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# Ferromagnetism on surface of $YBa_2Cu_3O_7$ particle

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ABSTRACT

In recent experiments, a special ferromagnetism of $YBa_2Cu_3O_7$ (YBCO) particles has been found at room-temperature. In this paper we mimic a YBCO particle using a small YBCO cluster and different YBCO surfaces. The magnetic properties of the small cluster and surfaces are calculated using *ab initio* density functional theory (DFT). According to our calculations, we infer that the ferromagnetism of the YBCO particle comes from the surfaces of the YBCO particle, which is contributed by both *p* electrons of oxygen atoms and *d* electrons of Cu atoms, and extends to several atomic layers beneath surface. The surface magnetism is similar to the itinerant magnetism and closely relative to low coordination number, spatial-inversion symmetry breaking and electric neutral condition. Our results indicate that the enhanced magneto-electric coupling induced by broken spatial inversion symmetry near surface layer plays an important role on the surface ferromagnetism of YBCO particle. The ferromagnetism on surface of YBCO particle can be significantly depressed in highly *c*-axis unique oriented films because the proportions of weak-links are small due to the reductions of pores, voids and micro-cracks.



## 1. Introduction

As ceramic materials, there are high-concentrations of micro-cracks, voids, dislocations and grain-boundaries constructed by random stacks of small grains or particles in brittle $YBa_2Cu_3O_7$ (YBCO). These defects are weak-links and suppress the transportation of super-current [1]. In recent magnetic measurements to YBCO and other cuprate superconductors (growing in non-equilibrium condition), the ferromagnetic or paramagnetic hysteresis loops are found at room temperature, which become the standard diamagnetic style in superconducting state below transition temperature $T_c$ [2–5]. For samples growing at equilibrium condition and having the proper annealing treatments, the ferromagnetic hysteresis loops disappear. These experiments have shown us that the possible origin of this kind of ferromagnetism is the ferromagnetism of small YBCO particles because growing in non-equilibrium state, the YBCO particles have smaller sizes with larger ratio of surface/volume and generally have different physical properties compared with those of crystals. These YBCO particles are loosely stacked together to form voids or pores so that the surface effects become very important. Some other experiments indicate that the films of cuprate superconductors are magnetic. For instance, the splittings of the zero bias conductance peaks of *ab*-orientated YBCO (Bi2212)/Insulator/Cu (Pb) tunneling junctions at lower temperature 7–8 K ($\ll T_c$) and zero magnet field [6,7] were explained as the breaking of time-reversed-symmetry induced by magnetic surface states [8].

In other metal oxides such as CuO [9], $HfO_2$ [10], ZnO, $CeO_2$, $Al_2O_3$ and MgO [11–14], the similar ferromagnetism has been found and is explained as the surface ferromagnetism of oxides particle induced by oxygen vacancy on surface [11,12]. Some researches based on theoretical models and *ab initio* simulations show that the partial occupations of *p* orbitals of the oxygen atoms near structural defects such as cation vacancies induce the ferromagnetism on these oxides [15,16]. In fact, a surface is a two-dimensional structural defect of a crystal and atoms near surface have lower coordination number than those in bulk. In a *ab initio* simulation of MgO, the formation energy of a cation vacancy in surface layer is lower than that in bulk so that the magnetic cation vacancies are easily formed near surface layer [17]. It is different from the above mentioned the insulating metal-oxides that YBCO is metal. The low coordination number will narrow the electronic bands of surface states of YBCO and increase the density of states (DOSs) near Fermi energy that consequently induces the instability of paramagnetic state and the formation of ferromagnetic state near surface by electron–electron exchange interactions.

The magnetism of materials is correlated to broken time-reversed symmetry. The mechanism inducing the ferromagnetism on surfaces of YBCO particles as well as other metal-oxides particles is a very interesting topic. It is obviously that the spatial-inversion symmetry is broken near surface because the atoms on one side of surface layer are lost. Based on Landau's magneto-electric coupling theory [18], the magneto-electric coupling will be enhanced because of the broken spatial-inversion symmetry.

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This means that in principle the electric field near surface can induce the spin-polarization or the orbital-polarization of surface electrons even without oxygen vacancies or cation vacancies, which generates the corresponding magnetic field near surface. However Landau's theory is only a phenomenological theory, the underlying microscopic mechanism of surface ferromagnetism of non-magnetic metal-oxides is deserved to investigate further.

Generally a YBCO particle has different facets (or outer surfaces) with different surface indexes so that it is difficult to calculate the electronic structures of these surfaces in a single calculation because experimentally the size of a YBCO particle is from nanometer to micrometer, which is too large for *ab initio* DFT calculations. In present work, we investigate magnetism of YBCO surface and small cluster to mimic YBCO particle approximately. Our main findings are (1) the YBCO surfaces have relative stable ferromagnetic state; (2) the surface magnetism is similar to the itinerant magnetism correlated to the electron gas on surface, in which the averaged magnetic moment is generally smaller than those induced by oxygen vacancies or cation vacancies; (3) the *p*-electrons of oxygen atoms have main the contributions to the ferromagnetic state, although the *d*-electrons of Cu atoms have the contributions to the ferromagnetism but small compared with those of the *p*-electrons of oxygen atoms; (4) beyond two-four atomic layers inside bulk the surface magnetism becomes very weak; and (5) the breaking of local inversion symmetry is the necessary condition for the ferromagnetic state of the YBCO surface, with that the driven forces are the electric neutral condition and the low coordination number near the YBCO surfaces.

## 2. The numerical methods of theoretical calculations

We calculate the electronic ground states and forces acting on atoms by the *ab initio* density functional theory, in which the Kohn–Sham equation is solved numerically based on the plane-wave pseudo-potential method. The pseudo-potential, which describes the interaction between valence electron and ion-core, is based on the projected argument wave method (PAW) [19,20]. The electrons with the configurations $4s^2 4p^6 5s^2 4d^1$, $5s^2 5p^6 6s^2$, $3d^{10} 4s^1$ and $2s^2 2p^4$ are treated as the valence electrons for Y, Ba, Cu and O respectively. The exchange–correlation functional beyond the local density approximation (LDA) adopts the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [21] with the generalized gradient approximation (GGA). As a comparison, part of our calculations adopt the Ceperley–Alder exchange–correlation functional [22] with the localized spin-density approximation (LSDA) [23,24]. The kinetic-energy cutoff of plane waves is about 420 eV in our all calculations. A YBCO crystal has Pmmm ($D_{2h}-1$) space group symmetry with lattice constant $a$ = 3.824 Å, $b$ = 3.8879 Å, $c$ = 11.6901 Å. We simulate two types of structures: surface and cluster, in particular, including the (100), (110) surfaces and (001) surfaces with different terminated atom layers. The simulation cells of surfaces and cluster have the large enough empty spaces to reduce the influence of structural images because of periodic boundary condition. In DFT calculation, the convergence state is generally not unique and numerically dependent on the initial conditions. In our self-consistent calculations, we choose different initial magnetic states such as ferromagnetic and non-magnetic states to find the reliable self-consistent ground state. The convergent state with the lowest free energy is defined the stable state in our calculations. The initial anti-ferromagnetic state is not included in our simulations of all surfaces because the anti-ferromagnetic state of perfect YBCO crystal is generally unstable in conventional GGA or LSDA calculation. In the simulations of surfaces, generally two k-point meshes centered at $\Gamma$ point are used for the integrations in the first Brillouin zone: the coarse $1\times1\times1$ mesh for the optimizations of surface structures and the $2\times2\times1$ mesh for the more accurate calculations of electronic structures of the optimized surface structures.

## 3. Ferromagnetism on YBCO (001) surface

A perfect crystal of YBCO is constructed by two types of structural units stacking along *c*-axis as shown in Fig. 1a and b, where the type A (TA) is BaO–CuO–BaO with CuO chains sandwiched between two BaO layers and the type B (TB) $CuO_2$–Y–$CuO_2$ with Y ions sandwiched between two $CuO_2$ layers. We first consider the (001) surfaces with the normal vector along the *z*-direction of the simulation cell. The (001) surfaces have six different types determined by the chemical compositions of the surface layers and their neighbors. The (001) surfaces with 208 atoms in the simulation cell are constructed by a crystal with the *a*-axis having an approximate 45° angle with the *x*-direction or the $[1\bar{1}0]$ direction of YBCO crystal parallel to the *x*-direction of the simulation cell. The sizes of the simulation cell are 10.907 Å, 10.907 Å, 33.380 Å along *x*, *y*, *z* directions respectively. Along the *z* direction the empty space above the top surface and below the bottom surface is about 10 Å under periodic boundary condition. The six different (001) surfaces belong to three simulation models in Fig. 1c–e. The top surface and bottom surface in each model are different types of surfaces. In our simulations, all the atoms and the shape of simulation cell are fully relaxed in order to find the stable structures of surfaces.

Our calculations show that the structural units TA and TB have positive charges 0.556e and negative charges −0.556e per crystal-cell respectively based on the numbers of valence electron of Y, Ba Cu, O in Table 1 obtained from Bader analysis[25]. By symmetry analysis we can find that the structural unit TA has $D_{2h}-1$ symmetry and TB $D_{4h}-1$ symmetry. Both of them have spatial inversion symmetry so there are no spontaneous polarization in the whole TA and TB. The polarization appears between the positive charged TA and the negative charged TB. This means that the structural units TA and TB are stable and electrically attracted each other to form the stable YBCO crystal. The two types of surfaces terminated by $CuO_2$ or BaO layers in Fig. 1c, which do not destroy the basic structural units TA and TB, can be formed by breaking the bonds between BaO layer and $CuO_2$ layer. As the magnetic density shown in Fig. 1c, the two surfaces (top and bottom) have no magnetism, which is closely related to the completeness of the structural units TA and TB.

The other four surfaces in Fig. 1d and e all destroy one of two basic structural units, that is the BaO and CuO terminated surfaces in Fig. 1d destroy the structural unit TA, and the Y and $CuO_2$ terminated surfaces in Fig. 1e destroy the structural unit TB. The results of these four surfaces in Fig. 1d and e are very different from those two surfaces in Fig. 1c because the self-consistent magnetic densities are dependent on the choices of the initial magnetic states. If the initial state of the slab model is ferromagnetic order for all the atoms in Fig. 1d, the final states of BaO and CuO surfaces are ferromagnetic, especially the bottom CuO surface in Fig. 1d is also ferromagnetic but with small number spin flips. It is important that the free energy in the ferromagnetic state is about 0.0396 eV (Table 2) lower than that in non-magnetic state. This means that the ferromagnetic surfaces in Fig. 1d is more stable state. The large magnetic moments in Fig. 1d appear at the oxygen atoms in the top layer (0.18–0.23$\mu_B$) and the copper atoms in the beneath $CuO_2$ layer (0.18–0.23$\mu_B$).

In Fig. 1e, there are two types of surfaces: the top surface terminated with $CuO_2$ layer and the bottom surface terminated with Y layer. The free-energies of the slab model are oscillating in our several self-consistent calculations by running about 400 scf cycles