3.1 Cuprate superconductors and Zhang-Rice physics

High temperature superconductivity was first observed in 1986 by Bednorz and Müller in a layered copper-oxide perovskite $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($T_C \sim 30\text{K}$) [1]. Since then a lot of attention was paid to design such cuprate materials. This resulted into superconducting transition temperature increased from 30K to 138K [2]. Although majority of high $T_C$ superconductors are hole doped, experimental database for $n$ doped compounds also exists. $\text{Nd}_{2-x}\text{SrCe}_y\text{CuO}_4$, $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ belong to the class of electron doped superconductor [3]. The structure of such cuprate compounds (both hole-doped and electron-doped) contain infinite CuO$_2$ planes which are the most important structural sub-unit. Due to the crystal field of square planner site symmetry $D_{4h}$, degeneracy of the $5d$ levels of atomic Cu is lifted completely, resulting into high lying Cu : $d_{x^2-y^2}$ state with a large energy separation from the rest. Similarly, crystal field of $D_{2h}$ symmetry also removes the degeneracy of oxygen $p$ states [5]. As a result O : $p$ states get splitted into $\pi_\parallel$, $\pi_\perp$ and $\sigma$ levels as shown in Fig. 3.1 where both $\sigma$ and $\pi_\parallel$ are composed of in-plane oxygen orbitals $p(x,y)$ (see Fig. 3.2) and $\pi_\perp$ stands for $p(z)$. Such hybridized $pd\sigma$ states

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<table>
<thead>
<tr>
<th>Cu</th>
<th>Crystal field of D_{4h} symmetry</th>
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<table>
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<tr>
<th>O</th>
<th>Crystal field of D_{2h} symmetry</th>
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<td>$\pi$</td>
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Figure 3.1: Crystal field splitting of Cu: d and O: p states and their covalent bonding as suggested by Damascelli et al. [5]. Strong hybridization between Cu: $d_{x^2-y^2}$ and O: $p_\sigma$ results bonding ($\sigma$) and anti-bonding ($\sigma^*$) bands.

<table>
<thead>
<tr>
<th>P_x</th>
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<td>$\sigma$</td>
<td>$\pi$</td>
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Figure 3.2: $\sigma$ (cyan) and $\pi$ (red) bonding in CuO$_4$ plane resulting from the orbital hybridization between Cu: $d_{x^2-y^2}$ (black) and O: $p_{x,y}$ (gray).

will produce broad bonding ($\sigma$) and antibonding ($\sigma^*$) bands as shown in Fig. 3.2, 3.3. Small mixing of $\sigma$ states of oxygen and Cu: $d_{3z^2-r^2}$ will produce narrow nonbonding band which has small contribution in the conductivity of cuprate superconductor [3]. Due to existence of large onsite Coulomb repulsion Cu: $d_{x^2-y^2}$ splits into two subgroups: upper Hubbard band (UHB) and lower Hubbard band (LHB) [4]. In the undoped case, valance band is formed by hybridized bonding $p$-$d$ band, mainly of O: $2p$ character. Empty con-
3.1. CUPRATE SUPERCONDUCTORS AND ZHANG-RICE PHYSICS

Figure 3.3: Different orbital hybridization (bonding phases) between Cu: \( d_{x^2-y^2} \) and O: \( p \) (a) bonding (b) anti-bonding (c) non-bonding. Phases of atomic wave-functions are separated by different colours. Adopted from [5].

Conduction band (UHB) consist of hybridized antibonding \( p-d \) states, primarily of Cu: \( d_{x^2-y^2} \) character. Valance and conduction bands are separated by charge transfer gap \( \Delta = \varepsilon_d - \varepsilon_p \) (see Fig. 3.4). As \( \Delta < U \), undoped cuprates are charge transfer insulators with half filled bands i.e. one hole per Cu site. Holes mainly occupy Cu: \( d_{x^2-y^2} \) state and interact with each other via superexchange [4–6].

Figure 3.4: Illustration of the \( p-d \) model with three bands, bonding (B), anti-bonding (AB) and non-bonding (NB). (a) metallic state for half filled AB band with \( U = 0 \) (b) \( \Delta > U > W \) (band width of \( p-d \) hybridized states) results the Mott Hubbard insulator (c) charge-transfer insulator for \( U > \Delta > W \). (d) Zhang-Rice singlet-triplet splitting. As a result of hole doping NB band splits into two subgroups: Zhang-Rice triplet (T) and singlet (ZRS) state. Doping of electron (hole) places \( \varepsilon_F \) at UHB (ZRS) (not shown in figure). \( \varepsilon_p \) and \( \varepsilon_d \) stand for band centers of 3\( d \) and 2\( p \) bands respectively. Reproduced from [5].

\( p-d \) model with 3 bands, Cu: \( d_{x^2-y^2} \), O: \( p_{x,y} \) shows formation of bands with different bonding characteristic in the CuO\(_2\) plane which is evident from Fig. 3.3, 3.4. In this context, three-band Hubbard model will lead to three different ground state (a) metallic
3.2. MOVTION BEHIND THE PROJECT

state of antibonding type for \( U = 0 \), (b) Mott-Hubbard insulator for \( \Delta > U > W \) (band width) and (c) charge transfer insulator for \( U > \Delta > W \) as shown in Fig. 3.4. Hole doping results new states for \( O : 2p \) types hole at the top of valance band while for electron doping introduces \( 3d_{x^2−y^2} \) types of electrons at the bottom of conduction band [7]. Therefore,

![Figure 3.5: Typical Zhang-Rice spin singlet state: \( pd\sigma \) antibonding between \( Cu : d_{x^2−y^2} \) and \( O : p(x,y) \). Doped holes at the \( pd\sigma \) hybridized states of \( O : p(x,y) \) couple antiferromagnetically with the hole at \( Cu : d_{x^2−y^2} \) band.](image)

the cuprate superconductors can be mapped onto an effective single band Hubbard model considering only \( Cu : d_{x^2−y^2} \) and \( O : p(x,y) \) hybridized orbital. In terms of a single band approach, Zhang-Rice described a simplified picture of the three band \( p\cdot d \) model [8–17]. They argued that doped hole at \( O \) site is antiferromagnetically coupled with the holes at \( Cu \) site (see Fig. 3.5). As a result of such mixing, \( Cu \) valency changes to \( d_{n+1}L \) (\( L \) denotes a ligand (oxygen) hole).† In addition to this, anti-symmetry of their wavefunction in spin coordinates suggests that in hole doped superconductors, any carrier excitation originates from this \( pd\sigma \) antibonding type spin singlet state.

3.2 Motivation behind the project

With a motivation to synthesis new compounds with square planar coordination of \( Cu \), recent high pressure synthesis was carried out [18]. This resulted into a new type of perovskite

\[ \text{total spin remains the same as that of } d^n \text{ configuration.} \]

†In absence of any \( p \)-hole at the transition-metal site, configuration of the undoped compounds with \( n \) numbers of \( d \) electrons takes the form of \( d^n p^6 \). In presence of the hole at the oxygen site, the configuration \( d^n p^6 \) breaks down and we have \( d^{n+1}p^5 = d^{n+1}L \). The interaction of the \( p \)-hole and transition-metal ion takes place in such a way that the quantum numbers remain conserved \( ie. \) total spin remains the same as that of \( d^n \) configuration.
structure which also shows such CuO$_4$ planes like the high $T_C$ cuprate superconductors. General composition of such oxide materials are given by AA$'$_3B$_4$O$_{12}$. Both A$'$ and B sites can in general, be occupied by transition metal ions. In the present study we will focus on compounds where the A$'$ site is occupied by copper. Experimental measurements on CaCu$_3$Co$_4$O$_{12}$ suggest that this compounds also shows Zhang-Rice like spin singlet state, despite the lack of superconducting ground state [19]. In this chapter we study the electronic properties of this compound intensively. For comparison, we also consider another isostructural compound, CaCu$_3$Cr$_4$O$_{12}$.

### 3.3 Computational Details

The DFT calculations were performed by using the plane wave basis set and pseudo-potentials scheme as implemented in the Vienna *Ab initio* Simulation Package (VASP) [25]. Electron-electron correlation was treated under the generalized gradient approximation (GGA) as suggested by Perdew-Burke-Ernzerhof [26]. Missing correlation beyond GGA was taken into account by means of GGA+U approach in a static mean-field way as implemented by Dudarev *et al.* [22] For the plane wave based calculations, we used projector augmented wave (PAW) potentials [23]. Wave functions were expanded in the plane wave basis set with a kinetic energy cutoff of 600 eV and Brillouin zone summations were carried out with a $6 \times 6 \times 6$ k-mesh. The U value of 5 eV on Cu site and 4 eV on B site were used for GGA+U calculations while the Hund’s rule coupling $J$ was fixed to 0.8 eV. The obtained results were further verified in terms of variation of U parameter. In order to determine the energy positions of the Cu-d, B-d and O-p levels as well as to generate the effective Wannier functions for Cu-d states, we used muffin-tin orbital (MTO) based N-th order MTO (NMTO)-downfolding [24] technique. Starting from a DFT calculations, NMTO-downfolding results at a few-orbital Hamiltonian by integrating out degrees (orbitals) which are not of interest. Our results were verified among the plane wave and LMTO [25] calculations in terms of total energy differences and related electronic properties, like density of states and band structures. All our theoretical results were further verified by experimental resonant soft x-ray absorption spectroscopy.
3.4 Results and Discussions

In order to study the microscopic electronic properties of A-site ordered quadruple perovskite \( \text{CaCu}_3\text{Co}_4\text{O}_{12} \) (\(\text{CCCOO}\)) and \( \text{CaCu}_3\text{Cr}_4\text{O}_{12} \) (\(\text{CCCrO}\)), first we have to understand their structural properties.

### 3.4.1 Crystal Structure

\( \text{AA}^2\text{B}_4\text{O}_{12} \) crystallizes in body centered cubic structure given by space group group symmetry \( \text{Im}\overline{3} \) (space group number 204). \( \text{B} \) ions sit within octahedral cage formed by the oxygen ions while \( \text{Cu}-\text{O} \) forms square planner geometry (see Fig. 3.6). \( \text{BO}_6 \) octahedra are corner shared type. Each oxygen is shared in-between two \( \text{B} \) ions and a copper ion. In this present study, \( \text{BO}_6 \) and \( \text{CuO}_4 \) polyhedra in both \( \text{CCCOO} \) and \( \text{CCCrO} \) show “trigonal” distortion which results a small deviation in \( \text{O}-\text{B}-\text{O} \) bond angle from 90°. We have used optimized structural parameters for our theoretical purpose. Optimization of atomic positions were carried out keeping the lattice parameters same as obtained in the experiment. Comparison of the optimized and experimental structures of both \( \text{CCCOO} \) and \( \text{CCCrO} \) are shown in Table 3.1, 3.2. Theoretically optimized structures show good agreement with the experimental measurements. In the following, we present the calculated electronic structure of the two compounds.

### 3.4.2 Electronic Structure

In order to assign the spin and valance states of different components correctly, one needs to carry out spin-polarized calculations even through the compound may not be ordered magnetically. Figure 3.7 shows the spin polarized density of states and band structure of \( \text{CaCu}_3\text{B}_4\text{O}_{12} \) (\( \text{B} = \text{Cr}, \text{Co} \)). Due to octahedral crystal field, five degenerate \( \text{B} : d \) states are splitted into two subgroups: triply degenerate \( t_{2g} \) states and doubly degenerate \( e^\pi_g \) states. Further due to trigonal distortion, three fold degeneracy of the \( t_{2g} \) states are removed partially, giving rise to singly degenerate \( a_{1g} \) and doubly degenerate \( e^\sigma_g \) states. Square planer crystal field also introduces splitting within the energy level positions of \( \text{Cu} : d \) states, which results into high lying \( \text{Cu} : d_{x^2-y^2} \) state with large energy separation from
3.4. RESULTS AND DISCUSSIONS

Table 3.1: Wyckoff Positions of Ca, Cu, B (=Cr, Co) and O in CaCu$_3$B$_4$O$_{12}$ (B=Cr, Co). For, CCCrO, theoretically optimized (experimental) values of x, y i.e. the free position parameters of oxygen become 0.3017 (0.3056) and 0.1825 (0.1797), while optimized (experimental) values of x, y in CCCoO become 0.3069 (0.3076) and 0.1773 (0.1765).

<table>
<thead>
<tr>
<th>Site</th>
<th>Symmetry</th>
<th>Multiplicity</th>
<th>Wyckoff letter</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>m$^3$</td>
<td>2</td>
<td>a</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>Cu</td>
<td>mmm</td>
<td>6</td>
<td>b</td>
<td>(0, 1/2, 1/2) (1/2, 0, 1/2), (1/2, 1/2, 0)</td>
</tr>
<tr>
<td>B</td>
<td>$\bar{3}$</td>
<td>8</td>
<td>c</td>
<td>(1/4, 1/4, 1/4) (3/4, 3/4, 1/4) (1/4, 3/4, 3/4) (3/4, 1/4, 3/4)</td>
</tr>
<tr>
<td>O</td>
<td>m</td>
<td>24</td>
<td>g</td>
<td>(x, y, 0) (x, -y, 0) (-x, y, 0) (-x, -y, 0) (x, 0, y) (x, 0, -y) (-x, 0, y) (-x, 0, -y)</td>
</tr>
</tbody>
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Table 3.2: Optimized lattice constants and selected bond-lengths and angles of CaCu$_3$B$_4$O$_{12}$ (B=Cr, Co) with the corresponding experimentally measured values within the parentheses.

<table>
<thead>
<tr>
<th></th>
<th>CCCrO</th>
<th>CCCoO</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-B bond-length (Å)</td>
<td>3.642 (3.627)</td>
<td>3.598 (3.561)</td>
</tr>
<tr>
<td>B-O bond-length (Å)</td>
<td>1.923 (1.926)</td>
<td>1.918 (1.901)</td>
</tr>
<tr>
<td>Cu-O bond-length (Å)</td>
<td>1.963 (1.921)</td>
<td>1.887 (1.860)</td>
</tr>
<tr>
<td>$\angle$ B-O-B$^\circ$</td>
<td>142.5 (140.6)</td>
<td>139.5 (139.0)</td>
</tr>
<tr>
<td>$\angle$ O-B-O $^{(90\pm\delta)}$, $\delta$ =</td>
<td>0.38 (0.16)</td>
<td>0.1 (0.2)</td>
</tr>
<tr>
<td>$\angle$ O-Cu-O $^{(90\pm\delta)}$, $\delta$ =</td>
<td>4.76 (4.52)</td>
<td>4.9 (4.9)</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>7.284 (7.253)</td>
<td>7.197 (7.123)</td>
</tr>
</tbody>
</table>

the rest of the states. From Figure 3.7, strong mixing among Cu : $d$, B : $d$ (B= Cr, Co) and O : $p$ states can be noticed near the Fermi energy ($\epsilon_F$). Such a strong mixing results into metallic ground state, in agreement with the experimental observations. Considering Cu : $d$ states, we can see that Cu : $d_{x^2-y^2}$ in CCCrO is occupied in majority spin channel, while it is empty in minority spin channel, suggesting Cu$^{2+}$ like oxidation state. Cu :
3.4. RESULTS AND DISCUSSIONS

Figure 3.6: Structural building blocks of CCCrO. (a) Crystal structure of CCCrO. (b) CrO$_6$ octahedra are corner sharing type. (c) All 3 Cu ions form CuO$_4$ square planner network parallel to Cartesian $xy$, $yz$, $zx$ planes. (d) Every oxygen ion is shared in-between two B ions and a Cu ion.

$d_{x^2-y^2}$ in CCCoO compound is empty in either spin channel suggesting metastable Cu$^{3+}$ like behavior. Unoccupied Cu : $d_{x^2-y^2}$ results $\sim 0.07 \mu_B$ moment at Cu site in CCCoO, while single unpaired electron at Cu : $d_{x^2-y^2}$ in CCCrO results in 0.5 $\mu_B$ spin moment.

Considering Cr : $d$ states from Figure 3.7, we can see that only occupied states are $e^\pi_g$ in the minority spin channel resulting low spin configuration of Cr in CCCrO. Two occupied $e^\pi_g$ electrons give rise to 2.2 $\mu_B$ moment at Cr site. Applying similar type of analysis, we can conclude that Co shows intermediate spin configuration resulting from $\sim 1.7 \mu_B$ spin
3.4. RESULTS AND DISCUSSIONS

Figure 3.7: Spin polarized density of states and band structure for CCCrO (left panel) and CCCoO (right panel). Black and red line corresponds to B : $t_{2g}$ and B : $e_g$ states respectively. Cu : $d$ and O : $p$ are shown by green and blue colour. Number of bands correspond to an orbital, have been shown by the digit within the parenthesis. Top and bottom panel stands for majority and minority spin channels. Zero energy represents Fermi energy.

moment. Considering nominal valance of Ca and O as $2^+$ and $2^-$, we get nominal valance of Cr and Co as $4^+$ and $3.25^+$ respectively i.e. d electron occupancy for Cr and Co becomes 2 and 5.75 respectively.

In order to determine the precise energy level positions of B : $d$, Cu : $d$ and O : $p$ states, NMTO downfolding calculations are performed considering B : $d$, Cu : $d$ and O : $p$ states
3.4. RESULTS AND DISCUSSIONS

Figure 3.8: Crystal field splitting of B: d (red line), Cu: d (black line) and O: p (green line) states. High T_c cuprate like almost degenerate Cu: d and O: p energy levels can be noticed for either perovskite. Energy is measured with respect to the Cu: d_{x^2−y^2} state of CCCrO compound.

as active and downfolding rest orbitals. From the energy-level position in Fig. 3.8, we can

Figure 3.9: Effective Cu: d_{x^2−y^2} Wannier function plot for (a) CCCrO and (b) CCCoO. For a selective isosurface, lobs with different sign have been shown by different colours.

see that Cu: d states are nearly degenerate with oxygen: p orbitals leading to a situation
very similar to that in high $T_C$ cuprates. Such hybridized states further interact with B : $d$ states which is evident from Fig. 3.7. The formation of such a mixed state is also evident in the Wannier function plot of an effective Cu : $d_{x^2-y^2}$ Wannier function obtained by keeping only Cu : $d_{x^2-y^2}$ state active and downfolding or integrating out all the other degrees of freedom (see Fig. 3.9). As clearly seen, the Wannier functions centred at the Cu site have the orbital character of $d_{x^2-y^2}$ symmetry, and the tail is shaped according to the symmetry of the orbitals mixed with it. Both compounds show strong $pd\sigma$ antibonding (see Fig. 3.3) state formed between Cu : $d_{x^2-y^2}$ and O : $(p_x, p_y)$ which further bind to B : $d$ states. For CCCoO, such $pd\sigma$ antibonding states will interact with empty Co : $e_g$ band while Cr : $t_{2g}$ will bind to Cu : $d_{x^2-y^2}$ and O : $p_\sigma$ antibonding orbitals. Mixing of $pd\sigma$ antibonding orbitals with B : $d$ states is found to be less for CCCrO. Such typical $pd\sigma$ antibonding states, degenerate O : $p$- Cu : $d$ levels and finite moment at O-site (0.08 $(0.20) \mu_B$ for CCCo(Cr)O ) bear “Zhang-Rice” like signature similar to the hole doped cuprate superconductors. All our theoretical results are further experimentally verified, as discussed in the following section.

3.4.3 Experimental Observation

Resonant soft x-ray absorption spectroscopy (XAS) is an ideal tool to investigate the microscopic electronic structure of materials [10,14–16,26–28]. Results of soft XAS measurements on the Cu L$_{3,2}$- and O K edges are summarized in Figure 3.10 for CaCu$_3$B$_4$O$_{12}$ (B= Cr, Co) along with LaCuO$_3$ (LCO) and optimally doped superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO). YBCO and LCO are recalled as the standard references for Cu$^{2+}$ and Cu$^{3+}$ oxidation states respectively. We will discuss the CCCrO compound first. From the absorption line shape of Cr compound, the sharp peak $\sim$ 930 eV corresponds to the transition from ground state $d^9$ to $d^{10}$ ($\zeta$ denotes a core hole) excited $d$ state. This transition introduces a single hole in the Cu $d_{x^2-y^2}$ band. Shoulder seen at 931.5 eV [29,30], a direct signature of ZR singlet state, is transition from the ground state $d^{10}L$ to the $\zeta d^{10}L$ excited state [10,13,15,27,28]. In both transitions Cu remains nearly at 2+ oxidation state, while in the latter case a ligand hole is distributed over neighbouring oxygen ions as shown in Fig. 3.5. Cu L edge spectrum of CCCrO shows excellent similarities with that of YBCO,
Figure 3.10: Left panel shows the XAS measurements on Cu $L_{3,2}$-edge for both CCCrO and CCCoO. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) and LaCuO$_3$ (LCO) are considered for standard reference for Cu$^{2+}$ and Cu$^{3+}$ oxidation states. Right panel shows O-K edge XAS results. Prepeak $\sim$ 528 eV bears the signature of ZR state.

starting from initial $d^9$ state followed by ZR shoulder. Similarly it can be seen very easily that the ZR spin singlet state has the dominant contribution to the ground state for both Co and LCO. Absorption line of CCCoO is shifted $\sim$ 1 eV away from the $d^9$ line which is evident for Cu$^{3+}$ like state. A three peak fit is used for the $L_3$ data of CCCoO which are centered at 929 eV (impurity peak) [31], 930 eV ($d^9$) and 931.4 eV ($d^9L$). This impurity peak is subtracted from the original data which is represented by dotted line in Fig. 3.10. Multiple split peak observed $\sim$ 940 eV corresponds to transition from meta-stable $3d^8$ state to excited $cd^9$ state. Such ionic Cu$^{3+}$ state is completely absent for YBCO. As seen from O-K edge spectra, prepeak $\sim$ 528 eV shows direct signature of ZR state, which is evident from the comparison with YBCO [14–16, 26].
3.5 Conclusion

Applying first principles GGA+U calculations we have studied two A site ordered perovskite oxides CaCu$_3$B$_4$O$_{12}$ (B = Cr, Co). Our calculations reveal that choice of B site cation is an effective tool to manipulate the degree of B-O-Cu hybridization. For CCCoO, Cu shows metastable 3$d^8$ ($d^9$ $L$) like behavior, while substitution of Co by Cr results into stable ionic Cu$^{2+}$ state. Analysis of energy level position and Wannier function calculations support the direct experimental observation that Zhang-Rice like state present in both compounds, despite the lack of the superconducting ground state. Our findings further demonstrate that the charge and spin state of Cu, fundamental to the intriguing physical properties the cuprates display, can be effectively controlled by a suitable choice of the B-site cation on isomorphic lattices that circumvent the chemical disorder and lattice modulation intrinsic to other doping methods.


