

## Charge redistribution at YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>-metal interfaces

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Charge redistribution at interfaces is crucial for electronic applications of high- $T_c$  superconductors, since the band structure is modified on a local scale. The authors address the normal-state electronic structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (YBCO) at an YBCO-metal contact by first principles calculations for prototypical interface configurations. They derive quantitative results for the intrinsic doping of the superconducting CuO<sub>2</sub> planes due to the metal contact. Their findings can be explained in terms of a band-bending mechanism, complemented by local screening effects. The authors determine a net charge transfer of 0.09–0.13 electrons in favor of the intraplane Cu sites, depending on the interface orientation. © 2007 American Institute of Physics. [DOI: 10.1063/1.2737397]

Electronic transport in wires and tapes from high- $T_c$  materials is seriously affected by structural defects and interfaces. In contrast to most conventional superconductors, bending of the band structure due to local variations of the charge distribution is strong enough to control the transport properties.<sup>1,2</sup> This results from large dielectric constants and small carrier densities, characteristic for high- $T_c$  materials.<sup>3</sup> The Thomas-Fermi screening length, over which band bending is effective, therefore reaches the order of magnitude of the superconducting coherence length.

The specific contact resistivity of YBCO-metal thin films is known to depend on the details of the contact geometry.<sup>4</sup> In particular, the transport in micron-sized YBCO-metal heterojunctions is strongly affected by the orientation of the YBCO crystallographic axes with respect to the direction of the current flow.<sup>5</sup> From the theoretical point of view, effects of charge modulation at the surface of high- $T_c$  superconductors have been studied by Emig *et al.*<sup>6</sup> It turns out that surfaces are covered by dipole layers due to a local suppression of the gap function. Nikolić *et al.*<sup>7</sup> study the charge imbalance at the boundary between a short coherence length superconductor and a normal metal by means of a self-consistent microscopic approach. However, first principles electronic structure calculations taking into account the details of the crystal structure are missing so far, probably due to a high demand on CPU time.

The technical optimization of interfaces calls for insight into the electronic structure close to the contact, which we address in the following for characteristic YBCO-metal interfaces. Since the electronic properties depend on the local atomic configuration, it is necessary to start from the details of the crystal structure in order to obtain reliable results. We present findings of band structure calculations for two prototypical YBCO-metal interface configurations fulfilling this requirement. Our calculations are based on density functional theory and the generalized gradient approximation, as implemented in the WIEN2K program package.<sup>8</sup> This full-potential linearized augmented-plane-wave code is known to be particularly suitable for dealing with structural relaxation and charge redistribution in complex geometrical arrangements.<sup>9–11</sup> We obtain quantitative results for the band-bending magnitude and, therefore, for the intrinsic doping of

the superconducting CuO<sub>2</sub> planes due to the metal contact.

Since band bending is proposed to take place on the length scale of the YBCO lattice constant, the electronic structure of YBCO-metal interfaces becomes accessible to a supercell approach with periodic boundary conditions. In the following, we address supercells both parallel and perpendicular to the crystallographic  $c$  axis. In each case, we start from the experimental YBCO bulk lattice constants<sup>12</sup> and optimize the atomic coordinates in order to minimize the atomic forces. In a second step, the structural relaxation of the supercells is carried out.<sup>13,14</sup> Figure 1 shows the interface configurations under consideration, which we call the parallel (a) and the perpendicular (b) interfaces, referring to their orientation with respect to the CuO<sub>2</sub> planes.

It is convenient to choose fcc Pd as the metallic substituent because of a minimal lattice mismatch of about 0.7%.

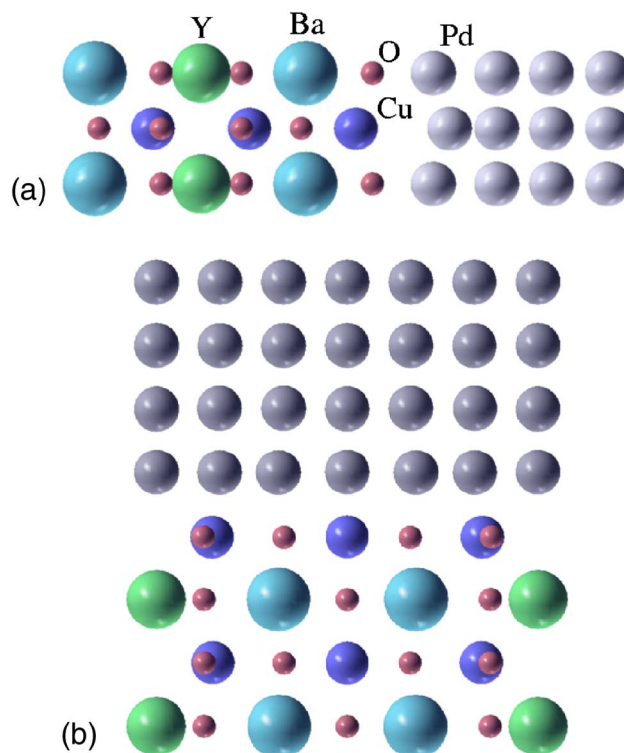


FIG. 1. (Color online) YBCO-metal interface configurations: (a) parallel and (b) perpendicular. The naming refers to the orientation of the interface with respect to the CuO<sub>2</sub> planes.

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TABLE I. Selected bond lengths at the parallel and perpendicular YBCO-metal interfaces, as resulting from the structure optimization.

	Parallel	Perpendicular
$d_{\text{Cu-Pd}}$ (Å)	3.32, 3.79	2.62, 2.74, 2.77
$d_{\text{O-Pd}}$ (Å)	2.12, 3.87	2.02, 3.15
$d_{\text{Cu-O}}$ (Å)	2.02	1.94
$d_{\text{Cu-O}_{\text{Ba}}}$ (Å)	1.90	1.93

The supercell for the parallel interface consists of 2 YBCO unit cells, whereas 3 YBCO unit cells are used for the perpendicular interface. The YBCO domain in each case terminates with a Cu–O layer.<sup>15–17</sup> Furthermore, the metal domain comprises 3 and 4 Pd fcc unit cells for the perpendicular and parallel configurations, respectively. Relative shifts between the YBCO and metal domain parallel to the interface have not been taken into consideration since they do not affect our further conclusions.<sup>10</sup> Structure optimization results in a strong tendency towards Pd–O bonding, whereas repulsion is found between Cu and Pd atoms. Importantly, the structural relaxation affects almost only the first atomic layer off the contact. Bond lengths calculated for these sites are summarized in Table I for both supercells.

In the following discussion, we compare the electronic structures obtained for our YBCO-metal interfaces with the results of a bulk YBCO calculation. We therefore mention that our bulk YBCO density of states (DOS) agrees perfectly with previous theoretical and experimental findings, see Refs. 18–20 and the references given therein. Figure 2 shows partial Cu 3*d* DOS curves for Cu sites in the CuO<sub>2</sub> planes of bulk YBCO and our interfaces (a) and (b). In the latter cases, the results refer to the Cu sites second closest to the contact. As compared to bulk YBCO, additional Cu states appear in the vicinity of the Fermi energy for the Cu atoms actually forming the interface, which trace back to a modified Cu–O bonding. In contrast, the second closest Cu atoms resemble the bulk YBCO DOS very well and hence allow us to study the band bending. For the parallel interface, we observe an almost perfect agreement of the DOS curves, whereas some effects of the structural relaxation are left for the perpendicular interface. However, in both cases the bulk DOS has to be shifted to lower energies in order to reconcile the curves. The necessary shift amounts to 0.20 eV for the parallel interface, whereas 0.15 eV are sufficient in the perpendicular case.

Since the gross structure of the Cu 3*d* DOS is not affected by the interface, we can interpret these energetical shifts in terms of almost ideal down bending of the electronic bands due to a modified Fermi level. As a consequence, the hole count at the Cu sites is altered. To be specific, a shift of 0.20 eV corresponds to a reduction of 0.13 holes, and a shift of 0.15 eV comes along with a loss of 0.09 holes. Both these values and the calculated magnitudes of the band bending are expected to be independent of the metallic substituent used for the interface, which we have confirmed for silver contacts. Importantly, the charge transfer likewise depends only little on the orientation of the YBCO-metal interface with respect to the unit cell of the high-*T<sub>c</sub>* compound. An intrinsic doping close to 0.1 eV hence appears to be a general result for YBCO-metal contacts. Of course, oxygen defects close to the interface could modify the charge transfer.

Core levels at atomic sites near the interface show energetical shifts of about twice the magnitude reported for the

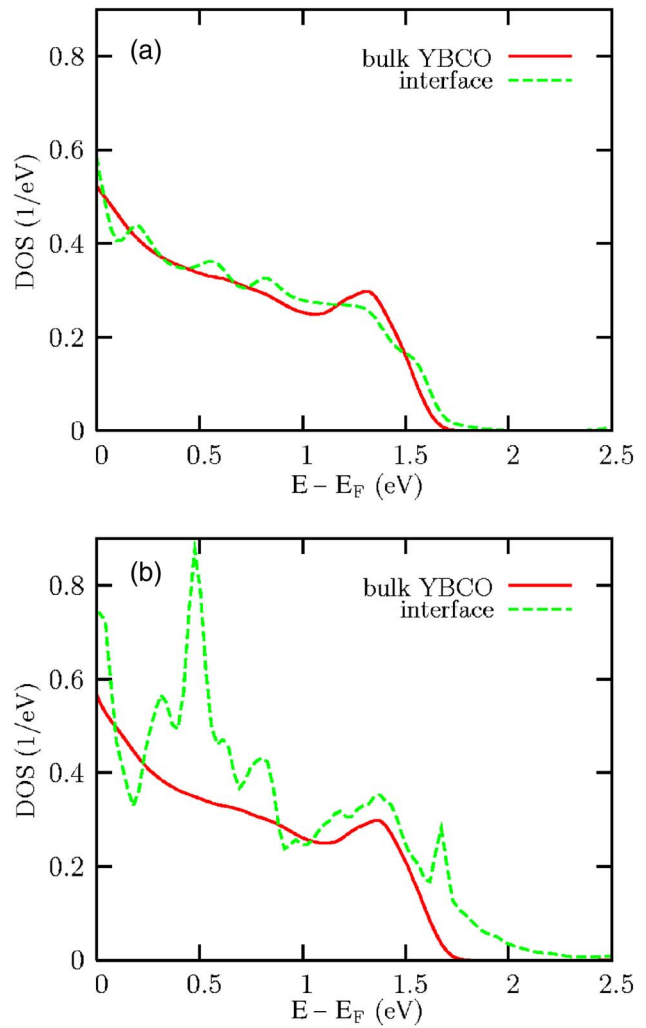


FIG. 2. (Color online) Partial Cu 3*d* densities of states for CuO<sub>2</sub>-plane sites in the vicinity of the parallel (a) and perpendicular (b) interface. The gross shape of the interface DOS resembles the bulk DOS when the latter is shifted by 0.20 eV (a) and 0.15 eV (b) to lower energies, respectively, which corresponds to charge carrier reductions of 0.13 and 0.09 holes per Cu site.

Cu valence states. To understand this fact, electronic screening has to be taken into consideration. Screening is more efficient for the Cu 3*d* states than for any core states since the former have finite weight at the Fermi energy. In general, the electrostatic screening length is only a few nanometers in high-*T<sub>c</sub>* cuprates, and the crystal structure is very inhomogeneous. Conventional band-bending models based on a continuum description of the charge distribution thus cannot be applied. Nevertheless, electronic screening results in a significant reduction of the band-bending magnitude at YBCO-metal interfaces and, therefore, in a reduced charge transfer.

Xu and Ekin report on specific resistivities for YBCO–Au interfaces of 10<sup>−4</sup>–10<sup>−3</sup> Ω cm<sup>2</sup> at low temperatures.<sup>21</sup> However, our calculations for normal-state YBCO-metal interfaces do not show a relevant reduction of the Cu 3*d* DOS at the Fermi energy. Even though no insulating layer is formed in the vicinity of the YBCO-metal contact, the observed interface resistivity can be explained in terms of screened band bending. Since the charge carrier density in the CuO<sub>2</sub> planes is significantly reduced, a local breakdown of the superconductivity is to be expected.

We have presented electronic structure calculations for prototypical contact configurations between the short coher-

ence length superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and a normal metal. In particular, we have discussed the charge redistribution in high- $T_c$  materials induced by normal metal interfaces. Calculations for well-relaxed supercells show that the charge redistribution can be interpreted in terms of an intrinsic doping of the superconductor on a nanometer length scale, in correspondence with the experimental observation of charge carrier depletion. The net charge transfer in favor of the copper sites in the  $\text{CuO}_2$  planes amounts to 0.13 electrons when the interface is oriented parallel to the superconducting planes and to 0.09 electrons for the perpendicular orientation.

This weak dependence of the charge transfer magnitude on the orientation of the interface lets us expect that the intrinsic doping at YBCO-metal interfaces is given by some 0.1 electrons for any contact geometry, as long as the YBCO domain terminates with a Cu–O layer. Moreover, the mechanism of screened band bending and the net charge transfer are almost independent of the specific high- $T_c$  material and metal forming the contact. Therefore, the results are very general and can be applied to a large variety of interfaces.

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