Calculation of combinative energy between perovskite and rocksalt blocks in $YBa_2Cu_3O_{7-\delta}$

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Based on a block model, separating the unit cell of $YBa_2Cu_3O_{7-\delta}$ into perovskite and rock salt blocks, the combinative energy between the two blocks in the $YBa_2Cu_3O_{7-\delta}$ with the different δ value, from 0.07 to 0.62, was calculated. A close relationship between the superconducting transition temperature and the combinative energy in $YBa_2Cu_3O_{7-\delta}$ is established, and the change of the combinative energy is closely related to the transformation from orthorhombic I to II. The results also give a clue to reconsider the role of the orthorhombic I and II in $YBa_2Cu_3O_{7-\delta}$. The calculation of the holes in different planes supplies abundant information about the charge distribution in $YBa_2Cu_3O_{7-\delta}$, which may possibly connect the electronic phase diagram and the fluctuations of the stripe phase. The results show that the interaction between the two blocks is of great importance for high T_c superconductivity.

All the high T_c superconductors are structurally composed of two different blocks, the perovskite, and the rock salt. Recently, we[1] developed a model to deal with the interaction between the two blocks. The model is quite different from the present theories about the high T_c superconductivity. The present theories mostly focus on the behavior of the Cu–O plane, which is indeed the most important part in the high T_c superconductors. They have led to some important understanding, but so far, no theory has the final word about the mechanism of high T_c superconductivity. Our model calculations show that the interaction between the two blocks has a close correlation with superconductivity. Finally to resolve the mechanism of high T_c superconductivity, the interaction of the two blocks should be taken into account.

It is well known that the superconducting transition temperature of $YBa_2Cu_3O_{7-\delta}$ decreases with the increase of oxygen deficiency, and there is a plateau at about 60 K, with the corresponding oxygen deficiency between $\delta \sim 0.35-0.55$.[2–5] There have been different ways to explain it. The main explanation[6–8] is that there are two different orthorhombic phases in $YBa_2Cu_3O_{7-\delta}$. When $\delta \sim 0.35-0.55$, the superconducting phase is orthorhombic II (orth II); when $\delta < 0.35$, the superconducting phase is orthorhombic I (orth I). As the oxygen deficiency increases, the superconducting phase transforms from the orth I to II at $\delta \sim 0.35$. But so far, few physical characteristics have been connected with the phase transformation from the orth I to II. In this report, based on our model, the combinative energy between the two blocks in $YBa_2Cu_3O_{7-\delta}$ is calculated and correlated with the superconducting transition temperature. The change of the combinative energy is closely related to the transformation from the orth I to II. We believe that the result is very helpful for understanding the superconductivity in the $YBa_2Cu_3O_{7-\delta}$.

The calculating method has been given in Ref. 1. According to Pauling's rule,[9] the ionic character between the Cu–O bond is 47%, Ba–O 77%, and Y–O 67%. It is reasonable to consider that $YBa_2Cu_3O_{7-\delta}$ is partly an ionic compound. But, obviously, $YBa_2Cu_3O_{7-\delta}$ has some covalent character. In the Cu(2)–O plane, the Cu3d and O2p orbitals hybridize and are responsible for the carriers. In order to compensate for the deficiency of a purely ionic model for $YBa_2Cu_3O_{7-\delta}$, we directly put some holes in the Cu(2)–O plane, the number of which depends on the oxygen deficiency. The whole cell is kept electrically neutral. This method is consistent with the experimental fact that the holes are mainly concentrated in the Cu(2)–O plane. In this way, the covalence is approximately considered, which makes the calculation more precise and the model more reasonable.

There are two ways to calculate the interaction between the different parts in a unit cell (hereafter, it is called combinative energy, to differentiate it from the cohesive energy of the unit cell). The first way is to separate all Cu–O planes and the rest of the cell. This way has been demonstrated in detail in our former work.[1] Another way is to treat the cell as two different blocks, the so-called perovskite and rock salt blocks. The perovskite block is the active block where the Cu(2)–O planes are located and the carriers concentrate. The rock salt block corresponds to the charge-reservoir block, which supplies the carriers to the Cu(2)–O planes.

The combinative energy is calculated by the two methods mentioned above. The data about the change of T_c value and the structural parameters with the oxygen deficiency are taken from Ref. 3. By analyzing the results of the first method we find a plateau at about 60 K in the T_c curve, but no such plateau in the combinative energy curve. Therefore we think that the first method is not ideal. In our former work,[1] calculating the combinative energy in five different superconductors of the Hg system, this method did not give a reasonable result. The previous results of the Hg system and $YBa_2Cu_3O_{7-\delta}$ hint that separating the cell into independent planes and considering the interaction between them is not sufficient for superconductivity.

Figure 1 demonstrates the calculated results by the second method, namely, considering the cell as two different blocks. The results demonstrate a very close relationship between the T_c value and the combinative energy. As the T_c value increases, the combinative energy decreases too. At about 60 K, the T_c value shows a plateau, and the combinative energy

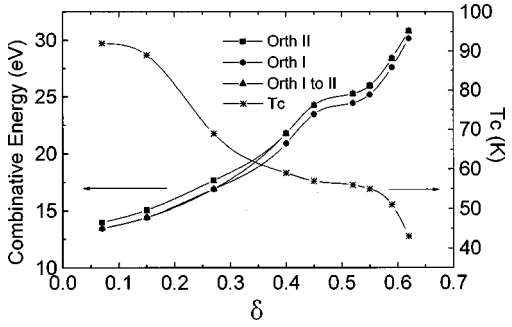

FIG. 1. The variation of T_c and the combinative energy E_c with different oxygen deficiency δ, calculated by the second method. The results are obtained for different phases in $YBa_2Cu_3O_{7-\delta}$.

also shows a plateau at about $\delta \sim 0.45$ (corresponding to $T_c = 60$ K). This result suggests that the interaction between the two blocks is of great importance for superconductivity.

Figure 1 shows the combinative energy calculated from the orth I, II, and when $\delta < 0.35$, using the orth I, when $\delta \geqslant 0.35$, using the orth II, respectively. The difference between the three curves is very small. This raises the question about the importance of the orth I and II phases, which should be discussed next. Former works[2–8] showed that there exists two different orthorhombic phases. Structurally, the difference between the two phases lies in the arrangement of oxygen defects in the Cu(1)–O plane, or basal Cu–O plane. Figure 2 illustrates the oxygen order in the two types of orthorhombic phases (orth I and orth II) in the basal Cu–O plane. The structure of the orth II is the one where every other Cu–O chain is missing in the basal Cu–O plane. The marked domains show the two cells of the orth I and one cell of the orth II in the basal Cu–O plane. The calculated results in Fig. 1 are based on these structures. From the results shown in Fig. 1, the difference between the three curves is very small. Accordingly, it is supposed that the plateau at about 60 K is not caused by the phase transformation from the orth I to orth II, but the native properties of $YBa_2Cu_3O_{7-\delta}$. No matter what phase it is, when the oxygen deficiency is in the range of $\delta \sim 0.35-0.55$, the plateau appears in the T_c curve. The main evidence for the existence of

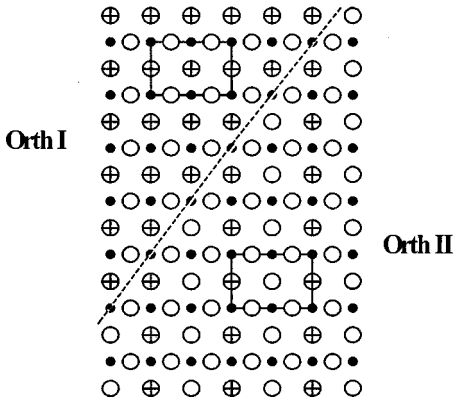

FIG. 2. The scheme of the two types of orthorhombic oxygen order (orth I and orth II) in the basal Cu–O plane. The dashed line separates the orth I and orth II. ○ denotes sites available for oxygen atoms and ⊕ denotes occupied oxygen sites. The Cu atoms are indicated by ●.

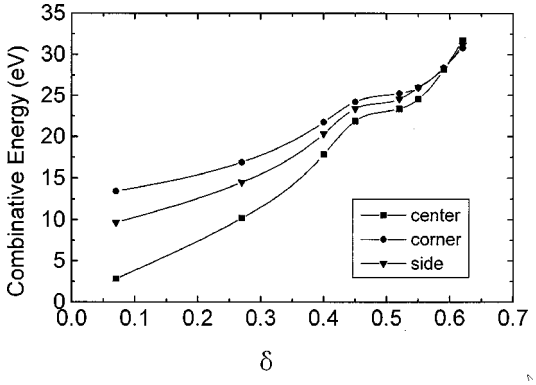

FIG. 3. The relationship between the combinative energy and the δ value with the holes in the Cu(2)–O plane. The coordinates of the corner site in a square plane are (0, 0), side (0, 1/2), and center (1/2, 1/2).

the orth II phase[10] was observed by electronic diffraction, which can just detect a very tiny area. We suppose that the orth I and orth II coexist in $YBa_2Cu_3O_{7-\delta}$. Maybe at $\delta \sim 0.35-0.55$, there is more orth II than orth I, but the existence of the orth II seems not to be the reason for the plateau in the T_c curve. This is an important problem for $YBa_2Cu_3O_{7-\delta}$. The authors of Ref. 6 suggested that the orth I to orth II transition is the dominant factor to the plateau at about 60 K. Recently, it was recognized that this is not the case.[11] The result in the present work just gives some hints to reconsider the role of the order of oxygen defects and its effect on superconductivity in $YBa_2Cu_3O_{7-\delta}$. This problem should be studied further.

In order to know the influence of charge distribution on the combinative energy, the holes in the Cu(2)–O plane, Cu(1)–O plane, and Ba–O plane were calculated, respectively. The holes in the Cu(2)–O plane were calculated at three different positions, on the corners, center, and sides. Figure 3 shows the results, which match Fig. 1, but some difference can be seen. As the oxygen deficiency (δ value) is low, i.e., the concentration of holes is high; the combinative energy differs for different positions. As the δ value increases, the combinative energy gradually tends to be the same. This result indicates that the distribution of holes influences the combinative energy in the region of high concentration but not at low concentration of holes.

The relationship between the combinative energy and the position of holes on the Cu(2)–O plane in the range of $\delta \sim 0.07-0.62$ is shown in Fig. 4. The bottom of the insets shows the hole's positions in the Cu(2)–O plane. The coordinates of these positions are as follows: 1 (1/2,1/2), 2 (0,1/2), 3 (0,0), 4 (0,1/4), and 5 (1/4,1/4). These positions are typical in the Cu(2)–O plane. According to the theory of the stripe phase, as a hole moves from one position to another, it causes the fluctuations of the stripe and the energy. The positions are chosen to know the influence of the movements of the holes on the energy. It is clearly demonstrated that as the δ value is low and the hole concentration is high, the effects of the hole's position on the combinative energy is significant. As the δ value increases, the effect becomes more and more ambiguous. At $\delta \sim 0.59$, the hole's position has no effect on the combinative energy. It should be mentioned that $\delta \sim 0.60$ is considered as the boundary of the superconduct-

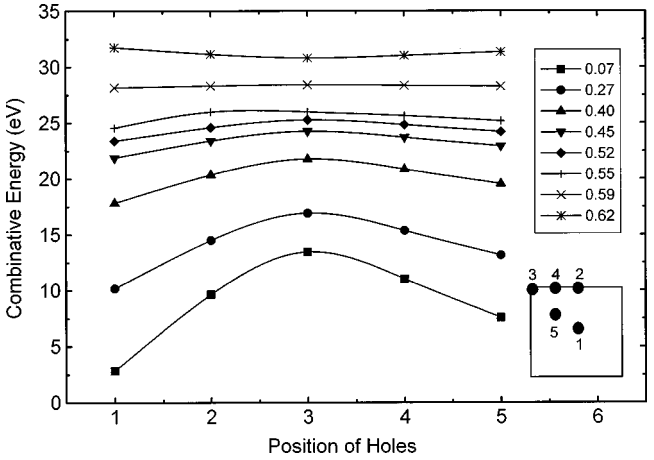

FIG. 4. The relationship between the combinative energy and the position of holes in the Cu(2)–O plane in the range of $\delta \sim 0.07-0.62$. The top of the insets shows the δ value and the bottom shows the position of holes.

ing and nonsuperconducting in $YBa_2Cu_3O_{7-\delta}$. As $\delta > 0.59$, the shape of the curve shows an opposite trend to the curve of the $\delta < 0.59$.

According to the electronic phase diagram[12] of the high T_c superconductors, the phase neighboring the superconducting region, in the underdoped region, is a strange metal with a pseudogap, which has attracted a lot of attention; but in the overdoped region, it is an ordinary metal. (Recently, some people argued this point of view.) The above results of the combinative energy demonstrate different trends in the region of low and high carrier concentrations. Approaching the strange metal region, or the region of the low carrier concentration, the combinative energy is not affected by the holes in the different positions. Approaching the ordinary metal region, or the region of high carrier concentration, it is obviously affected by the holes in the different positions. Comparing this result with that shown in the electronic phase diagram, it hints some relationship between the electronic phase diagram and the combinative energy, which should be studied further.

When the holes are assumed to be in the Cu(1)–O plane, the results differ from those in the Cu(2)–O plane as shown in Fig. 5. The curves show the same trend as that in Fig. 3, but the plateau in the range of $\delta \sim 0.35-0.55$ is different. Above $\delta \sim 0.55$, the plateau remains, and the energy does not

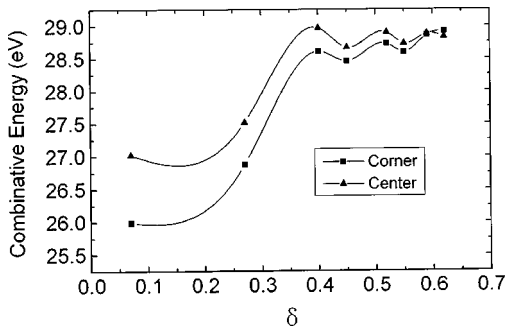

FIG. 5. The relationship between the combinative energy and the δ value as the holes are in the Cu(1)–O plane.

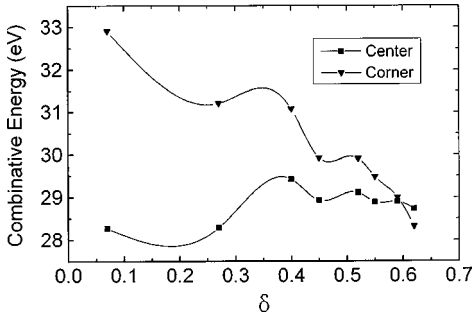

FIG. 6. The relationship between the combinative energy and the δ value as the holes are in the Ba–O plane.

increase, opposite to the case when the holes are in the Cu(2)–O plane (Fig. 3). The results show that as the carrier concentration is high, the behavior of the holes in the Cu(1)–O plane is very similar to that in the Cu(2)–O plane. This matches the description that the Cu(1)–O plane is a carrier reservoir. A strange phenomenon appears in the curves. The combinative energy shows some fluctuations, especially in the range of $\delta \sim 0.40-0.60$.

As the holes are in the Ba–O plane, the calculated results are quite different from that in the Cu(2)–O plane. As demonstrated in Fig. 6, the trend of the curves is opposite to the curves in Figs. 3 and 5. This proves that the carriers in $YBa_2Cu_3O_{7-\delta}$ are mainly distributed in the Cu–O planes, but not in the Ba–O plane.

The phenomenon of the energy fluctuation shown in Figs. 5 and 6 is very interesting. It is caused by changing the δ value, or changing the hole concentration. Comparing this result with the fluctuation of the stripe phase,[13] which has been studied extensively, it will hint to something very important. In the cuprate superconductors, the copper atoms have an odd number of electrons, and thus have an excess electron spin, giving these atoms a net magnetism. In these superconductors, opposite spins attract each other. Adjacent copper atoms do their best to align their spin moment in opposite orientations, creating an up-and-down pattern. As a hole moves to another copper atom, that spin moves to the hole's previous location, disrupting the orderly up–down arrangement of spins that results in fluctuation of the stripes. The above analysis shows that changing the holes causes all the fluctuation of stripes and the energy. So far, the role of the stripe phase is not clear. The results in our work possibly show that the fluctuation of the stripes has something to do with the holes in the Cu(1)–O plane and the Ba–O plane. This is just a preliminary result. Further study about the connection between the combinative energy and the superconductivity is badly needed. The combinative energy, calculated from the holes in the different planes, connects with the electronic phase diagram and the stripe phase demonstrates that the interaction of the two blocks in the high T_c superconductors is very important.

In conclusion, there is a close relationship between the combinative energy and the superconducting transition temperature in $YBa_2Cu_3O_{7-\delta}$. The study raises an important question about the relationship between the orth I, II, and T_c value, which deserves more attention. When the holes are

assumed to be in different planes, some interesting phenomena are found. The combinative energy indicates some connections with important characteristics of high T_c superconductors. We think that to fully understand the mechanism of the high T_c superconductivity, not only the behaviors of the Cu–O plane, but also the interaction of the two structural blocks should be considered.

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[1] H. Zhang, L. L. Cheng, X. C. Qin, and Y. Zhao, Phys. Rev. B **61**, 1618 (2000).

[2] N. C. Yeh, K. N. Tu, S. I. Park, and C. C. Tsuei, Phys. Rev. B **38**, 7087 (1988).

[3] J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus, and W. K. Kwok, Phys. Rev. B **41**, 1863 (1990).

[4] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Phys. Rev. B **36**, 5719 (1987).

[5] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Nature (London) **329**, 423 (1987).

[6] H. F. Poulsen, N. H. Andersen, J. V. Andersen, H. Bohr, and O. G. Mouritsen, Nature (London) **349**, 594 (1991).

[7] T. Zeiske, D. Hohlwein, R. Sonntag, F. Kubanek, and T. Wolf, Physica C **194**, 1 (1992).

[8] R. Sonntag and D. Hohlwein, Phys. Rev. Lett. **66**, 1497 (1991).

[9] L. Pauling, Phys. Rev. Lett. **59**, 225 (1987).

[10] Y. Kubo, T. Ichihashi, T. Manako, K. Baba, J. Tabuchi, and H. Igarashi, Phys. Rev. B **37**, 7858 (1988).

[11] D. Monster, P. A. Lindgard, and N. H. Anderson, Phys. Rev. B **60**, 110 (1999).

[12] For example, B. J. Batlogg, R. Buhrman, D. Gubser, D. Larbalestier, D. Lieber, J. Rowell, R. Schwall, D. Shaw, and W. Sleght, J. Supercond. **10**, 583 (1997).

[13] R. F. Service, Science **283**, 1106 (1999).