¹³ By internal charge transfer, the Cu $3d_{3z^2-r^2}$ orbital is occupied in fully oxidized YBCO due to bonding to the apical O_{Ba} . The $d_{x^2-y^2}$ superconducting pair state is stable within a wide range of doping.¹⁴

We first address the effects of hole doping on YBCO. This can be achieved by replacing trivalent Y by divalent Ca. In our supercells, we substitute one out of four Y by Ca, which means that the distance between two adjacent Ca impurities amounts to twice the a/b lattice constant. Assuming that this doping affects only the two adjacent CuO_2 planes, we consequently dope on average 0.5 holes to the Cu atoms adjacent to the Ca. The valence of these atoms changes to $3+$ (if the doping is confined to nearest neighbours). Experimentally, the effects Ca doping have been investigated in some detail in the context of critical currents

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across grain boundaries, since Ca doping of grain boundaries can enhance the critical current.^{15,16} In general, the hole doping should be reflected by a shift of the electronic states to higher energy, as less states are occupied. It is our aim to disclose in the following where the additional holes are located and how the charge gets redistributed near the Ca impurity.

The most common and technologically relevant defect in YBCO is the O vacancy. We model such O vacancies by a YBCO supercell in which we remove each second O atom from each second CuO chain, see Fig. 1. We hence deal with a $\text{Y}_4\text{Ba}_8\text{Cu}_{12}\text{O}_{27}$ supercell. Assuming that the additional charge assembles on the four Cu atoms in the CuO_2 planes next to the vacancy, the formal valence of these Cu atoms is $2.25+$. In the case of electron doping the electronic states shift to lower energy, as more states are occupied. Notice that our vacancy system still is in the metallic range.¹⁷ Possible effects of clustering of O vacancies are not taken into account in our calculations.¹⁸

The structural relaxation of our Ca doped and O deficient supercells leads to modifications of the Cu-O bond lengths. The results are summarized in Table I. For the Ca doping, a deformation affects the CuO_2 planes which slightly reduces the distance to the Y, while the distance to the Ca grows. In the vicinity of a Ca atom, the Cu-O bonds are shorter than around a Y atom. For the O vacancy, the CuO_2 planes are virtually not distorted. The calculated bond lengths of Table I agree nicely with the experimental values reported in Ref. 3.

In the following, the electronic structure of ideal (i.e., undistorted) YBCO will act as a reference for the interpretation of our results. We mention that our electronic structure of ideal YBCO agrees well with previous calculations using the local density approximation and also reveals good agreement with experimental observations, see Ref. 4 and the references given therein.

As almost only the Cu $3d$ and O $2p$ states contribute at the Fermi level, we subsequently focus on these states. With respect to the bulk YBCO density of states (DOS), Ca doping and O deficiency are known to shift the states towards higher and lower energy, respectively. However, the partial $3d$ DOS of the Cu atoms in the CuO_2 planes remains almost unchanged. In contrast, shifts in energy are found for the partial $2p$ DOS of the O atoms in the CuO_2 planes. Corresponding results are shown in Fig. 2 for Ca doping (top) and O

FIG. 1. Top and side view of the 2×2 YBCO supercell, with one O vacancy in the right CuO chain (arrow). Y/Ca, Ba, Cu, and O atoms are depicted as large grey, huge mint, medium brown, and small blue spheres, respectively.

TABLE I. Bond lengths obtained by structure optimization, as compared to ideal YBCO.

	Ideal	Ca doped	O deficient
$\text{Cu}_{\text{chain}}\text{-O}_{\text{Ba}}$	1.90	1.89	1.89
$\text{Cu}_{\text{chain}}\text{-O}_{\text{chain}}$	1.94	1.94	1.93
$\text{Cu}_{\text{plane}}\text{-O}_{\text{plane}}$	1.95–1.96	1.94–1.97	1.95–1.96
$\text{Cu}_{\text{plane}}\text{-O}_{\text{Ba}}$	2.24	2.243	2.25
$\text{O}_{\text{plane}}\text{-Y/Ca}$	2.39–2.40	2.41–2.42	2.39–2.40
$\text{Cu}_{\text{plane}}\text{-Y/Ca}$	3.22	3.21	3.22

deficiency (bottom). For the Ca doped YBCO, the overall shift amounts to about 0.1 eV. Moreover, we observe some minor alterations of the DOS shape in the vicinity of the Fermi level. For the O deficiency, the shift is smaller but still significant around the Fermi level. It turns out that doping effects are not confined to the O atoms close to the dopant or vacancy. This fits nicely to the common picture of localized spins at the Cu sites and mobile holes in the O $2p$ orbitals.

The effects on the different Cu $3d$ orbitals are further analyzed in Fig. 3. Even though the partial Cu $3d$ DOS changes little, we observe that both the Cu $3d_{x^2-y^2}$ DOS (which dominates at the Fermi energy) and the Cu $3d_{xy}$ DOS are subject to strong energetical shifts. While the Cu $3d_{3z^2-r^2}$ DOS is almost unchanged, substantial alterations are found for the in-plane orbitals. Especially, the Cu $3d_{x^2-y^2}$ orbital is depopulated.

FIG. 2. Partial O $2p$ DOS of Ca doped (top) as well as O deficient (bottom) YBCO for O atoms in the CuO_2 plane next to the impurity, as compared to undoped YBCO.

FIG. 3. Partial Cu $3d_{x^2-y^2}$ (top) and Cu $3d_{xy}$ (bottom) DOS of Ca doped YBCO for Cu atoms in the CuO_2 plane next to the impurity, as compared to undoped YBCO.

The charge density difference maps in Fig. 4 show the difference between the charge density in ideal YBCO and the density in the modified supercells without relaxation (to only highlight the doping effect). We again study the CuO_2 planes. Positive values are shown in red, negative values in blue. Regions in which holes accumulate, thus, are red and regions in which the electron density grows blue. In the case of Ca doping, see the top part of Fig. 4, a Ca atom is located in the center of the plot but above the depicted plane. We see that the hole accumulates in the interstitial region between the Cu and O sites and on the Cu-O bonds. However, surprisingly there are also regions in which the electron density increases. These include small pockets near the O atoms, pointing towards the Ca. Moreover, the occupation of the Cu d_{xy} orbital increases, while the $d_{x^2-y^2}$ orbital loses electrons. The trefoil structure of the in-plane Cu $3d$ orbitals is slightly distorted due to the proximity of the Ca atom. Ca doping, hence, reduces the electron density in most parts of the CuO_2 planes, but there are also regions in which the opposite effect is observed. Nevertheless, the hole is well delocalized over the entire CuO_2 plane.

In the O deficient case, see the bottom part of Fig. 4, we show a charge density difference map of a section of a CuO_2 plane with O atoms in the corners and center. The O vacancy is located in a plane below the central O atom. Instead of a simple loss of holes in the Cu $3d$ orbitals, we observe a strong spatial redistribution of charge. Moreover, the shape of the affected area does not reflect the shape of a specific $3d$ orbital but is rather spherical. As a consequence, it is not a single orbital which gets populated with additional charge or loses charge, but several orbitals are involved. In contrast, electron doping due to O deficiency exhibits for the neighbouring O atoms a clear orbital characteristic. The O $2p$ orbitals which point towards the Cu atoms lose holes, as to be expected. However, the perpendicular O $2p$ orbitals behave opposite: The occupation decreases significantly. For this

FIG. 4. Difference valence charge density in the CuO_2 plane (parallel ab -plane). Top: Ca doped YBCO (Cu in the corners; Ca in the center, but above the plane). Bottom: O deficient YBCO (O atoms in the corners and center). Red and blue colors represent a gain and loss of holes with respect to ideal YBCO, respectively.

reason, the effects of electron doping because of O deficiency in YBCO cannot be described in terms of a uniform filling of the hybridized Cu-O orbitals. The spatial pattern of the charge redistribution is more complicated.

Both for Ca doping and O deficiency, we find that the impurity does not affect all valence orbitals similarly but leads to orbital ordering. This ordering, in turn, will be reflected by the symmetry of the superconducting state.¹⁹ Consequently, it is not sufficient to describe YBCO in terms of the Cu $3d_{x^2-y^2}$ orbitals, which form covalent bonds with the O $2p_{xy}$ orbitals. In addition, the charge ordering leads to energetic modulations of the electronic states, which explains corresponding results by scanning tunneling microscopy.²⁰ Observed subdominant symmetries of the order parameter may also arise from local deviations in the charge density.

In conclusion, we have performed a set of *ab-initio* calculations of Ca doped and O deficient YBCO supercells to investigate the charge (re-)distribution in the vicinity of the dopant/vacancy. Both modifications have strong effects on the local electronic structure. Our results confirm an energy shift of the electronic states due to the fact that Ca doping overall creates additional holes, while O vacancies overall dope the system with electrons. However, when we go into more detail, we observe a complex spatial charge redistribution. For Ca doping, there exist regions in the CuO₂ planes in which the electron density even grows (reflecting a distinct orbital ordering). Similarly, for O deficiency both the Cu 3*d* and O 2*p* orbitals do not simply show the expected growth of the orbital occupations but there are also regions in which the electron density is significantly reduced. The orbital ordering clearly distinguishes the O 2*p* orbitals pointing towards the Cu atoms from those pointing perpendicular (within the CuO₂ plane).

We thank Zhiyong Zhu for fruitful discussions and acknowledge financial support by the Deutsche Forschungsgemeinschaft (TRR 80).

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