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# The electronic structure of grain-boundary of $YBa_2Cu_3O_7$ doped with 3d transition-metal atoms

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ABSTRACT

We systemically study the electronic structures of Σ5 grain-boundary of $YBa_2Cu_3O_7$ with and without dopants of 3d transition-metal atoms based on the density functional theory. The partial density of states (PDOS) shows that the electronic structure of grain boundary is very different from that of crystal and the interesting orbital-reconstruction of interface is found. Generally super-current will significantly decrease when transmitting across grain boundary. The main reasons for suppressed super-current are that (1) the carriers are not uniformly distributed near grain-boundary regions and (2) the number of $CuO_4$-squares in $CuO_2$ layer, which are essentially important to transport properties, sharply decreases near grain-boundary region. The preferentially substituting sites of 3d transition-metal atoms in $YBa_2Cu_3O_7$ are predicted and some of them such as Co, Ni and Zn are consistent with the reported experimental analysis.



## 1. Introduction

The cuprate high-temperature superconductors such as $YBa_2Cu_3O_7$ have been attracted most extensively attentions because of high transition-temperature ($T_c$) above the boiling point of liquid nitrogen (77 K). However in practice, the applications of cuprate superconductors are limited by low critical current because of the weak-links between grains in polycrystallines of the ceramic samples of cuprate superconductors. High-angle grain-boundaries (GB) are considered as weak-links in cuprate superconductors. The possible mechanisms that grain boundaries suppress critical current are the interface charging and band bending in regions of grain-boundary [1]. Generally the critical current decreases with increasing mis-orientation angle but there are exceptions that some specific high-angle grain-boundaries transport high super-current [2]. The theoretical calculation based on tight-bonding model had been proved that super-currents decrease exponentially with increasing mis-orientation angle [3]. The grain-boundaries play very contrary roles in superconductors. In magnetic field, the motions of fluxes can induce additional dissipations of super-currents. The grain-boundaries and other lattice defects can efficiently pin fluxes and decrease the dissipations of super-current induced by the motions of flux-lines [4]. More discussions on the properties of grain boundaries in copper-oxides superconductors can be found in reference [1].

The problem will become very complicated if the chemical substitutions are included [5]. Some experiments have demonstrated that the substitutions of Cu atoms by other transition-metal atoms such as Zn can improve critical current of cuprate superconductors [6,7]. The payment for the enhancements of critical current is that the $T_c$ probably decreases because of introducing impurities [8–12]. Understanding the underlying microscopic mechanism for improving superconductivity is a key step to design new applications of cuprate superconductors. Since the grain-boundaries can take as efficient flux pinning center, it is very important to find proper atoms whose preferentially substituted sites are in grain-boundary regions for that the critical current is significantly enhanced while $T_c$ has small changes. Experimentally over-doping Ca atoms in grain-boundaries of $YBa_2Cu_3O_{7-\delta}$ can enhance the super-current and keep $T_c$ small reductions by maintaining the grains at optimal doping level [13].

It is interesting that the grain-boundaries doped by proper magnetic impurities can be designed as $\pi$ Josephson junctions [14]. The high-angle grain-boundaries in copper-oxides superconductors serve as Josephson junctions. Some of experiments had determined the preferential positions of doping 3d transition metals at Cu (2) sites in $CuO_2$ layers ($CuO_2$ plane) or Cu (1) sites in CuO layers (CuO chain) in $YBa_2Cu_3O_7$ samples and other relative superconductors [15–20]. However, experimentally it is difficult to determine these doped atoms are located either in region of grains or grain-boundaries. Thus theoretical researches along this direction are very desired at current time. The elementary calculations of $YBa_2Cu_3O_7$ and other relative copper-oxides superconductors had been studied extensively based on the *ab initio* method with in density

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functional theory framework [21–23]. There are some works focused on the atomic and electronic structures in low doping region [24–26], which is generally more difficult because more atoms are required to get reliable results. The properties of interface and grain-boundary of cuprate superconductors have been studied using *ab initio* density functional theory and especially the electronic-structure difference between interface and crystal had been compared [27–29].

In this work, we present our theoretical calculations based on *ab initio* density functional theory performing on a large simulation cell. We study the substituted effects of Cu atoms by other 3d transition-metal atoms for both single crystal and high-angle Σ5 grain-boundary of $YBa_2Cu_3O_7$, in which we figure out the preferentially substituted positions for all 3d transition-metal atoms. The paper is organized as following. In Section 2 we introduce the theoretical method and other simulation details. In Section 3, we present the basic atomic structures and electronic structures of single crystal and grain-boundary of $YBa_2Cu_3O_7$. In Sections 4 and 5 we introduce the results of substitution effects of 3d transition-metal atoms to single crystal and grain-boundary of $YBa_2Cu_3O_7$, respectively. In Section 6, we present our predictions of the preferentially substituting sites of 3d transition metals in $YBa_2Cu_3O_7$.

## 2. Theoretical methods and simulation details

The coincident-site-lattice (CSL) model of grain-boundary is used to construct our grain-boundary model [30]. The $YBa_2Cu_3O_7$ film with CSL grain-boundary can be epitaxially grown on the substrate of MgO (or $SrTiO_3$) with the same type of grain-boundary [31]. We concentrate our attentions on the Σ5(3 1 0)/[0 0 1] grain-boundary of $YBa_2$ $Cu_3$ $O_7$ with mis-orientation angle $\theta = 2\arctan(1/3) = 36.87^\circ$ and the rotating axis along [0 0 1] direction. The Σ5 grain-boundary is generally found in crystal with cubic symmetry. To built Σ5 CSL model of $YBa_2Cu_3O_7$ with approximately tetragonal symmetry, we ignore the small difference between lattice parameters *a* and *b* and only consider rotation around *c*-axis. The approximation is not a problem because all initial structures will be fully optimized including the shapes and sizes of simulation cell as a whole. The unit cell of the super coincided-sites-lattice (CSL) includes 65 atoms, that is Σ (=5) times of the number of the original unit cell of $YBa_2Cu_3O_7$ lattice. Some of atoms have to be removed to avoid too small distances between different atoms near grain-boundary planes. The number of total atoms is 250, in which there are 20 Y atoms, 40 Ba atoms, 60 Cu atoms and 130 O atoms. The sizes of simulation cell are 24.34 Å, 12.17 Å and 11.69 Å along the *x*-axis, *y*-axis and *z*-axis, respectively. There are two grain boundaries in our simulation cell because of periodic boundary condition: one with grain-boundary plane at center and the other at boundary of the cell with their normals parallel to *x*-axis. For a general asymmetrical grain-boundary model, there are at least four grain-boundaries in simulation cell due to periodic boundary condition. The advantage of CSL model is that the number of grain-boundary is reduced to two. As a comparison, a single crystal including 208 atoms (with 16 Y atoms, 32 Ba atoms, 48 Cu atoms and 112 O atoms) is used to calculate electronic structure of $YBa_2Cu_3O_7$ crystal without grain-boundary.

The plane-wave method is used in this work to solve the Kohn–Sham equation self-consistently with the interaction between valence electrons and ions described by projected-augmented-wave methods [32,33]. The exchange-correlate functional is based on the generalized gradient approximations (GGA) [34]. All initial structures including their shapes and volumes of simulation cells are fully optimized based on conjugated gradient methods. When we optimize initial structures, Γ point is used in corresponding electronic-structure calculations. The accurate calculations of electronic structures of these optimized structures will be preformed using larger *k*-point mesh. The energy-cutoff of wave plane is about 400 eV for all calculations in this work.

## 3. The electronic structures of grain boundary and crystal of $YBa_2Cu_3O_7$

Before we study the effects on the substitutions of Cu atoms by 3d transition-metal atoms, it had better to introduce general electronic structures of single crystal and Σ5 grain-boundary of $YBa_2Cu_3O_7$. Basic electronic structure of $YBa_2Cu_3O_7$ single crystal had been extensively studied based on its unit cell. In this work we present results of a large simulation cell including 208 atoms. The purpose using large cell is that the same cell will be used as the basic structure for doping 3d transition-metal atoms in low doping region. The *ab initio* calculations of $YBa_2Cu_3O_7$ grain-boundaries are few in literatures [27–29]. The Fig. 1a–d shows four atomic layers of the optimized structure of Σ5 grain-boundary of $YBa_2Cu_3O_7$. Only small structural modifications are found after structural optimizations. From Y layer in Fig. 1d, we can see that there is a relative shift between two grains along *y* direction on grain-boundary plane. The perfect $CuO_2$ layer is square lattice with S (or S′) as its unit cell. The $CuO_2$ layer is generally considered as the superstructure on the square lattice with the $CuO_4$ squares or Zhang-Rice squares, such as at *D* in Fig. 1c, as basic building unit, which determine the properties of carriers. The number of $CuO_4$ squares sharply decreases near grain boundary instead the $CuO_3$ triangle and other irregular structures are found in the grain-boundary region. An O atom in CuO layer initially at grain-boundary plane modifies its position to neighbor CuO chain and the grain-boundary becomes asymmetric as shown in Fig. 1a.

The accurate electronic structures are calculated using larger *k*-points meshes $2 \times 2 \times 2$ and $1 \times 2 \times 2$ for single crystal and grain-boundary respectively. The local density of states (LDOS) around Fermi energy ±50 meV are plotted in Fig. 1. The distribution of LDOS in $CuO_2$ layer is the same as the expectation that the main conducting electrons are located in $CuO_2$ layer. Compared with $CuO_2$ layer, CuO layer are less conducting electrons. Further more we can see that O atoms (apex oxygen) near grain-boundary in BaO layer can provide conducting carriers but in the grains there are no distributions of conducting carriers in BaO layers. The full density of valence electron is very useful to understand the chemical bonds between different atoms. The Fig. 2 shows the strong Cu–O bonds in $CuO_2$ layers. In the region of grain boundary, the distribution of valence electron is very different from that in the bulk. The $CuO_3$ cluster in grain boundary is formed with three strong Cu–O bonds. The density of valence electrons is smaller in the atom-dilute region near grain-boundary plane. Thus very similar to conducting electrons in Fig. 1c, the distribution of valence electrons is not very uniform in grain-boundary region. In our calculations all atoms are non-magnetic although we apply spin-polarization calculations.

In order to make analysis more deeply, we calculate the partial and decomposed density of states of the optimized Σ5 grain-boundary and, as a comparison, the single crystal of $YBa_2Cu_3O_7$. In Fig. 3 the partial and decomposed density of states for single crystal are presented as the summations of spin-down and spin-up. We can find that the main conducting electrons in $CuO_2$ layer are contributed by Cu $d_{x^2-y^2}$ orbital in $YBa_2Cu_3O_7$ single crystal. The $p_x$ and $p_y$ orbitals of O atoms contribute conducting electrons and hybridize with $d_{x^2-y^2}$ orbitals of nearest-neighbor Cu atoms. Notice that we only present results of O atoms nearby Cu atom along *x*-axis so that only $p_x$ component is large. If we choose the nearest neighbor O atom along *y*-axis, $p_y$ component should be large. The CuO chains are parallel to *y*-axis in our model and