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Tailoring the Intrinsic Doping at $YBa_2Cu_3O_7$-Metal-Contacts

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Abstract. Charge redistribution at interfaces between high-T_c superconductors and metals is problematic for technological applications due to local variations in the electronic structure. In particular, the interface affects the charge density in the superconducting CuO_2-planes. For obtaining quantitative insight into effects of interface doping, we address YBCO-metal-contacts by means of first principle supercell calculations within density functional theory. On the one hand, we find that the CuO_2-planes are intrinsically electron-overdoped, i.e. hole-underdoped. On the other hand, very strong effects on the near-contact electronic states are also caused by electronegative impurities incorporated into the metal. Doping of such impurities consequently paves the way for a controlled re-extracting of charge from intrinsically doped interfaces and, therefore, for a tailoring of the interface properties.

1. Introduction

Electronic transport in wires and tapes from high-T_c materials is seriously affected by structural defects and interfaces [1, 2], due to large dielectric constants and small carrier densities [3]. In general, the local charge distribution in the CuO_2-planes near interfaces is of central interest for the transport properties of oxide high-T_c superconductors. By an electrostatic screening length of just a few nanometers and the inhomogeneity of the crystal structure, the conventional band bending models are not applicable. In this context, we have recently investigated the influence of the charge redistribution induced by a metallic interface on the local doping in $YBa_2Cu_3O_7$. It turned out that screening effects are important for understanding the charge transfer [4, 5], where the superconducting CuO_2-planes are subject to a strong intrinsic electron-doping. The net charge transfer amounts to 0.13 electrons per Cu site when the interface is oriented parallel to the CuO_2-planes, and to 0.09 electrons for a perpendicular orientation [5].

In this paper we deal with the question, how the charge transfer changes with perturbations of the contact. Additional impurities can support the electron transfer or compensate it, where we are interested in a method of compensating the local doping. In the context of defects and local doping in bulk YBCO and YBCO surfaces/interfaces, mainly the YBCO domain has been studied so far. Much attention has focussed on the influence of the O content, in the full range of the high-T_c phase diagram [6]. Furthermore, it has been observed that the superconducting properties of YBCO strongly alter under Ca substitution. The critical current at low magnetic fields and the critical temperature decrease with the Ca concentration [7]. In the case of grain boundaries, Ca doping thus is used to compensate local charge redistributions [8]. The YBCO

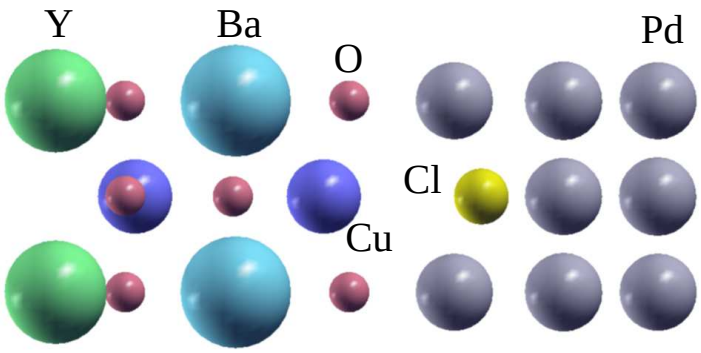

Figure 1. Cl-doped YBCO-metal-contact, where the interface is oriented parallel to the CuO_2-planes. Each second contact Pd atom is substituted by a Cl atom.

crystal structure is subject to drastic alterations under the incorporation of defects. Especially, the lattice parameters change as a function of the O stochiometry [9]. Instead of modifications of the YBCO itself, the present work deals with effects of impurities on the normal metal side of the interface. Already in the late eighties, experiments have indicated that an insertion of F/Cl into underdoped YBCO can enhance the critical temperature [10], where the F/Cl atoms tend to occupy the empty sites in the CuO-chains [11, 12]. Interestingly, insertion of the halogenides is accompanied by a higher hole content in the CuO_2-planes, which suggests that Cl impurities have also the potential to re-extract the excess charge arising at an YBCO-metal-contact.

2. Calculational Details

Our data are based on density functional theory and the generalized gradient approximation, as implemented in the WIEN2*k* package [13]. Since band-bending is proposed to take place on the length scale of the YBCO lattice constants, the electronic structure of YBCO-metal-contacts is accessible to a supercell approach with periodic boundary conditions [14]. It is most convenient to choose fcc Pd as the metallic substituent because of a minimal lattice mismatch of 0.7%.

In the following, we address interfaces parallel to the crystallographical *c*-axis, hence parallel to the CuO_2-planes. The supercells consist of 2 YBCO unit cells, terminated by the CuO-chain layer [15, 16], and 4 metal unit cells stacked in [001]-direction. We use the experimental YBCO bulk lattice constants $a = 3.865$ Å and $b = 3.879$ Å [17] also for the Pd domain, in the interface plane. In the direction perpendicular to the interface we chose the standard Pd lattice constant $c = 3.89$ Å. Layers are counted with respect to the interface, i.e. the 1st metal layer is attached to the 1st CuO-chain layer of the YBCO cell. At the contact, one half of the Pd atoms lays on top of the O atoms of the CuO-chains, the other half on top of the empty interstitial sites. For inserting an electronegative atom, we substitute the Pd atom without O neighbour by Cl. The structure is shown in Fig. 1, which already refers to the fully optimized interface.

3. Results and Discussion

Our optimized interface shows the same strong tendency towards Pd–O bonding as known from the clean interface, where the repulsion between Cu and Cl is weaker than between Cu and Pd. Distortions due to the Cl impurity are weak since the structural relaxation affects almost only the adjacent Pd atoms. Characteristic bond lengths are summarized in Table 1.

We first investigate the effect of the Cl substitution on the Pd electronic states. Fig. 2 shows the partial Pd 4*d* density of states (DOS) for the metal layer containing the Cl (1st Pd layer) as well as for the bulk-like 3rd Pd layer. For the 1st Pd layer, electronic states shift from the region

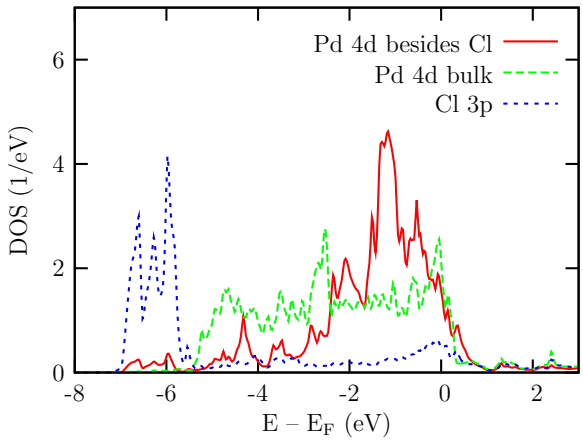

Figure 2. Partial Pd 4*d* DOS for a typical interface atom, compared to the bulk DOS. Strong effects of Pd–O and Pd–Cl bonding are visible, see also the corresponding partial Cl 3*p* DOS.

around −4 eV to higher energies, as compared to the bulk data, giving rise to a very pronounced structure around −2 eV. The latter is known to be connected to interface states due to covalent Pd–O bonding. In contrast to the Pd–O hybridization, the Pd–Cl hybridization is small for the metal sites in the 1st Pd layer, see the energy interval from about −7 eV to −5.5 eV. Of course, this behaviour is expected for an ionic bonding [18, 19]. The Pd 4*d* DOS of the 2nd metal layer is similar to the respective DOS of the clean interface, thus to the bulk DOS. However, the Pd admixtures in the Cl dominated energy range have increased. They are attributed to enhanced Pd–Cl bonding as reflected by the shortest Pd–Cl distance, see Fig. 1. Because the 3rd Pd layer is almost unaffected by the Cl, the structural screening length is short in the metal domain.

It is to be expected that the Cl extracts charge from the surrounding area, leading to a Cl^- state. Because no reduction of the Pd charge due to the Cl substitution is found, the extraction should affect the YBCO domain. For our supercell, which contains 7 Cu atoms, a naive electron counting indicates that the intrinsic charge transfer of 0.13 electrons due to the interface could be compensated almost exactly by this effect. We therefore compare the DOS of both the clean and the Cl-doped YBCO-metal-contact to bulk YBCO. We study the 2nd CuO_2-plane layer, as here the structural relaxation has already decayed. According to Fig. 3, the partial Cu 3*d* DOS confirms our speculation. Whereas a significant reduction of the unoccupied states is visible for the clean contact, this charge transfer is fully compensated in the case of the Cl-doped contact. The areas under the DOS curves on the right hand side of Fig. 3 coincide, reflecting an identical doping state of the CuO_2-planes.

	bulk	clean interface	Cl-doped interface
d_{Cu-Pd}	–	3.32	3.28
$d_{O-Pd/Cl}$	–	2.12, 3.87	2.12, 3.83
d_{Cu-O}	1.94	2.02	2.01
$d_{Cu-O_{Ba}}$	1.90	1.90	1.84

Table 1. Selected bond lengths (in Å) close to the YBCO-metal-contact, obtained by structure optimization. For comparison the bulk bond lengths are included.

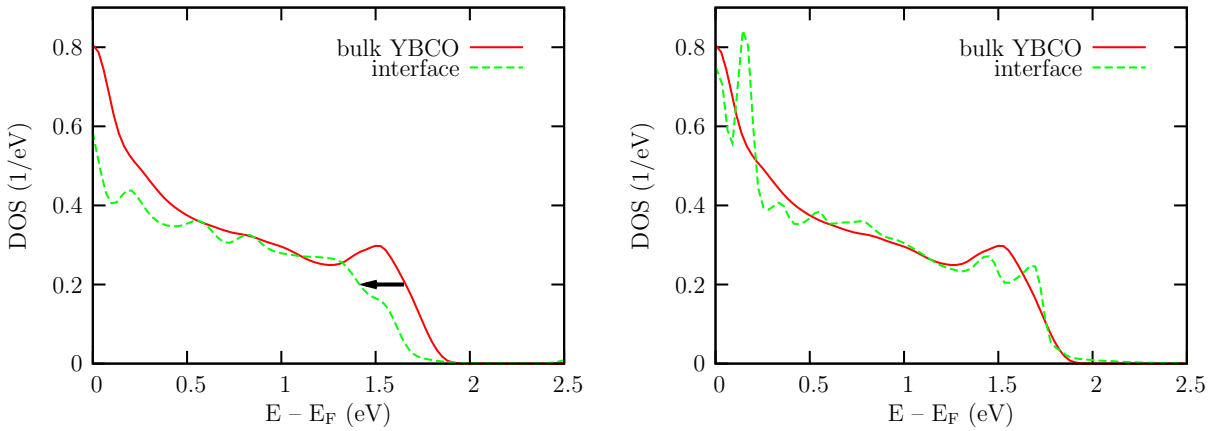

Figure 3. Partial Cu 3*d* DOS for the second CuO_2-plane off the interface (unoccupied states). Left side: clean interface [5]; right side: Cl doped interface.

4. Conclusion

We have discussed electronic structure calculations for a Cl-doped contact between $YBa_2Cu_3O_7$ and a normal metal, in order to analyze the impurity effects on the charge redistribution at the interface. Structural relaxation around the impurity is found to decay quickly within the metal domain. Moreover, the intrinsic charge transfer of some 0.13 electrons in favour of each Cu site in the CuO_2-planes is fully compensated. By means of an unexpected strong suppression of the charge transfer towards the YBCO domain, electronegative impurities consequently give rise to an ideal tool for adjusting an intrinsically doped interface.

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