Study on the effects of fluorine and oxygen deficiency on YBa$_2$Cu$_3$O$_7$ by *ab initio* method*

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Abstract The calculations of clusters modeling the fluorine-doping and oxygen deficiency of YBa$_2$Cu$_3$O$_7$ have been performed by the method of all-electron *ab initio* Hartree-Fock with self-consistent crystal field. Results show that in CuO planes electric charge significantly increases, the chemical valence of Cu decreases and the covalent bonding of Cu-O greatly weakens owing to oxygen deficiency, while the effect of F restores the local electronic structure of YBa$_2$Cu$_3$O$_7$. The reported opinion that F occupied the oxygen vacancy in Cu-O chains seems disputable according to the calculated bonding characteristics.

Keywords: YBaCuO, high-$T_c$ superconductivity, quantum chemical calculation.

The doping of halogen anions in YBaCuO has always been an attractive subject since high $T_c$ superconducting phenomenon was discovered. Many experiments have shown that the superconductivity of oxygen-deficient YBa$_2$Cu$_3$O$_{7-x}$ ($x > 0.5$), which is not a superconductor, could be recovered with $T_c$ being 88–92 K by doping halogen anions$^{[1,2]}$. The superconductivity could even be achieved in the $T'$-phase compound Nd$_2$CuO$_4$ by doping F$^{[3]}$. In order to understand these effects, it is desirable to first obtain the knowledge of local electronic structure of the crystal by carrying out cluster calculations. However, most of the existing calculations were performed by the local density functional approach LDFA or semi-experience methods without using electroneutrality models.

This paper presents the calculations of three clusters modeling pure crystal, doping of F and oxygen deficiency respectively by *ab initio* method of the all-electron Hartree-Fock with an SCF Madelung potential$^{[4]}$ and discussions of their local electronic structures.

1 Computational method

The cluster model of YBaCuO used as shown in fig. 1 in which the numbering and the structure parameters given by ref.$^{[5]}$ are adopted contains 13 atoms in a chemical formula unit in order that the cluster is a neutral system, which is necessary to exact investigation of an electric charge distribution in the cluster. Considering that the bonding between O(1) and Cu(1) belongs to a typical covalence because of their shortest distance (0.178 5 μm) in YBaCuO, the layer of Cu(1)-O(4), instead of the layer of Y, is put in the middle to keep two bonds of Cu(1)-O(1) in the calculation model and to make the correct description of chemical bonding characteristics.

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possible. To properly simulate the crystal field, $11 \times 11 \times 5$ ($a \times b \times c$) unit cells are made symmetrically distributed around the cluster. The atoms within these unit cells are represented by the corresponding Mulliken atomic charge obtained from SCF. Meanwhile, the Hartree-Fock surface potential proposed in ref. [6] is also used as boundary conditions.

To research the doping effect, the site of F in YBaCuO has to be definitely determined. Unfortunately, this is still an open problem. There are two different opinions about it: (i) the F anion is considered occupying the oxygen vacancy in the CuO chain according to a neutron diffraction and an LDF-LCAO calculation$^{[7,8]}$; (ii) the F is supposed to replace the apical O(1) of a CuO$_6$ octahedron based on the Raman spectroscopy, X-ray diffraction, Mössbauer spectroscopy and X-ray photoelectron spectroscopy$^{[2]}$. The present authors prefer to accept the latter instead of the former because of the following facts. On the one hand, the latter is determined by more experiments; on the other hand, the site of F should be similar to that of another halogen Br, which is considered to be at the apical site. In addition, the previous HF calculations have shown that the charge carried by the apical O(1) is closer to that by F as compared with other O atoms, and the apical O(1) is more easily replaced by F from the chemist's intuition$^{[4]}$. Therefore in the present work, the calculated cluster modeling the effect of F is to put it at the apical site.

Reference [9] proposes an "electron shift model" for studying the effect of oxygen deficiency, i.e. the oxygen deficiency in one unit cell will lead the remaining electric charge to shift out and to make other unit cells carry negative charge; by this model, $[\text{YBa}_2\text{Cu}_3\text{O}_7]^x-$ represents the effect of $x$ electric charge arising from the oxygen deficiency. For investigating the tendency of the effect, 0.2, 0.4, 0.6 and 0.8 are chosen as the values of $x$, respectively.

The computational details, such as basis set, computer program and so on, are the same as those in the previous report$^{[4]}$. The size of clusters used is in fact very limited as compared with the whole crystal, but as an approximation for obtaining a qualitative knowledge, it should be acceptable, as has been proved by the study on the effect of Zn on YBaCuO$^{[10]}$.

2 Results and discussion

2.1 Effect of oxygen deficiency

Table 1 shows the electric charge distribution from calculation results. It could be found from the table that the charge of Ba, O(1), Y, Cu(1) or O(4) is influenced little by the effect of oxygen deficiency, while the effect on the CuO$_2$ plane is the main one, i.e. the positive charge of Cu(2) decreases and the negative charge of O(2) and O(3) increases significantly. As is well known, the high $T_c$ superconductivity of cuprate ceramics depends mainly on the CuO$_2$ planes, which should be emphatically discussed.