

Electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ —charge-self-consistent band structure calculations

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Abstract. Charge self-consistent LCAO band structure (CSCBS) calculations are reported for orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ and tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ assuming ordered vacancy models. The effective atomic charges are used to study the charge transfer. In $\text{YBa}_2\text{Cu}(1)_1\text{Cu}(2)_2\text{O}_7$, the two types of copper atoms have their energy bands almost overlapping with effective valency of each copper as $7/3$ (or effective valency of each oxygen as approximately $-13/7$), so that electron hopping can take place without any loss or gain of energy while in $\text{YBa}_2\text{Cu}(1)_1\text{Cu}(2)_2\text{O}_6$, $\text{Cu}(1)_1$ is monovalent and $\text{Cu}(2)_2$ are divalent with significant difference in their bands. Therefore, $\text{YBa}_2\text{Cu}_3\text{O}_7$ should conduct much better compared to $\text{YBa}_2\text{Cu}_3\text{O}_6$. This corroborates the experimental observations that $\text{YBa}_2\text{Cu}_3\text{O}_7$ is a (super)conductor while $\text{YBa}_2\text{Cu}_3\text{O}_6$ is not. The calculated effective charges and DOS support the above view.

Keywords. band structure; charge-self-consistent band structure.

1. Introduction

The 1:2:3 compounds $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq \delta \leq 1$) are oxygen-deficient perovskites. Their superconducting transition temperature T_c varies with oxygen stoichiometry (Cava *et al* 1987). It is widely accepted that for the high temperature superconducting phase the crystal structure is orthorhombic and there is transition to tetragonal phase as δ is increased somewhere near 0.6. There are several high T_c oxides whose structures are well characterized (Yvon and Francois 1989), the highest T_c being 125 K. Superconductivity in Bi–Sr–Ca–Cu–O (Maeda *et al* 1988) and Tl–Ca–Ba–Cu–O (Sheng and Hermann 1988) systems support the view that the two-dimensional Cu–O planes are necessary for high temperature superconducting behaviour. The structure of $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$ ($T_c = 103$ K) is essentially identical to 1:2:3 structure. Therefore, a complete understanding of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ systems is desirable. Further, their detailed theoretical and practical studies may help in understanding the mechanism of high temperature superconductivity in other higher T_c superconductors.

The ordered vacancy model of the unit cell that we consider is shown in figure 1. $\text{YBa}_2\text{Cu}_3\text{O}_7$ has two vacancies—one in the central Cu(1)–O plane and the other in the Y–O plane. There are two Cu atoms in the five-coordinated position, called Cu(2). The other, Cu(1), is closer to O(4) than Cu(2). The Cu(2)–O plane has a ‘dimpled’ appearance and forms a 2D network in contrast to 1D Cu(1)–O ‘ribbons’. Y and Ba atoms contribute to the crystal structure through electrostatic and steric effects. In $\text{YBa}_2\text{Cu}_3\text{O}_6$ that we consider the O(1) atoms are absent. As a result the ‘ribbons’ are replaced by O–Cu(1)–O ‘dumb-bells’.

There are several experimental studies which give information about the band structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ systems. Johnson *et al* (1987) conclude, from their valence band photoemission measurements, that the experimental binding energies are further

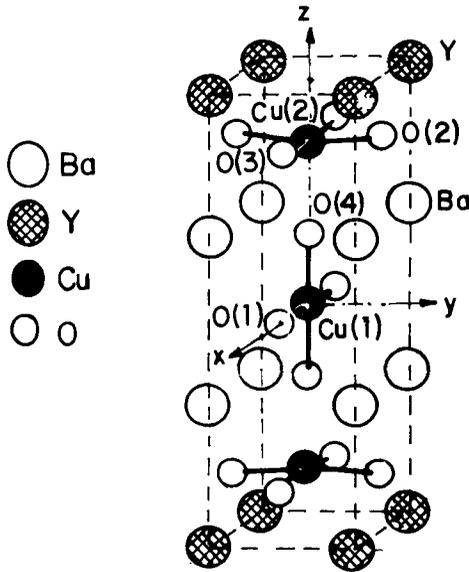


Figure 1. Unit cell of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$. The oxygen vacancy is shown by ●. In $\text{YBa}_2\text{Cu}_3\text{O}_6$ O(1) is absent in addition.

from Fermi level as compared to one-electron band calculations. Yarmoff *et al* (1987), from their photoemission, inverse photoemission and near-edge X-ray absorption studies, also find that occupied states are shifted down by about 2 eV. Their results indicate a near coincidence of Cu-3d and O-2p states. Fujimori *et al* (1987) conclude, from their photoemission studies that Cu-3d electrons are localized and find d^9 and d^{10} configurations as the ground state. Photoelectron and Auger spectroscopic studies by Sarma *et al* (1987) have shown that Cu^{3+} is absent and Cu^{1+} is present in $\text{YBa}_2\text{Cu}_3\text{O}_7$. Photoemission studies of Steiner *et al* (1987) also suggest that there is no Cu^{3+} . Kurtz *et al* (1987) used resonant photoemission to identify the chemical origin of the peaks in the spectra and they associate the peak nearest to E_F as due to Cu-3d orbitals and the next one to O-2p orbitals. Onellion *et al* (1987) reached similar conclusions. As almost all the experimental studies have concluded that the density-of-states (DOS) at the Fermi level is low, a non-BCS-like mechanism appears to be prevalent in these systems. The photoemission studies (Johnson *et al* 1987; Yarmoff *et al* 1987) suggest existence of strong electron correlation. Some of the experimental observations (Fujimori *et al* 1987) are consistent with a bipolaron or resonating-valence-bond theory (Anderson 1987).

There are several band calculations for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds. Mattheiss and Hermann (1987) have employed LAPW method to show the two-dimensional and one-dimensional features of the energy bands. Massida *et al* (1987) used FLAPW method to study the band structure. Ching *et al* (1987) studied the band structure by OLCAO method. Herman *et al* (1987) calculated the band structure for $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($x = 6, 7, 8$) using first-principles self-consistent pseudofunction method. They used an interpolation scheme to obtain DOS at the Fermi level for other values of x . Fujiwara and Hatsugai (1987) employed LMTO to study $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_8$ whereas

Temmerman *et al* (1987) used LMTO-ASA to study YBa₂Cu₃O₇. Band structure calculations using IEH scheme, which is non-self-consistent, have been reported by Orti *et al* (1987); Burdett and Kulkarni (1989) studied the electronic-geometric relationship in copper-oxide-based superconductors with their calculations. The self-consistent band structure calculations can provide vital details about the properties of solids that may be observed experimentally. This is the first report of systematic band structure calculations carried out for Y–Ba–Cu–O systems where self-consistency with respect to charge is incorporated.

2. Computational aspects

2.1 Methodology

In the CSCBS calculations the Bloch sums are used as the basis which are given by

$$X_a(\mathbf{k}; \mathbf{r}) = N_a(\mathbf{k}) N^{-1/2} \sum_t^N \exp(i\mathbf{k} \cdot \mathbf{R}_t) \phi_a(\mathbf{r} - \mathbf{R}_t), \quad (1)$$

where $\phi_a(\mathbf{r} - \mathbf{R}_t)$ are atomic orbitals centred at positions \mathbf{R}_t , $N_a(\mathbf{k})$ is the normalization constant and N is the number of lattice points which in the limit tends to infinity. The wavefunctions are linear combinations of Bloch sums given by

$$\Psi_i(\mathbf{k}; \mathbf{r}) = \sum_a C_{ai}(\mathbf{k}) X_a(\mathbf{k}; \mathbf{r}). \quad (2)$$

The overlap between two Bloch sums works out to be

$$S_{ab}(\mathbf{k}) = N_a(\mathbf{k}) N_b(\mathbf{k}) \sum_t \exp(i\mathbf{k} \cdot \mathbf{R}_t) S_{ab}^{AO}(\mathbf{R}_t) \quad (3)$$

where,

$$S_{ab}^{AO}(\mathbf{R}_1) = \int \phi_a^*(\mathbf{r}) \phi_b(\mathbf{r} - \mathbf{R}_1) d^3\mathbf{r}, \quad (4)$$

is the atomic overlap integral between the orbitals ϕ_a and ϕ_b centred at lattice points \mathbf{O} and \mathbf{R}_1 respectively. Similarly, the electronic Hamiltonian matrix would be

$$H_{ab}(\mathbf{k}) = N_a(\mathbf{k}) N_b(\mathbf{k}) \sum_t \exp(i\mathbf{k} \cdot \mathbf{R}_t) \int \phi_a^*(\mathbf{r}) \hat{H} \phi_b(\mathbf{r} - \mathbf{R}_1) d^3\mathbf{r}. \quad (5)$$

As in the case of extended-Huckel MO theory (Marathe *et al* 1980), the integral

$$\int \phi_a^*(\mathbf{r}) \hat{H} \phi_a(\mathbf{r}) d^3\mathbf{r} = h_{aa} \quad (6)$$

is taken as the negative of the sum of the ionization potential P_a^I of the electron in the orbital ϕ_a on atom A and the Madelung potential P_A^M at A . Therefore,

$$h_{aa} = -(P_a^I + P_A^M). \quad (7)$$

On the basis of Cusachs approximation (Cusachs 1965), the off-diagonal matrix

element is taken as

$$\int \phi_a^*(\mathbf{r}) \hat{H} \phi_b(\mathbf{r} - \mathbf{R}_1) d^3\mathbf{r} = h_{ab} = S_{ab}^{AO}(\mathbf{R}_1) [(1 \cdot 1 - 0 \cdot 6 |S_{ab}^{AO}(\mathbf{R}_1)|) (h_{aa} + h_{bb}) - (Q_A + Q_B)/R_{AB}]. \quad (8)$$

The effective atomic charges Q_A and Q_B of the atoms A and B , on which ϕ_a and ϕ_b respectively are located, are separated by distance R_{AB} . These approximations contained in (7) and (8) lead to the final expression for the Hamiltonian matrix $H(\mathbf{k})$, which can be evaluated for initial values of charge and potential. Then the Schrödinger equation in matrix form

$$H(\mathbf{k})C(\mathbf{k}) = S(\mathbf{k})C(\mathbf{k})E(\mathbf{k}), \quad (9)$$

is solved adopting a procedure described in Marathe *et al* (1980) for every value of \mathbf{k} to get the diagonal matrix of energies, $E(\mathbf{k})$, and the matrix of the coefficients, $C(\mathbf{k})$, of the linear combination of Bloch sums. The $C(\mathbf{k})$ values are used to calculate the density matrices for different \mathbf{k} 's. Using the Mulliken population analysis and the integration over \mathbf{k} space, the new effective charges Q_A 's are calculated (Lauer *et al* 1984), which would change the Madelung as well as ionization potentials. The new ionization potentials are calculated using the relation (Lauer *et al* 1984)

$$P_a^I = P_{a0}^I + \Delta P_a^I Q_A, \quad (10)$$

where P_{a0}^I is the atomic valence ionization potential. The new set of P_a^I and P_A^M derived from new effective charges Q_A 's, give rise to a new $H_{ab}(\mathbf{k})$ and hence, equation (9) can be solved iteratively till self-consistency with respect to atomic charges is reached. It is important to note that the overlap integrals $S_{ij}(\mathbf{k})$ were not omitted in the solution of (9) as is usually done in the conventional tight-binding approximation.

2.2 Computational details

The crystal structure data for $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ were taken from Beno *et al* (1987) and Santoro *et al* (1987) respectively. The basis consisted of Slater-type

Table 1. Slater exponent ξ , ionization potential P_{a0}^I and the incremental ionization potential ΔP_a^I of the atomic orbitals of the basis considered in the CSCBS calculations. The potentials are in Hartree.

Atom	Orbital	ξ	P_{a0}^I	ΔP_a^I
O	2s	2.25	1.30433	0.53
	2p	2.25	0.63192	0.53
Cu	4s	1.80	0.23795	0.45
	4p	1.80	0.09395	0.45
	3d	3.57	0.49074	0.45
Y	5s	1.90	0.19233	0.38
	5p	1.90	0.08294	0.38
	4d	2.38	0.19375	0.38
Ba	6s	1.90	0.15624	0.32
	6p	1.90	0.07689	0.32

single zeta functions whose exponents ξ were taken from Hehre *et al* (1986). Values of ξ , P_{a0}^I and ΔP_a^I of all the orbitals used in the calculation are given in table 1. The basis consisted of 72 and 68 orbitals for YBa₂Cu₃O₇ and YBa₂Cu₃O₆ respectively. The P_{a0}^I were estimated from atomic HF calculations (Clementi and Roetti 1974) and their incremental values ΔP_a^I were parametrized. The Madelung potentials were calculated using the direct sum procedure (Marathe *et al* 1983). A uniform mesh of 125 k points in the first BZ was considered for energy dispersion. The convergence condition was that the average charge difference per atom between two consecutive iterations is less than 0.05 e.

The DOS is calculated using the equation

$$n(E) = \Omega/4\pi^3 \int_{FBZ} \sum_i \delta[E_i(\mathbf{k}) - E] d^3\mathbf{k} \quad (11)$$

where δ is Dirac's delta function. In the actual calculation we obtained $n(E)$ by replacing the δ function by a Gaussian:

$$\delta(E_i - E) \rightarrow \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(E_i - E)^2}{2\sigma^2}\right], \quad (12)$$

where σ is the half-width of the Gaussian which in the present calculations is taken to be 0.002 hartree. For overlaps, all the atom-pairs within a distance of 30 Å were considered.

3. Results and discussion

The calculated effective atomic charges for both 1:2:3 systems are listed in table 2. Despite the fact that these compounds are expected to be ionic in nature, in both cases we find that the charges are far from integral values. This can be attributed to covalency effects and the very nature of the partitioning of overlap charges under Mulliken population analysis. In the Mulliken population analysis, the overlap density arising due to orbitals on different atoms is divided equally between the atoms.

We present our results of copper and oxygen valence bands in terms of total and partial DOS as most of the spectroscopic data can be compared with it. In figure 2 the total as well as partial DOS due to Cu in YBa₂Cu₃O₇ are given. The DOS at the Fermi level is 9.3 states/eV cell. The bands due to O-2p and Cu-3d are mixed with each other and O has larger contribution near E_F . This has been observed experimentally by Johnson *et al* (1987). However, Kurtz *et al* (1987) and Onellion *et al* (1987) differ in this regard. The calculated DOS shows two predominant peaks separated by about 1.3 eV which is relatively small compared to the experimentally observed value of about 2 eV. From the calculated electronic bands we conclude that all the three Cu sites are energetically equivalent with effective valency of each Cu

Table 2. Effective atomic charges of atoms in YBa₂Cu₃O₇ and YBa₂Cu₃O₆.

	Y	Ba	Cu(1)	Cu(2)	O(2)	O(4)	O(1)
YBa ₂ Cu ₃ O ₇	2.08	1.75	1.47	1.47	-1.42	-1.44	-1.49
YBa ₂ Cu ₃ O ₆	2.23	1.72	0.95	1.51	-1.54	-1.75	-

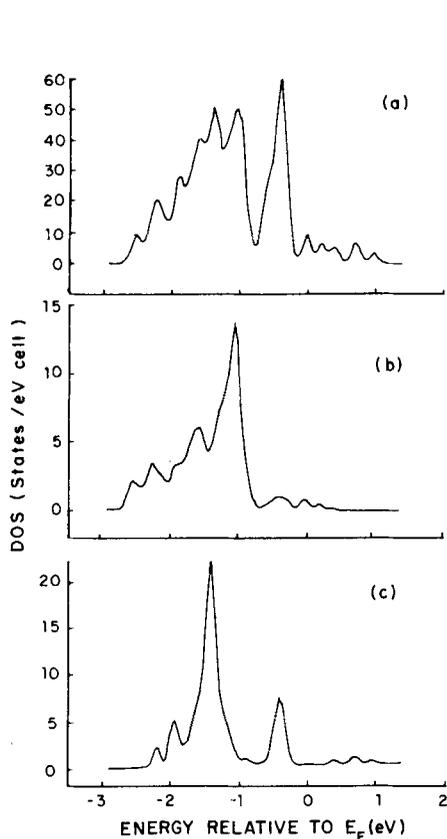


Figure 2. DOS picture of $\text{YBa}_2\text{Cu}_3\text{O}_7$ —(a) total DOS, (b) partial DOS of Cu(2) and (c) partial DOS of Cu(1).

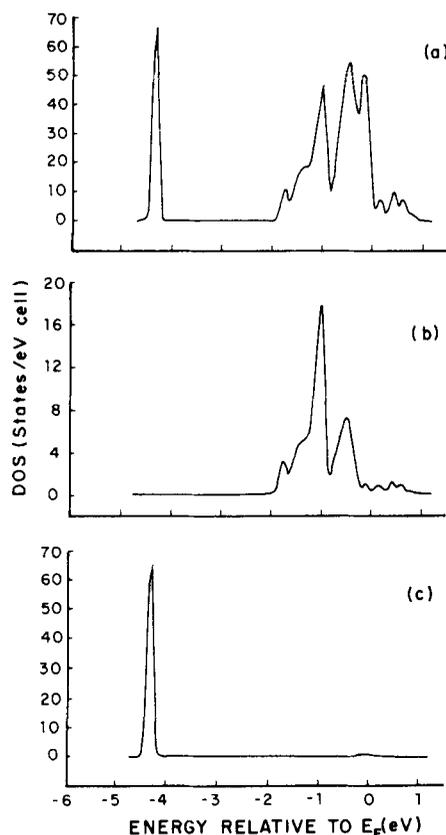


Figure 3. DOS picture of $\text{YBa}_2\text{Cu}_3\text{O}_6$ —(a) total DOS, (b) partial DOS of Cu(2) and (c) partial DOS of Cu(1).

as $7/3$ (or effective valency of each O as approximately $-13/7$). Therefore electron transport is favoured. This accounts for the (super)conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_7$.

A comparative study of the DOS of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ can give important information about the effect of oxygen stoichiometry on the electronic structure of oxygen-deficient perovskites. Our calculations on $\text{YBa}_2\text{Cu}_3\text{O}_6$ show that Cu(1) is monovalent whereas Cu(2)'s are divalent. The DOS results are presented in figure 3 in a manner similar to that of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The total DOS curve shows a gap of about 2.2 eV in the Cu(1)–O and Cu(2)–O valence bands in $\text{YBa}_2\text{Cu}_3\text{O}_6$. Its DOS at the Fermi level is about $7.2\text{ states/eV cell}$. Hence, $\text{YBa}_2\text{Cu}_3\text{O}_6$ consists of two Cu–O layers with a stable valency of copper as $+2$. These two layers are connected by a O–Cu(1)–O chain in which Cu(1) is monovalent with energy gap between Cu(1) and Cu(2) of 2.5 eV . There is no possibility of electron transport (hopping) mechanism favoured by energy considerations. Hence $\text{YBa}_2\text{Cu}_3\text{O}_6$ is an insulator. Experimentally, $\text{YBa}_2\text{Cu}_3\text{O}_6$ is an AF insulator. Stoffel *et al* (1987) studied the photoemission spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$, which has a tetragonal structure and concluded that Cu^{1+} is present in this compound. Both the compounds have a comparative value of DOS at the Fermi level but their conductivities differ drastically. Thus, our calculations clearly

indicate that the equivalent atoms with fractional valency is one of the necessary conditions for the observation of high(super)conductivity.

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