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# Effect of oxygen deficiencies and the substitution of fluorine on the electronic states in $YBa_2Cu_3O_{7-\delta}$ superconductors

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## Abstract

We present a systematic theoretical study of fluorine-substituted $YBa_2Cu_3O_7$ crystal based on accurate first-principles all-electron total-energy calculations, using the full-potential linearized augmented plane wave (FP-LAPW) approach in the framework of density functional theory (DFT), and the generalized gradient approximation (GGA) for the exchange-correlation term. The electronic structure, energy levels and the density of states (DOS) at equilibrium volume with different oxygen deficiencies distribution or F substitution are studied. The existence of oxygen vacancies and the substitution of oxygen by one, two and up to three fluorine atoms on several selective sites change the electronic band structure in $CuO_2$ plane between two Ba planes.

Thus, doping with charge carriers in the above materials is simulated and the resulting changes in the electronic distribution are compared to experimental and/or ab initio results.

*Keywords:* High-$T_C$ superconductivity; F-substituted $YBa_2Cu_3O_{7-\delta}$; First-principles; DFT/GGA; FP-LAPW; Electronic properties

## 1. Introduction

Since the discovery [1] in 1986 of superconductors with transition temperatures above 77 K much effort has been devoted to understanding the origin and mechanism of high-$T_C$ superconductivity and in a search for new high-$T_C$ materials. Investigation of the effects of changes in the structure and electron density of the material on the superconducting transition temperature holds the promise of furthering our understanding of the origin of superconductivity in oxide superconductors. Much of this work results in the production of extremely complex materials since it involves partial replacement of one chemical constituent of the basic material with another.

The compounds of the $(R)Ba_2Cu_3O_x$ class with oxygen content $x \approx 7$ superconduct at critical temperatures of about $T_C \approx 90$ K not only for Y on the rare-earth site but also for a wide variety of isoelectronic cation substitutions [2–4]. The orthorhombic crystal structure of $YBa_2Cu_3O_{7-\delta}$ consists of three simple perovskite units stacked one atop another [5].

The top and bottom units enclose a Ba atom, while the center units enclose a Y atom. The top and the bottom faces of the central unit are formed by $CuO_2$ layers, which form planes running throughout the crystal. In fully oxygenated samples, i.e., $\delta = 0$, the Cu and O atoms at the top and the bottom of the YBCO unit cell form two linear chains parallel to the planes. In order to form chain bonds, electrons leave the $CuO_2$ planes, leaving mobile holes behind. The $CuO_2$ planes are therefore metallically conducting and the holes in the plane can condense to form Cooper pairs when $T$ drops below $T_C$. The transition temperature $T_C$ depends on the O concentration in the chains. With decreasing O content $T_C$

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decreases, until for $\delta > 0.64$ the material no longer superconducts.

Many attempts have been made to synthesize or identify other multicomponent ceramic oxides with even higher $T_C$. One approach is to partially substitute the O in the $YBa_2Cu_3O_{7-\delta}$ with fluorine [6–8]. It was reported that superconductivity at 155 K or higher is possible in the Y–Ba–Cu–O–F system [8]. However, it is generally agreed that Y–Ba–Cu–O–F is extremely unstable, if it can be synthesized. The cycle of discovery, hope for applications, failure to realize them and despair has been repeated many times in the field of superconductivity up until the present day. However, if the F-substituted system can be stabilized, characterized and studied, not only does superconductivity with $T_C$ near room temperature becomes closer to reality, but it may also shed some light on the possible mechanism controlling the high-$T_C$ superconductivity.

In this paper, we report the results of the theoretical analysis of the electronic structure of the F-substituted $YBa_2Cu_3O_7$ crystal using the full-potential linearized augmented plane wave (FP-LAPW) method in the density functional theory (DFT) framework, with the generalized gradient approximation (GGA). Our objective is to examine these properties with a view to elucidating them using an accurate ab initio or first-principles technique, together with a comparison of the present study with existent measurements [9] and other theoretical calculations [8,10]. This comparison will provide a guideline for the use of methods in the cases for which similarly detailed analysis is impossible. We describe in the following section the calculation procedure underlying the present study. Section 3 is then devoted to the discussion of the results with a brief conclusion at the end.

## 2. Structural aspects and computational details

### 2.1. Crystal structure and symmetry

The $YBa_2Cu_3O_7$ orthorhombic crystal of *Pmmm* contains 13 atoms per unit cell distributed among eight distinct sites. Yttrium and the chain atoms Cu(1) and O(1) occupy sites with the full symmetry of the cell (*mmm*). For barium, the copper and oxygen atoms in the planes—Cu(2), O(2) and O(3)—and the bridging oxygen O(4) the symmetry is lower (*mm*). The following optimized lattice constants are adopted for $YBa_2Cu_3O_7$; $a = 7.1975$ a.u., $b = 1.017a$ and $c = 3.059a$. Since the electronic structure is very sensitive to the particular O site that was replaced by F [11–14]. We have limited ourselves to the study of the following substituted systems. (a) For $YBa_2Cu_3O_6F_1$, two cases were studied: one with F replacing O(1) and another with F replacing O(3). (b) For $YBa_2Cu_3O_5F_2$, three cases were studied: one with two F replacing two O(3), another with F replacing O(1) and O(3) and the third with F replacing O(1) and O(4). (c) For $YBa_2Cu_3O_4F_3$ we studied a case with three F substituting O(1) and two O(3) sites. We purposely concentrate on the substitution with O(1) site because this site is well recognized as the O vacancy site in $YBa_2Cu_3O_{7-\delta}$. $YBa_2Cu_3O_3F_4$ was not studied since experimentally it was indicated that this phase is nonsuperconducting [7] and involves another unknown phase instead of $YBa_2Cu_3O_7$. Fluorine addition to this material is believed to have an effect on the charge carrier concentration in the $CuO_2$ planes, as fluorine is more electronegative than oxygen. Furthermore, because the ionic radius of fluorine is smaller than that of oxygen, the crystal anisotropy may also change due to replacement of oxygen by fluorine.

### 2.2. Computational details

To predict the ground-state crystal and electronic structures, first-principles calculations are performed by employing the full-potential linearized augmented plane wave [15–18] method in the density functional theory framework [19,20] as embodies in the WIEN2k code [21], that has been shown to yield reliable results for electronic and structural properties of various complex crystals. The effects of exchange and correlation are treated within the generalized-gradient-corrected local-density-approximation using the parameterization scheme of Perdew et al. [22]. The FP-LAPW method makes no shape approximation to the potential or charge density. However, for computational convenience, space is divided up into volumes within nonoverlapping muffin-tin spheres plus the encompassing interstitial region. Core states are treated fully relativistically; valence and semi-core states are treated semi-relativistically. In this method the valence and core states origin energies have been separated, and the −6 Ry energy bound separating between the valence electrons and the core states was chosen. Recently, Sjöstdt et al. [23] suggested an important modification of the LAPW method. They introduced an APW-lo basis, where the APW's, are evaluated at a mixed energy and flexibility is added by including another type of local orbitals (los).

$$\varphi_{Kn} = \sum_{lm} [A_{lm,Kn} u_l(r, E_l)] Y_{lm}(\hat{r})$$

$$\varphi_{lm}^{\mathrm{lo}} = [A_{lm} u_l(r, E_{1,l}) + B_{lm} \dot{u}_l(r, E_{1,l})] Y_{lm}(\hat{r})$$

The local orbitals are evaluated at the same mixed energy as the corresponding APWs.

The two coefficients are determined by the normalization and the condition that the local orbital has zero value at the sphere boundary. In this version, $\dot{u}$ is independent of the PWs, since it is only included for a few local orbitals and not associated with every PW. The new scheme combines the best features of all APW-based method available [29]. However, the highest efficiency was found for a mixed basis set in which the "physically important" $l$-quantum numbers are treated by APW + lo but the higher $l$ by LAPW. In the calculations reported here, the $K_{\max} = 8/R_{\mathrm{mt}}$ parameters was used, which determines the matrix size (convergence), where