

## Quantitative calculations of charge-carrier densities in the depletion layers at $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ interfaces

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Charge redistribution at high- $T_c$  superconductor interfaces and grain boundaries on one hand is problematic for technological application. On the other hand, it gives rise to a great perspective for tailoring the local electronic states. For prototypical (metallic) interfaces, we derive *quantitative* results for the intrinsic doping of the  $\text{CuO}_2$  planes, i.e., for the deviation of the charge-carrier density from the bulk value. Our data are based on *ab initio* supercell calculations within density-functional theory. A remarkable hole underdoping is inherent to the clean interface, almost independent of the interface geometry. On the contrary, cation substitution as well as incorporation of electronegative impurities can compensate the intrinsic charge transfer and provide access to an exact adjustment of the superconductor's doping. The effects of oxygen deficiency are discussed.

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In recent years, interfaces incorporating a high- $T_c$  superconducting material are subject to a quickly growing interest, in both the experimental and theoretical communities. Due to the possibility of orbital reconstructions and a modified chemical bonding at interfaces, design of heterostructures with engineered physical properties has become a prosperous field. Much effort has focused on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -based interfaces, often attached to oxide compounds.<sup>1-3</sup> In the high- $T_c$  cuprates and nickelates, even a very small change in the crystal structure or the chemical composition, or the presence of structural strain or disorder, can result in fundamental alterations of the electronic properties.<sup>4-7</sup> From the structural point of view, large dielectric constants and small carrier densities amplify relaxation effects.<sup>8</sup> This fact is of special importance for the transport properties of the superconductor, since the local charge distribution in the  $\text{CuO}_2$  planes is seriously influenced near interfaces. Moreover, as a consequence of electrostatic screening lengths of a few nm and a strong structural inhomogeneity, conventional band-bending models cannot be applied for describing the charge redistribution.

Both the structural relaxation and the local electronic states at interfaces of high- $T_c$  compounds have been investigated for specific situations by various methods, including superlattices composed of different high- $T_c$  compounds,<sup>9</sup> doping induced by charge transfer from the localized states in a hopping insulator,<sup>10</sup> and cuprates in contact to manganites.<sup>11</sup> In this context, we have recently dealt with the influence of the charge redistribution at a metal interface on the doping in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO). It turns out that the superconducting  $\text{CuO}_2$  planes are subject to a strong intrinsic electron doping, where screening effects are important for describing the charge-transfer amplitude.<sup>12</sup> The net charge transfer amounts to 0.13 electrons per Cu site when the interface is oriented parallel to the  $\text{CuO}_2$  planes, and to 0.09 electrons for a perpendicular orientation.<sup>13</sup> In addition to this weak dependence on the geometry, the charge transfer is also robust against the specific metal forming the interface, thus giving rise to a “universal” behavior. In this Brief Report we deal with the question of how the intrinsic doping changes under different kinds of perturbations of the interface. In

particular, we give a *quantitative* evaluation of various mechanisms that can be used for *tailoring* the charge transfer, which provides a great technological potential for material optimization and design.

While for bulk high- $T_c$  compounds a formidable number of investigations of impurity effects are found in the literature, similar results for surfaces and interfaces are rather rare. In addition, studies of interfaces have predominately addressed the domain of the superconductor, whereas little deal with the interface itself. On the contrary, much attention has been focused on the influence of the O content—in the full range of the phase diagram.<sup>14</sup> Moreover, it has been observed that the superconducting properties of YBCO are strongly altered under substitution of Y by Ca. The critical current at low magnetic fields and the critical temperature decrease with the Ca concentration.<sup>15</sup> In the case of grain boundaries, Ca doping hence is used to compensate the local charge redistribution.<sup>16</sup> The YBCO crystal structure is subject to drastic alterations under the incorporation of defects. Especially, the lattice parameters change considerably as a function of the O stoichiometry.<sup>17</sup> Experiments in the late 1980s had already indicated that the insertion of F or Cl into underdoped YBCO can enhance the critical temperature,<sup>18</sup> where the F or Cl atoms tend to occupy the empty metal sites in the  $\text{CuO}$  chains.<sup>19,20</sup> Interestingly, this insertion of halogenides is accompanied by a higher hole content in the  $\text{CuO}_2$  planes, which suggests that a F or Cl impurity has the potential to re-extract the excess charge arising at an YBCO interface.

Our data are obtained from density-functional theory, applying the generalized gradient approximation and the Perdew-Burke-Ernzerhof scheme. We use the WIEN2K program package,<sup>21</sup> with a mixed linearized augmented plane wave and augmented plane wave plus local orbital basis. Moreover, we set  $RK_{\text{max}}=7$  when we investigate Cl impurities and  $RK_{\text{max}}=4.7$  otherwise. The radii of the muffin-tin spheres are (in Bohr radii) 1.8 for Cu, 2.2 for Cl, 2.25 for Ca, 2.3 for Y, 2.5 for Ba, 1.45–1.55 for O, and 2.1–2.4 for Pd.

Because band bending takes place on the length scale of the YBCO  $c$  lattice constant, the electronic structure of an interface is accessible to a supercell approach with periodic

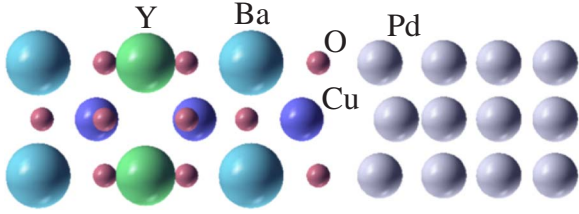


FIG. 1. (Color online) Interface between bulk Pd and YBCO (precisely the CuO-chain layer). The CuO<sub>2</sub> planes run parallel to the interface.

boundary conditions.<sup>22</sup> It is convenient to use as the metallic substituent fcc Pd, which has a minimal lattice mismatch of only 0.7% with respect to the YBCO  $a/b$  lattice constant. We have checked that our results do not depend on this choice by comparing the charge transfers at YBCO-Pd and YBCO-Ag interfaces, for which we find almost identical data in all relevant respects.<sup>12,13</sup> For illustrating the principle of the supercell setup, Fig. 1 displays the near-interface region of the supercell for a clean YBCO-Pd interface oriented parallel to the CuO<sub>2</sub> planes. It comprises two YBCO unit cells terminated by the CuO-chain layer, as indicated by experiment,<sup>23,24</sup> and four Pd fcc unit cells stacked in [001] direction. The supercells under consideration all have a similar size.

We use the experimental YBCO bulk lattice constants  $a=3.865$  Å and  $b=3.879$  Å,<sup>25</sup> which are likewise applied to the Pd region in order to avoid lattice mismatch in the contact plane. In the perpendicular direction, the standard Pd lattice constant  $c=3.89$  Å is an adequate choice. By the minor dependence of the charge transfer on the interface geometry, all subsequent results refer to the setup in Fig. 1. In the case of fully oxidized YBCO, one-half of the topmost Pd atoms consequently have an O bonding partner in the interface CuO-chain layer, while the other half are located next to an unoccupied site. We count atomic layers with respect to the interface; i.e., the first Pd layer is attached to the first atomic layer of the YBCO cell, formed by the CuO chains.

The following three mechanisms of tailoring the intrinsic doping are investigated. First, the incorporation of electronegative ions is realized by substituting each second interface Pd atom without an O neighbor by a Cl atom. This arrangement is shown in Fig. 2, after structure optimization. Second, cation substitution is studied for the replacement of Y by Ca, where we choose a Ca content close to the optimal value of  $\approx 30\%$  for grain-boundary doping.<sup>16</sup> To keep the computational effort manageable, we replace each fourth Y atom by

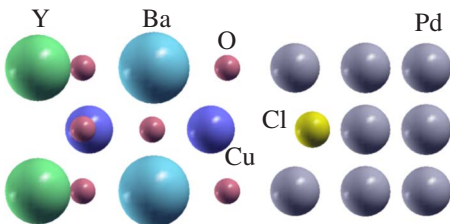


FIG. 2. (Color online) Cl-doped YBCO interface. Every second contact metal atom is substituted by Cl. The orientation of the CuO<sub>2</sub> planes is parallel to the interface, which is formed by CuO chains.

TABLE I. Selected bond lengths (in Å) for different interfaces (see the text for details), obtained by structure optimization. Bulk YBCO bond lengths are given for comparison.

	YBCO bulk	YBCO interface	YBCO <sub>6,75</sub> interface
$d_{\text{Cu-Pd}}$		3.32	2.83
$d_{\text{O-Pd/Cl}}$		2.12, 3.87	2.14
$d_{\text{Cu-O}_{\text{interf}}}$	1.94	2.02	1.88
$d_{\text{Cu-O}_{\text{Ba}}}$	1.90	1.90	1.87
	Y <sub>0.75</sub> Ca <sub>0.25</sub> BCO interface	Cl-doped YBCO interface	
$d_{\text{Cu-Pd}}$	2.76	3.28	
$d_{\text{O-Pd/Cl}}$	1.98	2.12, 3.83	
$d_{\text{Cu-O}_{\text{interf}}}$	1.94	2.01	
$d_{\text{Cu-O}_{\text{Ba}}}$	1.86	1.84	

Ca; i.e., we deal with Y<sub>0.75</sub>Ca<sub>0.25</sub>BCO. Third, the effects of O deficiency are addressed for YBCO<sub>6,75</sub>, where each fourth interface O atom, all from CuO chains, is removed. We note that the system therefore stays far in the metallic regime,<sup>26</sup> so that valid results are expected from a band-structure calculation using the present approximations.

Turning to the chemical bonding in the vicinity of the interface, there is always the same expected behavior. We find a strong tendency toward Pd-O bonding and a Cu-Pd repulsion. The Cu-Cl repulsion is weaker. Moreover, the Cl incorporation induces only weak structural distortions of the superconductor, whereas the first two Pd layers are subject to a finite relaxation. In fact, the relaxation in the superconductor domain declines quite quickly for all interfaces under investigation, so that the second CuO<sub>2</sub> plane is virtually undistorted. This is particularly true for the O-deficient case where we may anticipate a different behavior. Selected bond lengths are compared to each other in Table I. Reflecting covalent Pd-O bonding across the interface, the nearby Pd sites are subject to shifts of the valence electronic states from lower energy to about  $-2$  eV, with respect to the Fermi energy. This gives rise to a pronounced structure in the Pd  $4d$  density of states (DOS), characterized by a significant Pd-O hybridization. However, even for the second Pd layer, the DOS resembles the bulk Pd  $4d$  DOS very well, and a nearly perfect agreement is obtained for the third layer. As a consequence, structural distortions are screened quickly on both sides of the interface, which *a posteriori* justifies the size of our supercells.

We first investigate the effect of the Cl doping on the YBCO electronic states. Cl-Pd hybridization is tiny for atoms in the first Pd layer, according to an ionic bonding.<sup>27,28</sup> However, there are remarkable admixtures of the nearest-neighbor Pd atom (see Fig. 2) in the Cl-dominated DOS range, which we attribute to enhanced bonding because of a very short distance. Of course, it is to be expected that the Cl extracts charge from the surrounding area until a Cl<sup>-</sup> ion state is reached. Since no reduction of the Pd charge is observed under Cl doping, the extraction should affect only the YBCO region. Assuming that the charge reduction affects all seven Cu atoms per unit cell to a similar degree, naive elec-

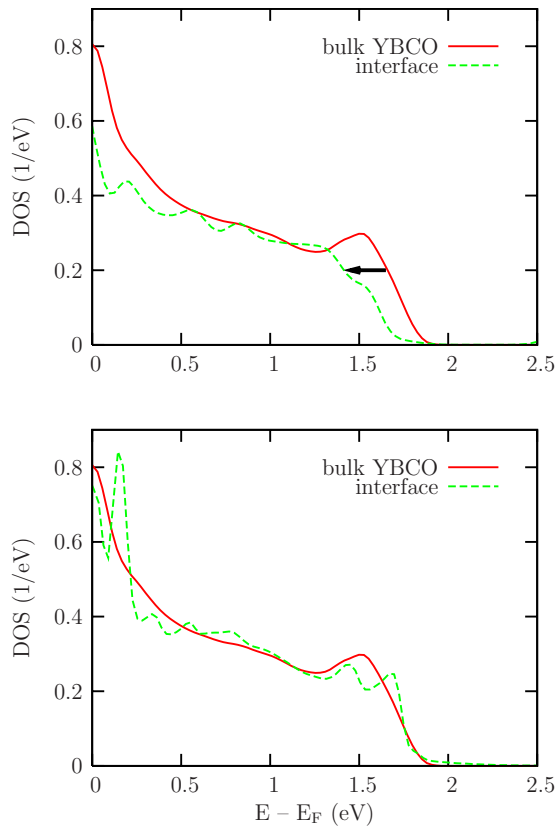


FIG. 3. (Color online) Partial Cu 3d DOSs for the second  $\text{CuO}_2$  plane off the clean (upper panel) and Cl-doped (lower panel) YBCO interfaces, as compared to the bulk DOS.

tron counting indicates that the intrinsic charge transfer due to the interface (0.13 electrons per Cu site) can be compensated by this mechanism quite well.

We therefore compare in Fig. 3 the DOSs for the clean and for the Cl-doped interfaces to that for bulk YBCO. The data refer to the second  $\text{CuO}_2$  plane, because here the structural relaxation has already decayed. According to Fig. 3, the Cu 3d DOS confirms our speculation. Whereas a strong reduction of the (unoccupied) states is visible for the clean interface, this charge transfer is fully compensated for the Cl-doped case. The areas under the DOS curves in the lower panel of Fig. 3 coincide almost perfectly, reflecting identically doped  $\text{CuO}_2$  planes. In fact, the suppression of charge transfer to the YBCO domain due to the Cl atoms is surprisingly strong. Electronegative impurities consequently seem to form a rather rigid potential barrier which prohibits any intrinsic doping.

Another way for overcoming the hole underdoping at interfaces is simultaneous overdoping: replacing  $\text{Y}^{3+}$  by  $\text{Ca}^{2+}$ . The initial doping state should be restored, since the introduction of Ca increases the hole concentration. The upper panel of Fig. 4 confronts the DOS of the pure YBCO interface with the results for an  $\text{Y}_{0.75}\text{Ca}_{0.25}\text{BCO}$  interface. Whereas differences in the Cu 3d DOS shape reflect remarkable alterations of the electronic states, in particular of the Cu-O bonding, their occupation fulfills exactly the trends mentioned before. The interface doping is even overcompensated for the configuration under investigation, which is visible in

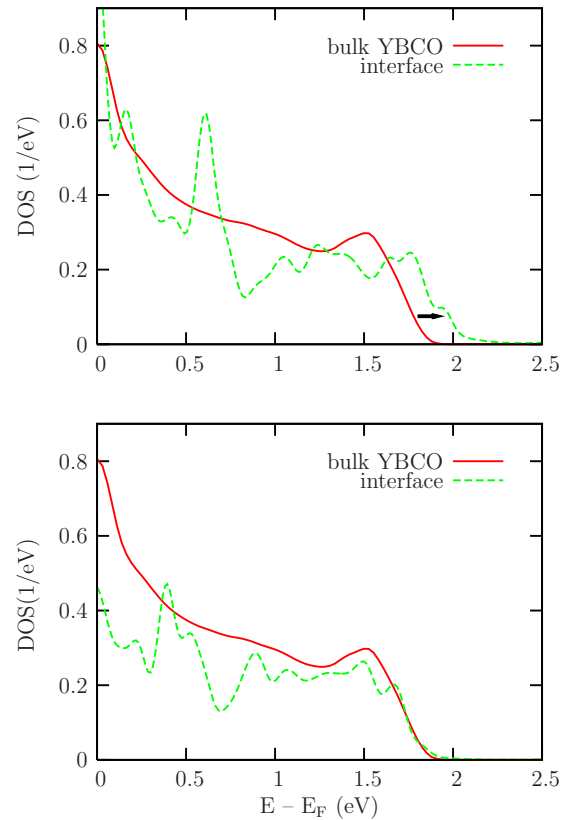


FIG. 4. (Color online) Partial Cu 3d DOSs for the second  $\text{CuO}_2$  plane off the  $\text{Y}_{0.75}\text{Ca}_{0.25}\text{BCO}$  (upper panel) and the O-deficient  $\text{YBCO}_{6.75}$  (lower panel) interfaces. In each case, the findings are compared to the corresponding DOS of bulk YBCO.

Fig. 4 by a shift of the DOS curve to higher energies. Further evaluation of the data gives a charge reduction of 0.08 electrons. 25% Ca doping thus comes along with an injection of 0.21 additional holes per Cu site into the  $\text{CuO}_2$  planes.

The fact that local Ca doping of grain boundaries can enhance the supercurrent density has been attributed to a reduction of the charge accumulation at grain-boundary dislocations, which causes a hole depletion.<sup>29</sup> The size of the perturbed regions seems to be smaller for Ca-doped samples and the interface conductivity thus is improved. Resistivity measurements in fact reveal changes in the height and the shape of the electrostatic potential barrier under Ca doping.<sup>30</sup> However, the experiments likewise indicate that such modifications cannot explain the observed effect of Ca doping on the transport properties. It therefore has been speculated that extra holes must be generated for some reason, which finally is substantiated by our findings. A grain boundary appears to be quite well described in terms of an interface between an unperturbed superconductor domain and the charge reservoir of the grain-boundary dislocations. Ca doping then compensates the intrinsic charge transfer present at this interface and so introduces additional holes.

As is known from many experiments, O deficiency has a very strong influence on the hole content of the  $\text{CuO}_2$  planes; see Ref. 31, for instance, and the references therein. In analogy to our previous proceeding, we now quantify this effect. Evaluating the DOS given in the lower panel of Fig. 4, we

obtain a reduction of the hole count in our YBCO<sub>6.75</sub> interface by 0.10 holes per Cu site. However, this reduction is not due to charge transfer, as we do not observe an energetical shift of the DOS curve, but traces back to a modified Cu-O bonding.

We have discussed electronic structure calculations for prototypical interfaces of a high- $T_c$  superconductor and a normal metal. In each case, we have evaluated *quantitatively* the interface charge transfer from the metal into the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  domain. The intrinsic underdoping of 0.13 holes per Cu atom (for  $\delta=0$ ) is fully suppressed by electronegative impurities. Cation substitution in the superconductor likewise leads to (over)compensation, where the ini-

tial hole concentration is restored for a 15% Ca content. Since O deficiency at the interface has just the opposite effect, it is therefore possible to exactly design the doping state of the superconductor. Reduction of the O content by  $\delta=0.25$  leads to an underdoping of 0.10 holes per Cu atom. We expect that all these values likewise apply to the intentional doping of grain boundaries, which paves the way for a systematic optimization of transport properties.

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