

tween Fe^{3+} and Fe^{4+} ions.

Acknowledgement. This work was supported by Post-Graduate scholarship from the Dae Woo Foundation in 1993 and also Grant No. 92-25-00-02 from the Korean Science and Engineering Foundation in 1992. Therefore we express our deep appreciation to the authorities concerned.

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Electronic Structure and Properties of High- T_c Substituted YBCO Superconductors: II. MO Calculations on Charged Cluster Models Relating to High- T_c Se-Substituted YBCO Superconductors

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Received February 7, 19994

Using the extended Hückel molecular orbital method in connection with the tight binding model, we have studied electronic structure and related properties of the charged cluster models relating to superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals in which O-atoms in regular sites were selectively replaced with Se atoms. In analogy to the isomorphism problem with molecules, we discuss all possible combinations of Se-substitutions in O-sites with one, two, and four Se atoms. The calculations are carried out within charged cluster models for analogues of YBa-copper oxide. Our results suggest that the electronic structure of the symmetrically Se-substituted or Se-added compound is closer to that of the YBCO superconducting compound than that obtained from the unsymmetrical substitution. This applies in particular if O is replaced with Se around the Cu(1) site. Symmetrical substitutions in the CuO_2 layers give rise to large variations in the electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$. This is consistent with the fact that superconductivity is very sensitive to the electronic population of the CuO_2 layers.

Introduction

Since the discovery of copper oxide with transition temperature T_c near 93 K in the Y-Ba-Cu-O systems,¹ a number of attempts have been made to increase T_c for High- T_c superconductors. These²⁻⁴ and other studies⁵⁻¹⁰ have stimulated research to modify the chemical composition by isomorphic replacement of the element in order to raise T_c and to examine the mechanism of High- T_c superconductivity by sub-

stituting various elements in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ compound. It was found that yttrium could be replaced with rare-earth metals² with no increase, *i.e.* enhancement, of critical temperature. Similarly, when barium is replaced with other alkaline earth metals,³ the overall trend is toward a continuous decrease of T_c . Also, 3d transition-metal substitution⁴ for Cu gives rise to a diminution of T_c as the doping is increased.

In the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ system, the superconductive properties are strongly correlated with its oxygen content.⁵ Several pa-

pers⁶ have reported the partial replacement of oxygen by fluorine. This may or may not lead to the stability of superconducting properties of the Y123 phase. In particular, the chalcogens, such as S, Se and Te, exhibit similar valence states to oxygen and are expected to form similar bond characteristics.

Superconductivity at 108 K in S-substituted Y-Ba-Cu-O has been reported,⁷ though it was not stable against heat cycling. Recently, it has been reported that sulphur can enter the lattice of YBa₂Cu₃O₇ and become substituted for oxygen atoms,⁸ and the non sulphur doped compound shows better superconducting behaviour than does the doped one.⁹

It has also been shown that the addition^{10a} of selenium at the O(5) sites in YBa₂Cu₃O_{7-x}, leads to an increase of the T_c (zero) value, accompanied by a sharpening of the transition to within 1 K. Recently, the substitution^{10b} of Se for oxygen of YBa₂Cu₃O_{7-x}Se_x has been shown to drastically decrease T_c as x increase and it equals 40 K at $x=0.25$.

It has been an attractive research goal to obtain the relations among superconductivity, structure and carrier concentration in the Y-Ba-Cu-O system. It is therefore important to understand how the hole concentration in the CuO₂ layers is affected by the Se-substitution. In this paper we study all possible combinations of O-substitutions by Se atoms in analogy to the isomerism problem of molecules, and we report a possible way of relating T_c with the extended Hückel molecular orbital (EHMO) results, explaining the preferential ordering of the dopants in the Y-Ba-Cu-O system, based on theoretical calculations.

In evaluating the influence of substitutions into the Y-Ba-Cu-O system, it appears that the precise lattice location is important. Experimentally, the preferred site for the Se could so far only be examined generally, not specifically. Therefore it appears to be desirable to explore theoretically the particular change in the electronic structure and properties of the Se-substituted, or Se-added Y123 compound as a function of the Se-concentration.

The calculations are based on the EHMO method¹¹ with the tight binding model. Even though the method can only lead to very approximate results, its fast computational speed allows one to study the envisioned complex systems which can only be handled with great difficulty in use of more sophisticated methods of calculation. It is shown to provide useful insights into the electronic structure and other physical properties of the solid in question.

Method and Investigation

To qualitatively study the bulk properties of YBa₂Cu₃O_{7-x}Se_x ($x=0.5, 1, 1.5, 2, 3$) and YBa₂Cu₃O₇Se_x ($x=0.5, 1$), we model these materials by clusters for the formula unit of the host material. We list cluster models representing each stoichiometric formula of substituted YBCO in Table 1. Here we use the notation Se_s[O(a), O(b) LN] to represent the Se-substituted system in which the subscript s is the number of Se atoms which substitute or add at sites a and b , and the L and N represent the lower layer and the negative direction oxygen in the local crystal structure plane of each copper atom when the position of Cu(1) atom is taken to be the origin of our coordinates.

For simplicity, we neglect lattice relaxation effects associa-

Table 1. Cluster models, cluster numbers, substitution-sites, and stoichiometric formulas

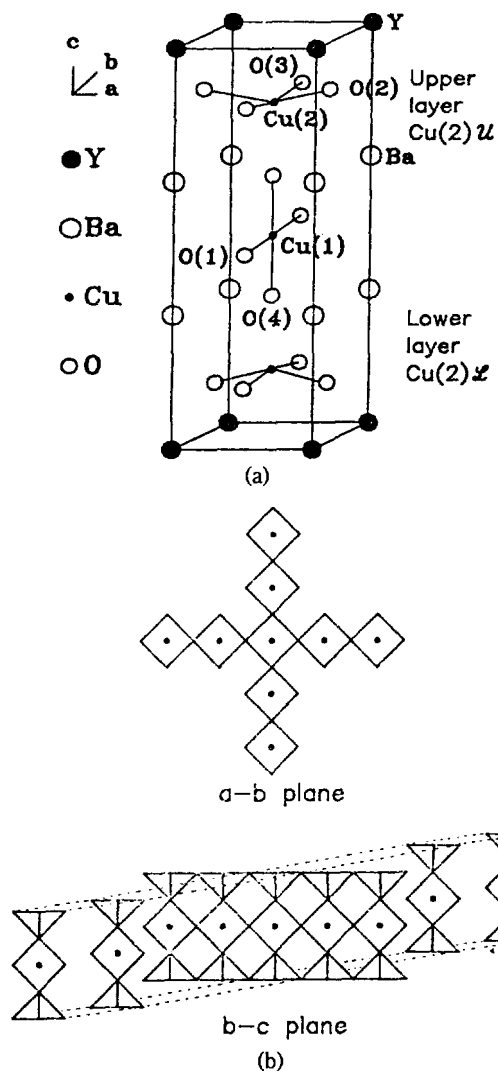
| Cluster models | Cluster numbers | Substitution-sites | Stoichiometric formulas | | |
|---|--|---|---|---|---|
| Cu ₃ O ₁₀ Se ₂ | 1: | Se ₂ [O(1), O(1)], | YBa ₂ Cu ₃ O ₆ Se | | |
| | 2: | Se ₂ [O(1), O(2) N], | | | |
| | 3: | Se ₂ [O(1), O(3)], | | | |
| | 4: | Se ₂ [O(1), O(3) N], | | | |
| | 6: | Se ₂ [O(2), O(2) N], | | | |
| | 7: | Se ₂ [O(2), O(2) L], | | | |
| | 8: | Se ₂ [O(2), O(2) LN], | | | |
| | 9: | Se ₂ [O(2), O(3)], | | | |
| | 10: | Se ₂ [O(2), O(3) L], | | | |
| | 13: | Se ₂ [O(3), O(3) N], | | | |
| | 14: | Se ₂ [O(3), O(3) L], | | | |
| | 15: | Se ₂ [O(3), O(3) LN], | | | |
| | Cu ₃ O ₁₁ Se | 5: | | Se ₂ [O(1), O(4)], | YBa ₂ Cu ₃ O _{5.5} Se _{1.5} |
| | | 11: | | Se ₂ [O(2), O(4)], | |
| | | 12: | | Se ₂ [O(2), O(4) N], | |
| 16: | | Se ₂ [O(3), O(4)], | | | |
| 17: | | Se ₂ [O(3), O(4) N], | | | |
| 18: | | Se ₂ [O(4), O(4) N], | YBa ₂ Cu ₃ O ₅ Se ₂ | | |
| 19: | | Se ₁ [O(1)], | YBa ₂ Cu ₃ O _{6.5} Se _{0.5} | | |
| 20: | Se ₁ [O(2)], | | | | |
| 21: | Se ₁ [O(3)], | | | | |
| Cu ₃ O ₁₂ Se ₂ | 22: | Se ₁ [O(4)], | YBa ₂ Cu ₃ O ₆ Se | | |
| | 23: | Se ₂ [O(5), O(5) N], | YBa ₂ Cu ₃ O ₇ Se | | |
| Cu ₃ O ₁₂ Se | 24: | Se ₁ [O(5)], | YBa ₂ Cu ₃ O ₇ Se _{0.5} | | |
| Cu ₃ O ₈ Se ₄ | 26: | Se ₄ [O(1), O(1) N, O(2), O(2) L], | YBa ₂ Cu ₃ O ₇ Se ₂ | | |
| | 27: | Se ₄ [O(1), O(1) N, O(3), O(3) L], | | | |
| | 30: | Se ₄ [O(2), O(2) N, O(2), O(2) LN], | | | |
| | 31: | Se ₄ [O(3), O(3) N, O(3), O(3) LN], | | | |
| | 32: | Se ₄ [O(2), O(3), O(2)L, O(3) L], | | | |
| | 25: | Se ₄ [O(1), O(1) N, O(4), O(4) N], | | YBa ₂ Cu ₃ O ₄ Se ₃ | |
| | 28: | Se ₄ [O(4), O(4) N, O(2), O(2) L], | | | |
| 29: | Se ₄ [O(4), O(4) N, O(3), O(3) L], | | | | |

The unsubstituted case is designated by 0.

ted with the specific substitutions of Se for O. In Table 2 we list the atomic coordinates of unrelaxed Y-Ba-Cu-O systems based on the crystal structure of Y-Ba-Cu-O obtained by Beno *et al.*¹² The possible crystal structure¹² and the charged cluster model of YBa₂Cu₃O₇ are shown in Figure 1, in which one central unit is taken to be our cluster model

Table 2. Atomic coordinates of substituted Y-Ba-Cu-O superconductor

| Atom | X/a | Y/b | Z/c* |
|-------------|-----|-----|--------|
| Cu(2) | 0.0 | 0.0 | 0.3556 |
| O(1), Se(1) | 0.0 | 0.5 | 0.0 |
| O(2), Se(2) | 0.5 | 0.0 | 0.3773 |
| O(3), Se(3) | 0.0 | 0.5 | 0.3789 |
| O(4), Se(4) | 0.0 | 0.0 | 0.1584 |
| Se(5) | 0.5 | 0.0 | 0.0 |

*Beno *et al.*¹², YBa₂Cu₃O₇: a=3.8231, b=3.8864, c=11.6807 Å.**Figure 1.** (a) Crystal structure of YBa₂Cu₃O₇, (b) Charged cluster model.

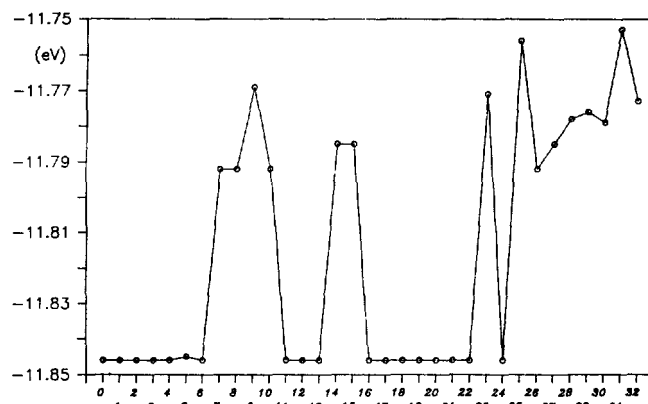
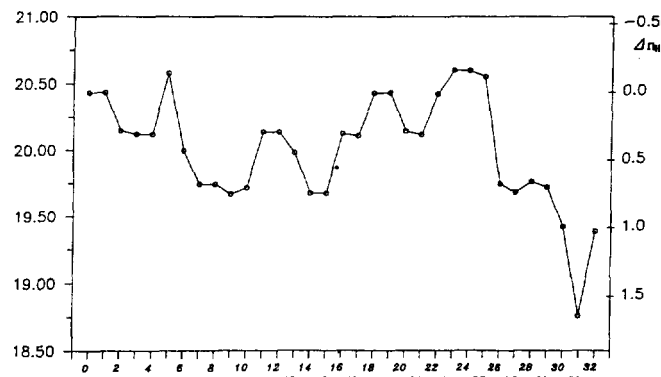
with the boundary effect. Here the boundary effect is supposed to be given by the rest of cluster.

In Table 3 we have listed the extended Hückel parameters¹³ for the valence orbitals of Cu, O, and Se atoms. The nominal charges of the individual ions have been chosen as follows: +7 for Cu₃; -2 for O and Se ions.

The highest occupied molecular orbital (HOMO) energy levels for charged cluster models are shown in Figure 2.

Table 3. Extended Hückel parameters for valence orbitals¹³

| Atom | orbital | H _i (eV) | ζ ₁ | c ₁ | ζ ₂ | c ₂ |
|------|---------|---------------------|----------------|----------------|----------------|----------------|
| Cu | 4s | -11.40 | 2.20 | | | |
| | 4p | -6.06 | 2.20 | | | |
| | 3d | -14.0 | 5.95 | 0.5933 | 2.30 | 0.5744 |
| O | 2s | -32.3 | 2.275 | | | |
| | 2p | -14.8 | 2.275 | | | |
| Se | 3s | -20.5 | 2.240 | | | |
| | 3p | -14.4 | 2.070 | | | |

**Figure 2.** HOMO energy levels for each charged cluster model.**Figure 3.** Average electron population of CuO₂ layer and relative hole concentration. Here the hole concentration difference (Δn_H) is obtained by taking the charge on a CuO₂ layer in the unsubstituted case (O) as a reference.

In this paper we present a comparative study using electron population analysis on one unit of the most central site for each charged cluster model following the method of Mülliken population analysis¹⁴ (Figs. 3, 4). The average variation of hole concentration of the central CuO₂ unit is shown in Figure 3. The electron population on the copper sites [Cu(1), Cu(2)] is shown in Figure 4.

Result and Discussion

We have studied the electronic structure and related properties of superconducting YBa₂Cu₃O₇ crystals with Se-sub-

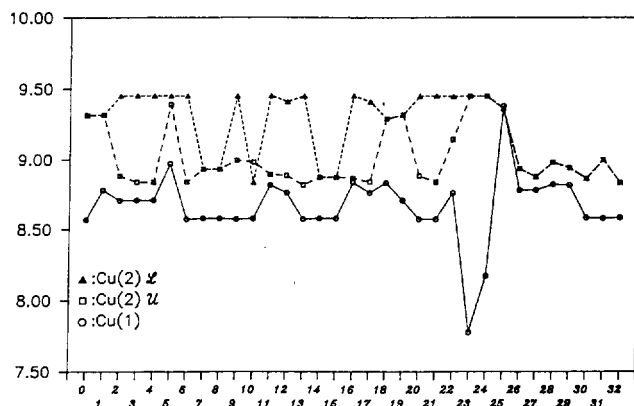


Figure 4. Electron population for each Cu site in charged cluster models. Here Cu(2) *L* and Cu(2) *U* are the Cu(2) atoms of lower and upper CuO₂ layers, respectively. Cu(1) is the Cu atom in the CuO₃ plane.

stitution at selective O-sites by using the EHMO method and charged cluster models in the tight binding model.

As shown in Figure 2, the HOMO energy level variation in every cluster model compared to the unsubstituted case (0) is less than 0.1 eV. Although the effect of the Se presence on the HOMO energy level in every cluster model is not very pronounced, we take the HOMO energy level to be a possible way of explaining preferential ordering of the dopants in YBCO. In the case of selenium substitution in the CuO₂ layer (2 Se atoms in unsymmetrical sites (7-10, 14, 15); >2 Se atoms in both unsymmetrical (26-29, 31) and symmetrical (30, 32) sites), one effect is of slightly higher HOMO energy levels compared to 0. Here the symmetry is referred to the *c*-axis. The effects of one Se atom substitution (19-22) on every HOMO energy level is negligible compared to 0. The effect of symmetrical Se substitution (6, 13) on every HOMO energy level in the CuO₂ layer is also negligible compared to 0. In the case of unsymmetrical, two-Se substitution (2-4, 11, 12, 16, 17), of which one Se is in the CuO₂ layer and the other is in the CuO₃ plane, the effect is negligible on HOMO energy levels compared to 0. In the case of two Se-substitution in the CuO₃ plane, of both symmetrical (1, 18) and unsymmetrical (15) Se-substitution, effect is minimal on HOMO energy levels compared to 0. It suggests that the electronic state of CuO₂ layers is more labile than that of a CuO₃ plane.

Substitution of two Se atoms at O(2)- and O(3)-sites in the upper CuO₂ plane forms the models in 6, 9, and 13. The HOMO energy levels of 6 and 13 are slightly lower than that of 9 because an effect of the vector direction of dipole moment between Cu(2) and Se, and [(Cu(2) and O)] is balanced in 6 and 13, but unbalanced in 9. The dipole moment is an electronic effect based on the local crystal field symmetry environment and the electronegativity difference between Se and O. The electronic effect is also shown in 7-10, 14, and 15. Thus, it suggests that the electronic effect of Se-substituents is important.

When we compare 23 (two Se-addition case for O(5)-sites) with 24 (one Se-addition case for O(5)-sites) the dipole moment of 23 is balanced but that of 24 is unbalanced, thus showing the electronic effect of 23 to be less than that of

24. But the HOMO energy level of 23 is slightly higher than that of 24. This is due to the difference of local crystal field symmetry environments around the CuO₃ plane. In 23, there is a distorted octahedral local crystal field symmetry environment, but 24 has the square pyramidal structure like the local crystal field symmetry environment of CuO₂ layers. When we compare the local crystal field symmetry environment of the CuO₃ plane in 25 with that in 0, both have the distorted square planar symmetry with the different covalent bonding character of Se and O. Model 25 is the HOMO level of four Se-substitution at both O(1)- and O(4)-sites. The different covalent bonding character of Se to O increases approximately 0.1 eV in HOMO energy. This suggests that the interaction of Cu(1) with Se is a little stronger than that of Cu(1) with O. As the Se-substitution for O in both CuO₂ layers and the CuO₃ plane increases, the orthorhombic structure can be easily deformed. It is related to the charged cluster models 26-32.

The number of electrons and the hole concentration differences for the CuO₂ layers in thirty-two different charged cluster models are shown in Figure 3. It should be noted that in unsymmetrical substitution cluster models there are two different types of Cu(2) sites that exist on CuO₂ layers; *i.e.*, just above, or below, a chain Cu(1)-site. There is a small difference between the charges at these Cu(2) sites because of difference between the charges at these Cu(2) sites because of differences in local crystal field symmetry environments. Due to considerations of simplicity this has been ignored.

An optimal hole density (n_H) in YBa₂Cu₃O₇, for which the T_c is maximum, is taken to be a reference point (*i.e.* zero point). The variation of n_H is little when the substitution of Se for O is at O(1)- or O(4)-sites. Thus it suggests that a small amount of substitution of O(1)- or O(4)-sites has resulted in negligible damage to the CuO₂ layer. When we compare our calculated results with the experimental results,¹⁰ in which the crystal structure for even a small concentration of Se is tetragonal, the substitution of O(1, 4) sites seems to be more probable than of O(2, 3) sites.

The electron population for each Cu site with a different local crystal field symmetry environment arising from the Se-substitution is shown in Figure 4. The upper and lower Cu(2) sites have different electron populations depending upon the shape of Se-substitution. Here we can easily see that the local crystal field effect of the selenium substitution of the charged cluster model is actually related to the electron populations of CuO₂ layers. The comparative damage strength of CuO₂ layers by Se-substitution is as follows: O(1) sites < O(4) sites < O(5) sites < O(2), O(3) sites.

Therefore we arrive at the result that the HOMO energy levels and electronic properties for the charged cluster models of the symmetrically Se-substituted YBCO are closer to those of high- T_c YBCO than to those of unsymmetrical substitutions. This applies in particular if O is replaced with Se in the O(1) site. Symmetrical substitutions in the CuO₂ layers give rise to large variations in the electronic structure of YBa₂Cu₃O₇. This is consistent with the well-known fact that superconductivity is very sensitive to electron populations of CuO₂ layers.

Acknowledgement. This paper was supported in part by NON DIRECTED RESEARCH FUND, Korea Research

Foundation, 1992 and BRSI-94-3438.

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Synthesis and Characterization of Dichloro and Dibromo(2-(dimethylaminomethyl)thiophene) Copper(II) Complexes

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Received February 8, 1994

The 2-(dimethylaminomethyl)thiophene (dmamt) complexes with copper(II) chloride and bromide were prepared and characterized by optical, EPR, XPS spectroscopies and magnetic susceptibility measurements. The low-energy absorption band above 850 nm and the relatively small EPR hyperfine coupling constant ($A_{\parallel} \approx 125$ G) indicate the pseudotetrahedral site symmetry around copper(II) ion both in Cu(dmamt)Cl₂ and Cu(dmamt)Br₂ complexes. The higher satellite to main peak intensity of Cu 2P_{3/2} core electron binding energy in XPS spectra also supports the pseudotetrahedral geometry around the copper(II) ions having CuNSX₂ chromophores. The distortion from square-planar to pseudotetrahedral symmetry is likely to arise from the steric hindrance of the bulky dmamt ligand in the complex. Magnetic susceptibility study shows that these compounds follow Curie-Weiss law in the temperature range of 77-300 K with positive Weiss constant exhibiting the ferromagnetic interaction between copper(II) ions in solid state.

Introduction

Blue copper proteins (Type I) exhibit unusual spectral and chemical properties in comparison with those of other copper (II) complexes¹. Such unusual properties are presumably justified with not only the nature of the donor atoms of ligands coordinated to copper(II) but also with the distorted tetrahedral geometry around copper(II) site in the proteins^{1,2}. Therefore, The pseudotetrahedral copper(II) complexes have been used as model compounds for the copper proteins. The degree of distortion from square plane to tetrahedron is highly

variable, being strongly influenced by the nature of the ligands coordinated to copper(II). In any case, the spectral and chemical properties of the complexes usually provide useful informations concerning their stereochemistry.

We prepared previously (-)-sparteine-copper(II) halides, which have pseudotetrahedral geometry around copper site, and examined the thermal³, electrochemical⁴, structural and magnetic⁵ properties, and also reported the result of the mechanistic investigation of the hydrolysis of these complexes⁶. The unusual properties of (-)-sparteine-copper(II) halides complexes were discussed in terms of the coordination geo-