

The Role of Oxygen for Expressing Superconductivity in La-Ca-Cu-O Compounds

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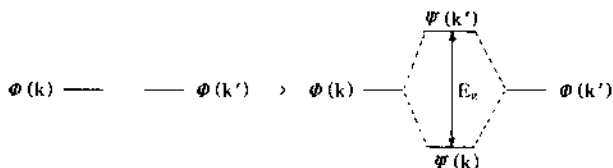
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Two $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6-\delta}$ (2126) compounds exhibited different properties depending upon how they were synthesized. The compound prepared under high oxygen pressure showed superconductivity. But the compound prepared under low oxygen pressure did not exhibit superconductivity, and showed a metal-insulator transition. Our study on these compounds shows that a small amount of additional oxygen intercalated into the superconducting phase plays an important role for superconductivity. The Fermi surface of non-superconducting 2126 compound possesses nesting phenomena, which is the reason for the M-I transition. On the other hand, the superconducting 2126 compound does not show Fermi surface nesting. This is because the additional oxygen removes some electrons from Cu d-orbitals, thereby bradking the Fermi surface nesting.

Introduction

After the discovery of superconductivity in strontium-doped lanthanum copper oxides,¹ a flood of analogues have been synthesized.²⁻⁹ The pristine lanthanum copper oxides do not show superconductivity but exhibit metal-insulator (M-I) transition.^{8,10} Fermi surfaces of these compounds are well nested, which is believed to be responsible for the M-I transition. Why the nested Fermi surface leads to an M-I transition has been an interesting subject for many scientists. Around the Fermi surface of a metal, by definition, the energy difference between occupied and unoccupied regions is very small. If a Fermi surface is nested, the strong interaction between occupied and unoccupied orbitals occurs in the whole nested region to form new sets of orbitals (see 1). Thus, an energy gap appears between new occupied and unoccupied orbitals, which means the metal becomes an insulator. Superconductivity arises only when the M-I transition is avoided. For a metal, therefore, its Fermi surface should not be nested to become a superconductor.

Two methods are well known in copper oxides to destroy the Fermi surface nesting by increasing the number of holes in the valence bands (*i.e.*, d-orbital of copper); cation substitution by divalent Sr or Ca for trivalent La and the insertion of additional oxygen into the compounds.



E_g ; band gap

k ; occupied wave vector

k' ; unoccupied wave vector

Weakly superconducting $\text{La}_2\text{CaCu}_2\text{O}_{6.04}$ [hereafter we denote this as 2126 compound], which is not doped with Sr, has been recently synthesized and investigated using neutron powder diffraction.¹¹ However, it has been found that 2126 compounds do not exhibit superconductivity if they are syn-

thesized in air or in 1-atm O_2 . This means the oxygen content is critical in the 2126 compound to be a superconductor. Because of the difficulty in controlling the oxygen content, a satisfactory superconducting 2126 phase had not been prepared for a time though special attention has been given to oxygen stoichiometry.

Kinoshita *et al.*¹² succeeded to synthesize two different 2126 compounds under different reaction conditions; non-superconducting $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_6$ was prepared under 2-atm of flowing oxygen and superconducting $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6-\delta}$ was synthesized by sintering the already prepared non-superconducting compound under 20% O_2 · 80% Ar at a total pressure of 2000 atm. The structures of both compounds were refined with time of flight (TOF) neutron powder diffraction. Superconducting and non-superconducting 2126 compounds were very similar in structure, but not in oxygen content. A small amount of additional oxygen was intercalated into superconducting phase which is believed to play an important role for superconductivity.

In the present paper, we examine the difference in electronic structures of superconducting and non-superconducting phases in terms of the band dispersions and associated Fermi surfaces by adopting the tight binding band calculation¹³ based on extended Hückel method.¹⁴

Structures of $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_6$

The structures of 2126 compounds were refined from the TOF neutron diffraction data. The materials exhibit $I4/mmm$ space group which consists of corner-sharing CuO_5 pyramidal planes and cations between the CuO_5 pyramids (See Figure 1). As shown in Figures 1 and 2, a CuO_5 slab faces another CuO_5 pyramid to form a CuO_5 - CuO_5 pair along the c-direction. In a unit cell there are two alternating CuO_5 - CuO_5 pairs. When no additional oxygen is intercalated, all environments around these two pairs are exactly the same. The bond distances between Cu and O in the CuO_5 pyramid are 2.31 and 1.91 for axial and equatorial Cu-O, respectively. Hereafter the equatorial oxygen in CuO_5 pyramid is denoted by O(1) and the axial one by O(2).

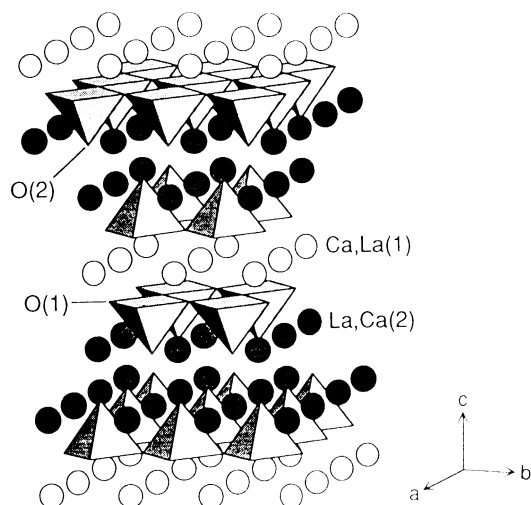


Figure 1. Crystal structure of $\text{La}_{2-x}\text{Ca}_{1-x}\text{Cu}_2\text{O}_6$. The CuO_5 blocks are expressed by pyramidal shape.

In the superconducting phase, additional oxygen [this is denoted by O(3)] intercalates between CuO_5 slabs [this is denoted by O(3)] to form distorted CuO_6 octahedra (*i.e.*, $\text{CuO}_5\text{-O-CuO}_5$, See Figure 2), although its occupancy is low. When oxygen intercalates into only one $\text{CuO}_5\text{-CuO}_5$ pyramidal to form a corner sharing octahedron pair, two $\text{CuO}_5\text{-CuO}_5$ pairs in a unit cell are not same anymore. Thus, two Cu form CuO_6 units and the other two form CuO_5 in a unit cell. According to the neutron diffraction data, the additional oxygen can be found in both $\text{CuO}_5\text{-CuO}_5$ pairs. Since the occupancy of the additional oxygen is not 100%, the insertion of oxygen can take place into one $\text{CuO}_5\text{-CuO}_5$ pair or into the other pair or into both pairs in a unit cell. In addition, these probable structures may not continue in the next unit cell (*i.e.*, the structure may become incommensurate). Thus, the insertion of oxygen with low occupancy can produce hundreds of possible structures.

The bond length between Cu-O(3) is 1.65 Å which is short compared with the regular axial Cu-O distances. However, this interstitial oxygen is not shown in the non-superconducting phase.

Results and Discussion

As mentioned in the previous section, there are hundreds of possible structures when oxygen is inserted. Since the main question to investigate in this study is how and to what extent the insertion of oxygen changes the electronic structure of the 2126 compound, especially the shape of the Fermi surface of this material, two simple structures are adopted for the band calculations; only one oxygen is inserted into a $\text{CuO}_5\text{-CuO}_5$ pair or two oxygen atoms are added into both $\text{CuO}_5\text{-CuO}_5$ pairs in a unit cell. In addition, the oxygen-inserted unit cell structures are extended continuously.

The band dispersion near the Fermi energy which is mainly contributed by the Cu d-orbital, is illustrated in Fig-

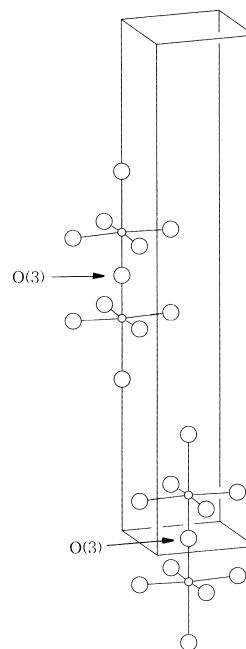


Figure 2. The $\text{CuO}_5\text{-CuO}_5$ pairs and inserted oxygen forming $\text{CuO}_5\text{-O-CuO}_5$ in a unit cell.

ure 3. These bands are obtained from the structure of the non-superconducting 2126 phase [Figure 3a], the superconducting 2126 phase with one additional oxygen atom [Figure 3b], and the superconducting phase with two additional oxygen atoms in a unit cell at room temperature. It is clear from the band dispersions that the orbital interactions are large along the x- and y-directions but zero along the z-direction which means that the compound is a 2-dimensional metal at room temperature. This result is consistent with the experiments. Since its structure is tetragonal the interactions along the x- and y-directions are the same. The shape of the valence band is similar to those of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$,¹⁵ Bi series,¹⁶ and Tl series¹⁷ superconductors. In Figure 3a, the valence band is quadruply degenerated because there are four environmentally identical CuO_5 slabs in a unit cell. But the band dispersion calculated for the superconducting 2126 phase with one interstitial oxygen (See Figure 2) per unit cell is different from that in Figure 3a. Quadruply degenerated bands are split into two different doubly degenerated bands which represent the Cu d-orbitals in the $[\text{CuO}_5\text{-O-CuO}_5]$ and $[\text{CuO}_5\text{-CuO}_5]$ pairs. When an additional oxygen is inserted, the Fermi energy is lowered from -11.51 eV to -11.54 eV. Consequently, the occupied region of the top portion of the valence bands decreases. Since the valence band of the superconducting 2126 phase without O(3) is almost similar to that shown in Figure 3(a), it is not illustrated. Fermi energy is further lowered if oxygen is intercalated into two $[\text{CuO}_5\text{-CuO}_5]$ pairs, and the unoccupied region becomes larger as shown in Figure 3c. Since the orbital interactions in $\text{CuO}_5\text{-O-CuO}_5$ are larger than that in $\text{CuO}_5\text{-CuO}_5$, the valence band is more dispersive.

Fermi surfaces associated with the top portion of the valence bands in Figures 3a, 3b, and 3c are shown in Figure

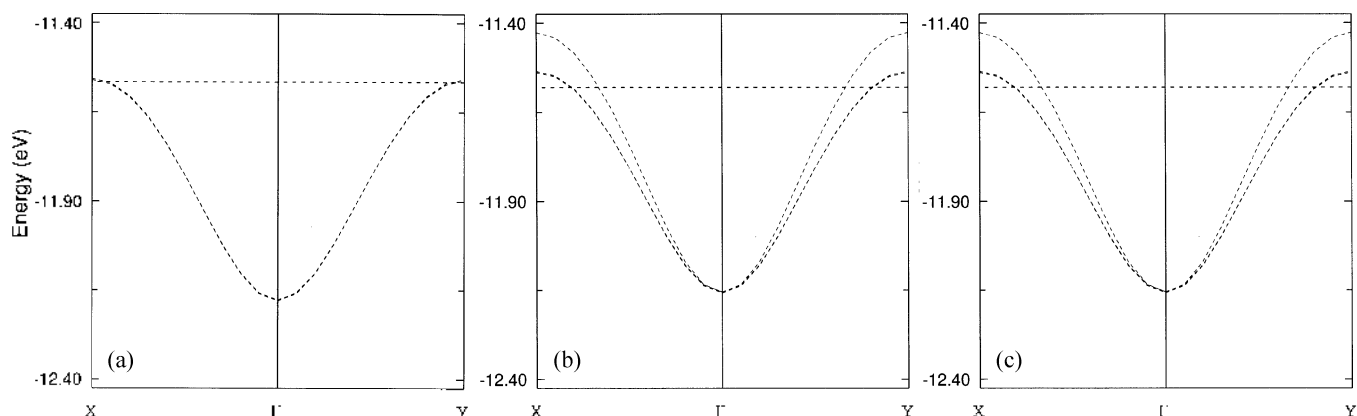


Figure 3. The band dispersion near the Fermi energy obtained from the structure of (a) the non-superconducting 2126 phase, (b) the superconducting 2126 phase with one additional oxygen, and (c) the superconducting phase with two additional oxygen atoms in a unit cell at room temperature.

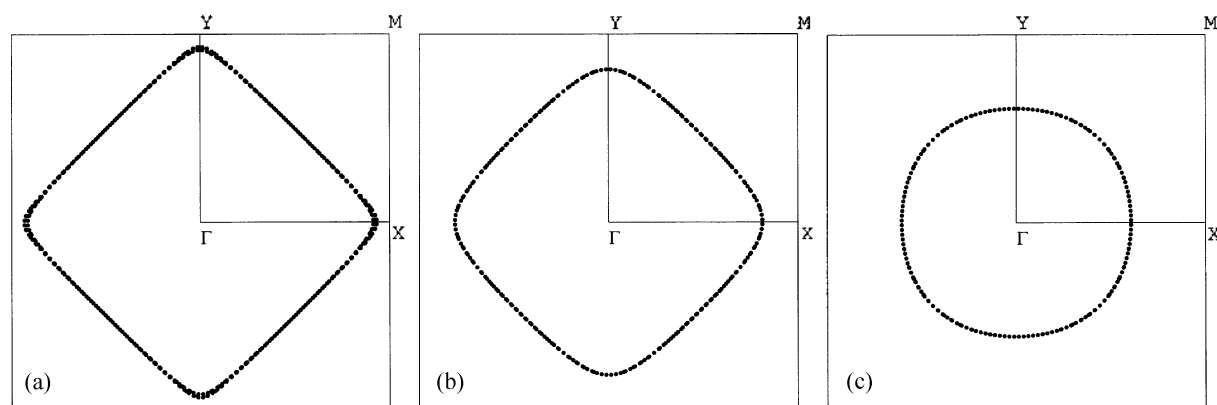


Figure 4. Fermi surfaces associated with the top portion of the valence bands in (a) Figure 3a, (b) Figure 3b, (c) Figure 3c, respectively.

4a, 4b, and 4c, respectively. The Fermi surfaces in Figures 4a, 4b, and 4c clearly illustrate that these compounds are 2-dimensional metals at room temperature. However, the shape of the Fermi surface of the non-superconducting compound is round-cornered square. This means the Fermi surface is well nested. Thus, this compound is expected to exhibit a metal-insulator transition. This is evidenced from the experiments in which the non-superconducting compound shows metal to insulator transition at ~ 50 K¹². (See Figure 5)

For a metal to become superconducting, it should avoid the electronic instability toward a metal-insulator transition caused by the nested Fermi surface. For the 2126 compound, the nested Fermi surface can be collapsed by subtracting the electrons from the Cu d-orbitals. The additional oxygen in superconducting 2126 compound acts as an electron withdrawer, thereby increasing the oxidation state of copper. Thus, the size of the occupied region in the First Brillouin Zone (FBZ) decreases and the Fermi surface becomes round shape [see Figure 4(b)] which is not nested. The intercalation of more oxygen, therefore, provides smaller occupied regions in the Fermi surface and the shape of the Fermi surface becomes more circular, as shown in Figure 4c. As mentioned earlier, the oxygen intercalation can take place in many ways. The results shown in this paper

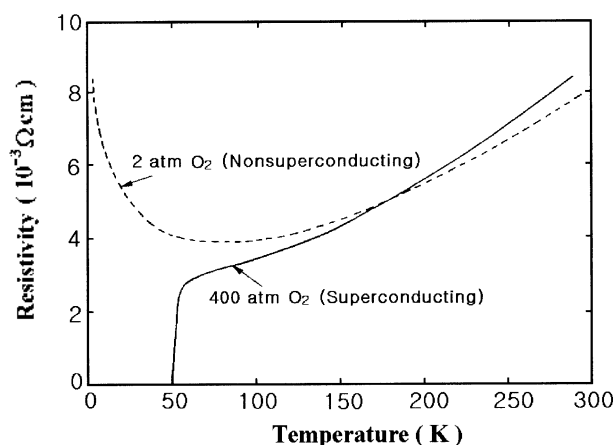


Figure 5. Electrical resistivity vs temperature for superconducting and non-superconducting $\text{La}_{1.85}\text{Ca}_{1.13}\text{Cu}_2\text{O}_6$.

is the simplest case that the only one oxygen intercalates into the CuO_5 - CuO_5 pair in every unit cell. The real structure would be an average of total possible structures with the probable occupancy of O(3). However, it is clear that the additional oxygen can take some electrons out of copper d-orbitals which results in the non-nested Fermi surface. Consequently, the additional oxygen plays an important role for the 2126 compound to become a superconductor.

Conclusions

Two $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6-\delta}$ compounds exhibited different properties depending upon how each was synthesized: showing superconductivity if prepared under high oxygen pressure, but no superconductivity if prepared under low oxygen pressure. Electronic structure study of these materials can provide appropriate reasons for the difference in their properties. The shape of the Fermi surface of the non-superconducting compound is round-cornered square which means the Fermi surface is well nested. Thus, the compound is expected to exhibit a metal-insulator transition. This is supported by the experiments that the non-superconducting compound shows metal to insulator transition at ~ 50 K. When some amount of oxygen is added, on the other hand, the compound becomes superconducting and does not show Fermi surface nesting. This is because the additional oxygen removes some electrons from Cu d-orbitals thereby breaking the Fermi surface nesting. Consequently, the additional oxygen plays an important role for the 2126 compound to become a superconductor.

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