The fixed triangle chemical bond and its effect in the \( Y_{1-x}Ca_xBa_{2-y}La_yCu_3O_z \) system from underdoped to overdoped

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Abstract. Samples of \( Y_{1-x}Ca_xBa_{2-y}La_yCu_3O_z \) (YCBLCO) were synthesized by the standard solid-state reaction with both \( x \) and \( y \) taking values from 0 to 0.5. Structural and superconducting properties have been investigated by x-ray diffraction, Rietveld refinement and dc magnetization measurement. The three-dimensional phase diagram in the YCBLCO system is obtained, describing the dependence of \( T_c \) on the content of two dopants simultaneously. By careful study of the chemical bond lengths related to the Cu(2)O\(_2\) plane and the Cu(1)–O chain, it is found that \( T_c \) has opposite dependences on the bond lengths of Cu(1)–O(4) or Cu(2)–O(4) in the underdoped (\( x < y \)) and overdoped (\( x > y \)) regions. In addition, calculation of the bond angles for the optimal-doped samples indicates that \( T_c \) is closely related to four pairs of bond angles, all of which characterize the curvature of the CuO\(_2\) plane. It is demonstrated that the interaction between the perovskite block and the rock salt block in a unit cell has a close relationship with the superconductivity. The calculation of bond lengths and angles indicates that Cu(2), O(2) and O(3) on the CuO\(_2\) plane form a ‘fixed triangle’, independent of the doping level in the system. It is suggested that the collective behavior of the fixed angle might result in a particular phonon mode, which may induce a special kind of electron–phonon coupling, different from that appearing in conventional superconductors. This may be of great importance for uncovering the elusive mechanism of high-temperature superconductivity.

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1. Introduction

Although an enormous amount of research has been done over two decades since the discovery of high-temperature superconductors, the origin of high-temperature superconductivity (HTSC) in copper oxides still remains elusive. It is well known that for cuprates, doping changes the crystalline structure and the carrier concentration simultaneously. So far, much more attention has been paid to understanding the dependence of superconductivity on the carrier concentration and a uniform conclusion has been achieved on the electronic phase diagram for high-$T_c$ superconductors \[1\]–\[4], but fewer researchers have focused on the structural effects. Understanding the role that the crystalline structure plays is of great significance for illustrating the underlying mechanism of HTSC.

The YBa$_2$Cu$_3$O$_y$ (YBCO) system has been investigated by many research groups for the situation of individual calcium or lanthanum doping \[5\]–\[18]. Generally speaking, cation doping in YBCO depresses $T_c$. Partial substitution of Ca$^{2+}$ at the Y$^{3+}$ site will supply hole carriers; hence, the carrier concentration or charge distribution in this system will be regenerated. The Ca substitution also leads to the reduction of the total oxygen content, little change in the effective copper valence and the depression of $T_c$. In contrast, La$^{3+}$ replacing Ba$^{2+}$ will provide electronic carriers. The La substitution at the Ba site causes the oxygen content to increase, the effective copper valence to slightly decrease and the $T_c$ also to decrease.

Previously, the $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_y$ (YCBLCO, $y = x$) system has been studied by several groups; it is of particular interest because the co-substitution of Ca (for Y) and La (for Ba) is electrically self-compensating. Researches show that the simultaneous substitution of Ca$^{2+}$ for Y$^{3+}$ and La$^{3+}$ for Ba$^{2+}$ keeps both the Cu oxidation state and the overall oxygen content nearly constant \[19\] and helps in improving the corrosion resistance and chemical stability of YBCO substantially \[20\], \[21\]. From this self-compensating system, it is found that even in some optimum doping states, $T_c$ is depressed. It demonstrates that the influence of the crystalline structure on the HTSC is independent of the carrier concentration since the latter remains constant but the $T_c$ value still evidently changes.

As is well known, the coupling between electrons and phonons drives the formation of the Cooper pairs responsible for conventional superconductivity \[22\]. But up to now, the role of the electron–phonon coupling on HTSC is still under debate \[23\]–\[25\], and no theory has the final word on the mechanism of HTSC. Researchers have paid much more attention to electronic behaviors, but less to phonons. According to the existence of the ‘fixed triangle’ configuration in YCBLCO, in this work, it is supposed that there exists a special electron–phonon mode in HTSC, which may result in some unknown phonon behavior, which in turn influences HTSC.
2. Experimental

The samples were synthesized by the solid-state reaction method. Pure oxides of $\text{Y}_2\text{O}_3$, CaCO$_3$, BaCO$_3$, La$_2$O$_3$ and CuO were mixed according to the chemical formula of $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_z$ with both $x$ and $y$ taking values from 0 to 0.5 in intervals of 0.1. The preparation process is similar to the preparation of the self-compensating YCBLCO ($y=x$) system [26].

The crystalline structures of the samples were characterized by x-ray diffraction (XRD) on an X’pert MRD diffractometer with CuK$\alpha$ radiation. Detailed structural parameters were obtained by the Rietveld refinement method, using the X’pert Plus software. The goodness of fit (GOF = $R_{wp}/R_{exp}$) of all the samples was less than 1.7, demonstrating that the refinement results are reliable. The $T_c$ of each sample was determined by dc magnetization measurement at 10 Oe field in the temperature of 30–100 K, using the Quantum Design MPMS system.

3. Results and discussion

To show explicitly the $T_c$ dependence on the content of Ca or La, respectively, $T_c$ is plotted as functions of both $x$ and $y$ for the YCBLCO system in figure 1, which is a three-dimensional
Table 1. Grouping of all 36 samples of YCBLCO according to the content of Ca (Ca-defined group).

| Group names | Group Elements $(x, y)$ |
|-------------|-------------------------|
| Ca-0        | (0,0), (0,0.1), (0,0.2), (0,0.3), (0,0.4), (0,0.5) |
| Ca-0.1      | (0.1,0), (0.1,0.1), (0.1,0.2), (0.1,0.3), (0.1,0.4), (0.1,0.5) |
| Ca-0.2      | (0.2,0), (0.2,0.1), (0.2,0.2), (0.2,0.3), (0.2,0.4), (0.2,0.5) |
| Ca-0.3      | (0.3,0), (0.3,0.1), (0.3,0.2), (0.3,0.3), (0.3,0.4), (0.3,0.5) |
| Ca-0.4      | (0.4,0), (0.4,0.1), (0.4,0.2), (0.4,0.3), (0.4,0.4), (0.4,0.5) |
| Ca-0.5      | (0.5,0), (0.5,0.1), (0.5,0.2), (0.5,0.3), (0.5,0.4), (0.5,0.5) |

(3D) phase diagram. An interesting phenomenon is that the maximum $T_c$ values are clearly along the diagonal of the basal plane, which correspond to the optimum doping samples, i.e. the self-compensated samples. But it is clearly shown that even if the sample is optimum doped or self-compensated, as the $x$ and $y$ values increase, $T_c$ is still gradually depressed.

The highest transition temperature is about 92 K for pure YBCO, which corresponds to the optimum oxygen content of 6.93 and the average copper valence of $+2.28$ [10]. If assuming that in the system, the average copper valence and the optimum oxygen content are both the same as that of pure YBCO (in fact, all the samples were fully oxygenated at 450°C for 24 h in a flowing oxygen), the optimum doped condition is $y = x$ according to the electric neutrality condition. This is consistent with the experimental result, i.e. the self-compensated YCBLCO ($y = x$) samples have higher $T_c$ values compared with samples that are un-compensated ($y \neq x$).

In the YCBLCO system, $\text{Ca}^{2+} (x)$ replacing $\text{Y}^{3+}$ will provide more hole carriers and depress $T_c$ in the manner of overdoping. But $\text{La}^{3+} (y)$ substituting for $\text{Ba}^{2+}$ will supply electronic carriers, which neutralize some of the holes caused by the Ca doping. When $y < x$ and the system remains overdoped, $T_c$ initially increases with increasing of La content. Once the content of La exceeds the optimum doping value, i.e. $y > x$, the excess electrons will neutralize more hole carriers and the sample becomes underdoped. As a result, $T_c$ decreases with further addition of La. In other words, with $x$ remaining constant and $y$ increasing, the system YCBLCO undergoes a transition from overdoped to optimum-doped at $y = x$, and finally to underdoped. Accordingly, the $T_c$ values exhibit a roof-shape in the 3D phase diagram, where the ridge represents the $T_c$ of the optimum-doped sample.

To distinguish the individual influence of Ca and La doping on the crystalline parameters, samples are divided into six groups according to the content of Ca (Ca-defined group). In every group, the Ca content remains constant, but the La content varies (see table 1). The samples are also divided into another six groups according to the La content (La-defined group). In every group, the La content remains constant, but the Ca content varies (see table 2). The definitions of the lattice parameters and the atom position in the unit cell are indicated in figure 2 for the convenience of later discussions.

The lattice constants of the $c$-axis of the Ca-defined (solid line) and La-defined (dotted line) groups are plotted versus the doping content in figure 3. It is clear that the $c$ parameter decreases monotonously with increasing La content in the six Ca-defined groups. This result is due to the substitution of large $\text{Ba}^{2+}$ ions (1.42 Å) by small $\text{La}^{3+}$ ions (1.16 Å). In contrast, for the La-defined groups, as the vertical dotted line shows, the $c$ parameter increases in the...
Table 2. Grouping of all 36 samples of YCBLCO according to the content of La (La-defined group).

| Group names | Group elements (x, y) |
|-------------|----------------------|
| La-0        | (0,0), (0.1,0), (0.2,0), (0.3,0), (0.4,0), (0.5,0) |
| La-0.1      | (0,0.1), (0.1,0.1), (0.2,0.1), (0.3,0.1), (0.4,0.1), (0.5,0.1) |
| La-0.2      | (0,0.2), (0.1,0.2), (0.2,0.2), (0.3,0.2), (0.4,0.2), (0.5,0.2) |
| La-0.3      | (0,0.3), (0.1,0.3), (0.2,0.3), (0.3,0.3), (0.4,0.3), (0.5,0.3) |
| La-0.4      | (0,0.4), (0.1,0.4), (0.2,0.4), (0.3,0.4), (0.4,0.4), (0.5,0.4) |
| La-0.5      | (0,0.5), (0.1,0.5), (0.2,0.5), (0.3,0.5), (0.4,0.5), (0.5,0.5) |

Figure 2. The orthorhombic structure of YCBLCO.

six groups with Ca substitution, which is an indication of the eightfold-coordinated $Y^{3+}$ ions (1.02 Å) replaced by larger eightfold-coordinated $Ca^{2+}$ ions (1.12 Å).

Another interesting fact is the orthorhombic–tetragonal (O–T) transition with the addition of La, as is illustrated in figure 4. In all six Ca-defined groups, the difference between the lattice constants $a$ and $b$, which is usually named ‘orthorhombic distortion’, becomes smaller and smaller with the addition of La, and such a difference vanishes simultaneously at La content $y = 0.5$. In other words, it is independent of Ca content. The O–T transition of the YCBLCO system occurs provided the La content reaches the critical value of $y = 0.5$. On the other hand, this difference has no direct correlation with the addition of Ca in the La-defined groups. The interesting phenomenon of the O–T transition in the system is under study.

To study the correlation of the superconductivity and the structural parameters, the lengths of some chemical bonds around the Cu atoms are calculated. It is found that the bond lengths of Cu(1)–O(4) and Cu(2)–O(4) change systematically with the content of two dopants. In the Ca-defined groups, the substitution of La shortens the Cu(2)–O(4) bond length and lengthens...
Figure 3. Lattice constant along c-axis versus La content in the Ca-defined YCBLO system. The standard deviation of c is less than 0.0007 Å. The anomalous behavior of the (0.3,0.3) sample is probably due to the unhomogeneity of that sample.

Figure 4. Orthorhombic distortion (a–b) versus La content in the Ca-defined YCBLO system. The standard deviations of a and b are less than 0.0004 Å.

the Cu(1)–O(4) bond length simultaneously. On the other hand, in the La-defined groups, the addition of Ca results in the shortening of the Cu(1)–O(4) bond and the lengthening of the Cu(2)–O(4) bond. These results are plotted in figure 5. These behaviors could be interpreted by considering the different roles of Ca and La ions in doping and detailed charge transfer mechanism. In the YBCO system, the apical oxygen, the O(4) atom, plays a vital part in charge transfer because of its crucial location between the Cu(2)O₂ plane and the Cu(1)–O chain and is thus named the ‘bridge atom’. It has been recognized that this bridge atom moves in a direction opposite to the hole transfer [5]. When Ba²⁺ is replaced by La³⁺, the density of holes in the Cu(2)O₂ plane decreases, i.e. holes move away from the plane and enter the reservoir layer. Meanwhile, the O(4) atom comes near the Cu(2)O₂ plane, making the Cu(2)–O(4) bond...
Figure 5. The dependence of the bond lengths of the Cu(1)–O(4), Cu(2)–O(4) on the content of La in Y$_{0.9}$Ca$_{0.1}$Ba$_{2-y}$La$_y$Cu$_3$O$_z$ (a) and on the content of Ca in Y$_{1-x}$Ca$_x$Ba$_{1.8}$La$_{0.2}$Cu$_3$O$_z$ (b). The standard deviations of the bond lengths are less than 0.015 Å.

Figure 6. The correlation between the $T_c$ and the bond length of Cu(2)–O(4). The standard deviation of the bond length is less than 0.015 Å.

constrict and the Cu(1)–O(4) bond prolong accordingly. The substitution of Ca$^{2+}$ for Y$^{3+}$ has the opposite effect due to the creation of extra holes, and the O(4) atom moves far from the Cu(2)O$_2$ plane.

Furthermore, the relationship between $T_c$ and the bond lengths of Cu(2)–O(4) and the Cu(1)–O(4) is investigated and illustrated in figures 6 and 7. It is evident that the dependence of the $T_c$ on the bond length of Cu(2)–O(4) has better linearity than on that of Cu(1)–O(4). It is quite interesting that the relationship between the $T_c$ and the bond lengths is different for the underdoped ($x<y$), optimal-doped ($x=y$) and overdoped ($x>y$) samples.

In the underdoped region, $T_c$ increases linearly with the lengthening of the Cu(2)–O(4) bond and the constriction of the Cu(1)–O(4) bond. That is reasonable in order to consider the charge transfer mechanism. The variations of the two bond lengths indicate that the bridge atom O(4) moves far from the Cu(2)O$_2$ plane and accordingly, the hole carriers transfer toward the
**Figure 7.** Correlation between the $T_c$ and the bond length of the Cu(1)–O(4). The standard deviation of the bond length is less than 0.015 Å.

**Figure 8.** A block model, dividing the structure of a high-$T_c$ superconductor into perovskite and rock salt blocks. The blue triangle shows the ‘fixed triangle’ on the boundary of the perovskite and rock salt blocks. The green arrows illustrate the opposite movements of O(2) and O(3) as the doping content varies.

Cu(2)O$_2$ plane. From the result of the electronic phase diagram and in the underdoped region, a larger hole carrier concentration on the Cu(2)O$_2$ plane implies a higher $T_c$.

The positive correlation between $T_c$ and the Cu(2)–O(4) bond length in the underdoped region can be understood by the block model we proposed before [27]. In this model, the crystalline structure of a high-temperature cuprate is divided into two blocks, the perovskite block, where the Cu(2)O$_2$ planes are located, and the rock salt block, which is considered as a charge-reservoir (figure 8). It is found that the interaction between the two blocks is closely related to the electronic phase diagram.
related with the superconductivity. In a pure YBCO system with different oxygen content, which could be considered as underdoped in to different degrees, it was reported that as the combinative energy between the two blocks decreases, the $T_c$ value increases [28]. The Cu(2)–O(4) bond is just located between the perovskite block and the rock salt block and connects them. It can be said that the weakening of the interaction between the two structural blocks corresponds to the lengthening of this chemical bond and then the increase of $T_c$. This is exactly the situation in the underdoped region of the YCBLCO system (figure 6).

However, in the overdoped region, $T_c$ decreases linearly with the prolongation of the Cu(2)–O(4) bond and the constriction of the Cu(1)–O(4) bond, which is also consistent with the charge transfer mechanism and the electronic phase diagram. As the Cu(2)–O(4) bond lengthens, the O(4) atom moves far from the Cu(2)O$_2$ plane and hole carriers transfer toward that plane, the same direction as in the underdoped region. But in the overdoped region, more hole carriers to the Cu(2)O$_2$ plane are disadvantageous to the superconductivity and hence reduce $T_c$.

In the optimal-doped samples, it is suggested that the correlation between $T_c$ and the Cu(2)–O(4) bond length is negative, similar to the overdoped region. It should be emphasized that for the optimal-doped samples, the electronic phase diagram is no longer applicable for interpreting the variation of $T_c$ since the carrier concentration in this system remains invariant. Thus the variation of $T_c$ in the optimal-doped system can only be attributed to the corresponding structural change. It is clearly seen from figures 6 and 7 that the interaction between the two structural blocks, which is represented by the bond lengths of Cu(1)–O(4) and Cu(2)–O(4), is exclusively responsible for the superconductivity in the optimal-doped system (as the blue curves show).

According to the above results, it is believed that the coupling between the perovskite block and the rock salt block in the form of the Cu(2)–O(4) and Cu(1)–O(4) bond lengths changing is an important factor to HTSC from the underdoped region to the overdoped region. Most recently, superconductivity has been observed on the interface between insulating oxides [29] and the interface between metallic and insulating copper oxides [30]. These results clearly show that the interaction between the different crystalline structures can induce superconductivity, which is strong circumstantial evidence for our block model.

Owing to their special locations, the bond lengths and angles related to the atoms in the Cu(2)O$_2$ plane are now discussed. The careful calculation of the bond lengths of Cu(2)–O(2), Cu(2)–O(3) and O(2)–O(3) demonstrates that these three bonds belong to quite stable chemical bonds in the unit cell. As illustrated in figure 9, the bond lengths between each other in the triangle formed by Cu(2), O(2) and O(3) atoms have little fluctuation with the addition of Ca or La (see tables 3 and 4). Furthermore, the computation of the bond angle of O(2)–Cu(2)–O(3) shows that it fluctuates in the range from 88.4° to 89.2° among all the 36 samples with a maximal difference of 0.8°, which could be regarded as nearly constant. Consequently, it is reasonable to treat the three atoms as a ‘fixed triangle’. It should be pointed out that the ‘fixed triangle’ is located on the boundary of the perovskite block and the rock salt block.

The optimal-doped YCBLCO ($y = x$) samples deserve more attention because they are electrically self-compensating. In these samples, the correlations among the superconductivity and some other bond angles are investigated and it is demonstrated that $T_c$ is closely related to the change of the four pairs of the bond angles, which are considered to characterize the curvature of the CuO$_2$ plane to some extent. As an instance, the correlation between $T_c$ and the bond angles of the Cu(2)–O(2)–Cu(2) and the Cu(2)–O(3)–Cu(2) is illustrated in figure 10.
Table 3. Data of the bond length values plotted in figure 9(a).

| La content | 0   | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|------------|-----|-----|-----|-----|-----|-----|
| Cu(2)–O(2) Å | 1.960 | 1.953 | 1.957 | 1.964 | 1.985 | 1.944 |
| Cu(2)–O(3) Å | 1.938 | 1.943 | 1.946 | 1.947 | 1.946 | 1.944 |
| O(2)–O(3) Å | 2.724 | 2.722 | 2.722 | 2.724 | 2.731 | 2.725 |

Table 4. Data of the bond length values plotted in figure 9(b).

| Ca content | 0   | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|------------|-----|-----|-----|-----|-----|-----|
| Cu(2)–O(2) Å | 1.950 | 1.947 | 1.949 | 1.944 | 1.945 | 1.953 |
| Cu(2)–O(3) Å | 1.943 | 1.950 | 1.946 | 1.955 | 1.946 | 1.943 |
| O(2)–O(3) Å | 2.729 | 2.731 | 2.727 | 2.731 | 2.727 | 2.722 |

Figure 9. The bond lengths between each other in the triangle formed by Cu(2), O(2) and O(3) versus La content in Y$_{0.5}$Ca$_{0.5}$Ba$_{2}$-$\gamma$La$_{y}$Cu$_{3}$O$_{z}$ (a) and Ca content in Y$_{1-x}$Ca$_{x}$Ba$_{1}$La$_{0.1}$Cu$_{3}$O$_{z}$ (b). The standard deviations of the bond lengths are less than 0.015 Å.

It is found that O(2) and O(3) atoms move in opposite directions along the c-axis as the doping content changes, which implies that the ‘fixed triangle’ changes its gradient as the doping level varies. Here some more discussion on the ‘fixed triangle’ is given. It is well known that the coupling between electrons and phonons results in the formation of the Cooper pairs and conventional superconductivity. But the real mechanism remains elusive for HTSC. Whether the interaction between electrons and phonons (or some other Boson mode) should be responsible for HTSC is still controversial. However, researchers have found some evidence for electron–phonon coupling in HTSC and it seems quite likely to be included in its mechanism. Cohen et al [31] proposed a model that was capable of explaining the small oxygen isotope effect in YBa$_2$Cu$_3$O$_y$ within the framework of phonon-mediated electron pairing. Lanzara et al [32] observed a dispersion anomaly (‘kink’) from an angle-resolved photoemission (ARPES) experiment. They considered it to be direct evidence for the ubiquitous strong electron–phonon coupling in high-temperature superconductors, but there is no complete agreement on this [33]. Meevasana et al [23] found that the weight of the self-energy in the
overdoped Bi-2201 system shifted to higher energies, which was related to a change in the coupling between electrons and \(c\)-axis phonons. The above results indicate that it is hardly possible to exclude the electron–phonon coupling from HTSC. But how the coupling works in HTSC, and how much it affects it, are still very ambiguous.

From our experimental result, it is strongly hypothesized that the mystery of HTSC lies on the particularity of the phonon mode due to the structural specialty of the high-\(T_c\) cuprate. It is likely that the atoms in the vital superconducting \(\text{CuO}_2\) plane probably behave collectively since \(\text{Cu}(2), \text{O}(2)\) and \(\text{O}(3)\) atoms form a ‘fixed triangle’. Such an atom group with a colossal effective mass is sure to represent a special kind of phonon mode that is different from a single atom. Furthermore, the coupling between electrons in the unit cell and that exceptional phonon might differ from that shown in conventional superconductors. The vibration of the ‘fixed triangle’ should be much weaker than that of the individual atom. The interaction with electrons should also be much weaker, and the potential energy in the system should be lower. The ‘fixed triangle’ is strongly coincident with the theory of Varma [34]–[36], who believes that there exists a loop current among \(\text{Cu}(2), \text{O}(2)\) and \(\text{O}(3)\) atoms and then determines HTSC. The location of the loop is exactly at the ‘fixed triangle’. Here it is necessary to point out an experiment connected with our result. Friedl et al [37] discovered that there is an anomalous broadening of the \(B_{1g}\)-like phonon of \(\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}\) as a function of the phonon frequency in Raman spectra, which involves the combined vibrations of the \(\text{O}(2)\) and \(\text{O}(3)\) atoms, but the \(B_{3g}\)-like mode involving the vibrations of the \(\text{Cu}(2)\) atoms does not show an obvious effect. It seems difficult to match with our ‘fixed triangle’ proposal which emphasizes a massive vibration of those three atoms.

\textbf{Figure 10.} The correlation between \(T_c\) and the bond angles of \(\text{Cu}(2)\)–\(\text{O}(2)\)–\(\text{Cu}(2)\) (angle 7) and \(\text{Cu}(2)\)–\(\text{O}(3)\)–\(\text{Cu}(2)\) (angle 8). The standard deviation of the bond angles is less than 0.8°.
Figure 11. Possible physical origin of the two-gap phenomenon associated with the lattice scattering (a). Lattice scattering of electrons in the YBCO unit cell (b). The green plane represents all the other phonons.

The Raman result may not conflict with our result. We give a simple explanation, i.e. the anomalous broadening of the $B_{1g}$-like linewidth and the lack of the $B_{2g}$ mode involving the vibration of the Cu(2) atoms in the CuO$_2$ planes may come from the cooperation of the Cu weight to O(2) and O(3) because of the fixed triangle. We also observed the opposite-direction move of O(2) and O(3) (see figure 8), which is to some extent similar to the $B_{1g}$-like phonon mode.

To better elucidate the possible significance of the ‘fixed triangle’, the electron–phonon interaction term is separated from the Hamiltonian of the system and expressed as

$$H_{\text{ep}} = H_{\text{ep}1} + H_{\text{ep}2},$$

(1)

where $H_{\text{ep}}$ is the total electron–phonon interaction Hamiltonian, $H_{\text{ep}1}$ the interaction Hamiltonian between electrons and the ‘fixed triangle’ on the CuO$_2$ plane, and $H_{\text{ep}2}$ the interaction Hamiltonian between electrons and other phonons in the crystal. The physical process of the electron–phonon interaction in the YBCO unit cell is illustrated in figure 11(b), assuming that the ‘fixed triangle’ behaves as a phonon mode with a collective wavevector $\vec{q}$, and one electron (hole) with a wavevector $\vec{k}$ is scattered by it to another electronic state denoted by $\vec{k}'$. In this process, the energy of the system may be lowered, and may form a pseudogap (figure 11(a)). When it goes through the CuO$_2$ plane, it is scattered to the third electronic state with a wavevector $\vec{k}''$ by absorbing other phonons (all of which are included in a wavevector $\vec{q}'$) in the unit cell. In this process, it is likely to induce the formation of Cooper pairs, which may have something to do with the superconducting gap and HTSC.

Here, we clarify the conjecture. It is well known that there are pseudogaps and gaps in HTSC [38], but so far, a definitive statement about the two gaps has not been made. As illustrated in figure 11(a), the Fermi surface of the electrons is supposed to lower in two stages due to lattice scattering. Firstly, it lowers (as the red curve shows) after the Hamiltonian $H_{\text{ep}1}$ when scattered by the ‘fixed triangle’, and a pseudogap is formed. Secondly, it lowers further due to the Hamiltonian $H_{\text{ep}2}$ when scattered by other phonons in the unit cell, and superconductivity occurs. It should be mentioned that in the conjecture (formula 1), the $H_{\text{ep}1}$ could be due to the scattering by other phonons and the $H_{\text{ep}2}$ could be due to the ‘fixed triangle’ phonon.
From that point of view, the final mechanism of the HTSC may possibly be approached. If the conjecture is correct, then the exceptional nature of the collective phonon mode and its coupling with electrons might be represented in various experimental measurements, such as the electronic quasi-particle dispersion expressed in ARPES, the isotope effect, the temperature dependence of the resistivity, the Raman spectrum and so on. In another paper, we will study this exceptional nature of the phonon in our co-doped samples systematically.

4. Conclusion

The structure and superconductivity in the YCBLCO system were investigated. An overall three-dimensional phase diagram dependent on the content of two dopants simultaneously is given from the underdoped region to the overdoped region. The change of the $T_c$, besides the carrier concentration, depends mostly on the crystalline structure (some special bond lengths and bond angles) and the interaction of the two structural blocks. In addition, the ‘fixed triangle’ model in the superconducting CuO$_2$ plane is proposed. From this model, an exceptional phonon mode and its coupling with electrons in the unit cell can probably be induced. This hypothesis may be of significant help in understanding HTSC.

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