

Interaction between two structural blocks and superconductivity in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Ba}, \text{Sr}$)

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The combinative energy between two structural blocks in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Ba}, \text{Sr}$), with different M concentration, has been calculated with holes in different positions in the CuO_2 planes on the basis of a block model. The relationship between the combinative energy and superconductivity has been investigated. The results indicate that there is an interesting correlation among the combinative energy, the T_c value, and the positions of the doped holes, which are originated from the substitution of Ba^{2+} or Sr^{2+} for La^{3+} . Although there are some similarities in correlation between $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.03 < x < 0.25$) and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.075 \leq x \leq 0.3$), there are also some notable differences which may be originated from different properties of the substituted elements: barium and strontium. The results not only suggest that the interaction between perovskite-type and rocksalt-type blocks plays an essential role in high- T_c superconductivity, but also give us some clues of the influence of the position of the holes within the CuO_2 plane.

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I. INTRODUCTION

Among a variety of high- T_c superconductors known today, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ is the first high- T_c superconductor.¹ The structure and superconductivity of this system and its related system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have been extensively studied.²⁻⁸ It is well known that both systems have optimum Ba (Refs. 2 and 5) or Sr (Refs. 3 and 4) concentration, at which the maximum T_c are achieved. For $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$,^{5,6} the suppression of T_c when $x = 0.125$ has something to do with the structural transition (phase transition from a tetragonal, space group $I4/mmm$, to an orthorhombic structure, space group $Bmab$). As to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, some authors proposed many possibilities such as the effects of increasing oxygen vacancies,⁹ structural phase transition,¹⁰ chemical phase separation,⁸ etc., to explain the suppression of superconductivity. But others have found these contentions contrary to their experiment results. For example, Kamiyama *et al.*¹¹ studied samples containing various Sr concentrations prepared under different synthetic conditions by neutron powder diffraction and showed that oxygen defect formation is not the main reason that causes T_c to drop above $x = 0.15$. They argued that the suppression of T_c is attributed to the deviation of the holes concentration from an optimum value. Also, Nagano *et al.*¹² suggested the structural phase transition theory. Similarly, work on chemically homogeneous samples has cast doubt on chemical inhomogeneous theory.¹⁰ So far, there are still controversies concerning the properties of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ as a function of M content.

In our previous work,^{13,14} we calculated the combinative energy of the Bi, Hg, Tl, and Y systems on the basis of a block model. At first, we had successfully established a close relationship among the combinative energy, the T_c value, and the number of the CuO_2 planes in the Bi, Hg (Ref. 13), and Tl (Ref. 14) systems. Later, we found an intimate correlation among the combinative energy, the T_c value, and the amount of the oxygen deficiencies in the Y system. Yet it had re-

mained to be seen if this model would work in systems with cation substitution. For this reason and the striking features possessed by the $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Ba}, \text{Sr}$) systems, we have calculated their combinative energy. Further, these materials possess comparatively simple structures and are distinct from the other systems we had previously investigated. The results indicate that there is a correlation between the interaction of the two blocks and the superconducting transition temperature. Nevertheless, these two systems have distinct differences as far as the position of the holes is concerned. The important reasons controlling the T_c of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Ba}, \text{Sr}$) as a function of M are discussed in view of these results.

II. CALCULATING METHOD

According to the classical theory, the cohesive energy of the crystal can be written as a sum of the Madelung energy E_M , repulsive energy of ions E_r , and the electron affinity energy E_α , namely,

$$En = E_M + E_r + E_\alpha \quad (1)$$

and

$$E_M = 1/2c \sum e_i e_j / r_{ij}, \quad (2)$$

$$E_\alpha = \alpha e^{-1/\rho}, \quad (3)$$

$$E_\alpha = \sum \sum \varepsilon_{ij}. \quad (4)$$

Here e_i and e_j are the electric charges of the different ions, r is the distance between two different ions, and ε_{ij} is the ionization energy if the j atoms in the cell and α , ∞ coefficients. We discard the electron affinity energy since once the atom becomes an ion, the ion has a closed shell then and the electron affinity energy will have little effect on other electrons or vacancies. For that some authors have demonstrated the ion model can be used to deal with the high-

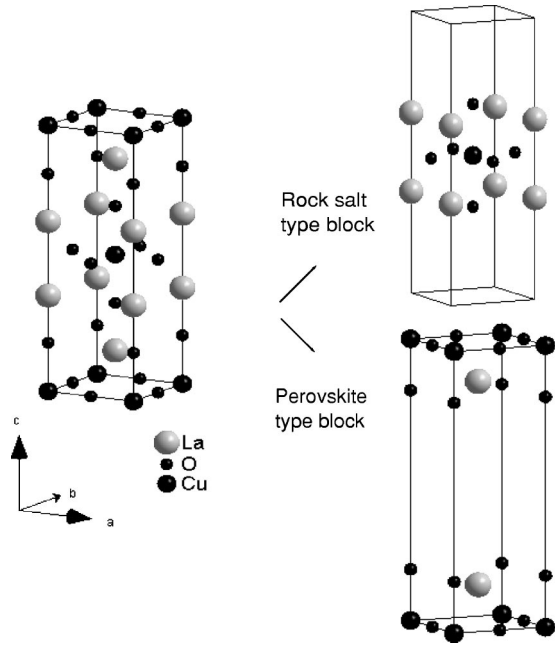


FIG. 1. The division of the two blocks in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

temperature superconductors.^{15,16} We use the ionic model to simplify the problem. To make the calculation more precise and the model more reasonable, the covalence is also approximately considered.

To calculate the Madelung energy, we use the standard Evjen method,¹⁷ in which the distribution of the charges in a cell is balanced and the summation is highly convergent. In calculation of the repulsive energy, we use a Bohr approximation. The accuracy and reliability of the calculation method have been well tested in Refs. 13 and 14.

The structure of $\text{La}_{2-x}M_x\text{CuO}_4$ ($M = \text{Ba}, \text{Sr}$) can be described in terms of alternating layers of perovskite-type (LaCuO_3) and rocksalt-type (LaO) units along the c axis. In our block model, we have divided the cell into two parts accordingly: the so-called rocksalt-type block and perovskite-type block as shown in Fig. 1. To study the interaction between the two blocks, we have defined the combinative energy between the two blocks: combinative energy between the two blocks = the total cohesive energy of the cell – the cohesive energy of the perovskite-type block – the cohesive energy if the rocksalt-type block.

We calculated the combinative energy of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.03 < x < 0.25$) and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.075 < x < 0.3$) on the basis of the block model mentioned above. The data about structural parameters (see Tables I and II) with different Ba or Sr concentrations and the T_c value are taken from Refs. 2 and 3, respectively. When Ba^{2+} or Sr^{2+} substitutes La^{3+} , there will be holes in this system to keep the whole cell electrically neutral.

In $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, there is an obvious orthorhombic-to-tetragonal (O - T) structural transition, which occurs at $x = 0.125$. We take it into account in our calculation. It may be argued that the substitution of Sr^{2+} for La^{3+} might induce oxygen deficiencies in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system, but Rada-

TABLE I. Lattice parameters at 115 K for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and T_c . Space groups of the materials change from orthorhombic $Bmca$ isomorphous to the standard $Cmca$ to tetragonal $I4/mmm$ at $x = 0.17$ (for more detailed parameters see Ref. 2).

x	a (Å)	b (Å)	c (Å)	T_c (K)
0.03	5.34070(13)	5.40540(13)	13.1554(3)	1.8
0.08	5.34141(9)	5.38390(9)	13.2060(2)	25
0.125	5.33915(9)	5.35882(9)	13.2414(2)	4.2
0.17	3.77993(6)		13.2885(2)	26
0.24	3.77866(7)		13.3235(3)	1.8

deul *et al.*³ showed that the number of oxygen vacancies is very small. Especially in our calculating range ($0.075 < x < 0.25$), they can almost be neglected. That is why we have not considered the oxygen deficiencies in our calculation. In this way, we can make an unambiguous understanding of the correlation among the combinative energy, the dopant concentration, and superconductivity in these two systems.

III. RELATIONSHIP AMONG THE COMBINATIVE ENERGY, THE M CONTENT, AND THE T_c VALUE IN $\text{La}_{2-x}M_x\text{CuO}_4$ ($M = \text{Ba}, \text{Sr}$)

In Fig. 2, it is easy to see that there is an obvious relationship between the combinative energy of the two blocks and the T_c value versus the Ba concentration in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ when holes are at position 1 (the definition of the positions of the holes is shown in Fig. 3). A similar correlation also exists in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as displayed in Fig. 3. When T_c reaches the maximum, the combinative energy between the two blocks also reaches the maximum. It indicates that the slacking of the interaction between the two blocks does contribute to the change of the T_c in these sys-

TABLE II. Lattice parameters at 295 K for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ oxygen-annealed samples and T_c . The space group change similar to Table I happens at $x = 0.1125$ (for detailed atomic positions see Ref. 3).

x	a (Å)	b (Å)	c (Å)	T_c (K)
0.0750	5.3508(1)	5.3664(1)	13.2030(1)	18
0.0875	5.3492(1)	5.3588(1)	13.2076(1)	25
0.1000	5.3489(2)	5.3543(1)	13.2126(1)	28
0.1125	5.3471(1)		13.2205(1)	27.8
0.1250	5.3466(1)		13.2266(1)	26.5
0.1375	5.3449(1)		13.2281(1)	33.5
0.1500	5.3422(1)		14.2317(1)	37.5
0.1625	5.3401(1)		13.2364(1)	37.2
0.1750	5.3381(1)		13.2420(1)	37
0.1875	5.3371(1)		13.2458(1)	36
0.2000	5.3353(1)		13.2469(1)	34
0.2125	5.3330(1)		13.2419(1)	28
0.2250	5.3316(1)		13.2538(1)	23
0.2375	5.3304(1)		14.2572(1)	20
0.2500	5.3292(1)		14.2539(1)	12.5

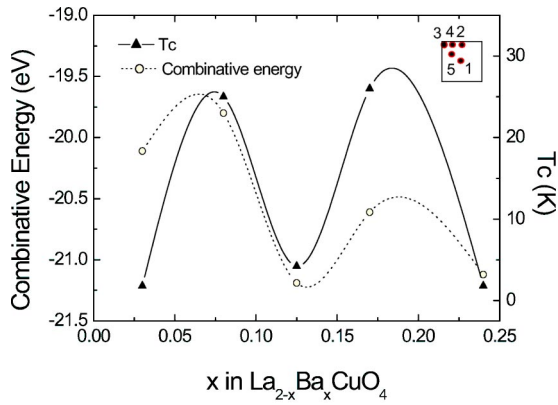


FIG. 2. The combinative energy (circles) and the value of T_c (triangles) vs x in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with holes at position 1 (0.5,0.5) in the CuO_2 planes.

tems. The combinative energy begins decreasing with increasing of the Ba concentration when $0.08 < x < 0.125$ and $0.17 < x < 0.24$ and of the Sr concentration above $x = 0.15$ as T_c decreases. The results indicate that the increasing of the interaction between the two blocks may have something to do with the suppression of superconductivity in these systems. These results are consistent with that of our earlier work.^{13,14} Such a correlation might result from the importance of the cooperation between the two blocks to the superconducting properties of the materials. A further study is still necessary.

IV. EFFECTS OF THE POSITION OF HOLES ON SUPERCONDUCTIVITY IN $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Ba}, \text{Sr}$)

In order to find out whether the position of the holes would influence the superconductivity of these systems, we have calculated the combinative energy between perovskite-type and rocksalt-type blocks when holes are at different positions (1,2,3,4,5) as shown in Fig. 4. Surprisingly, when holes are at position 1, the curves of combinative energy versus the dopant concentration are quite different from that

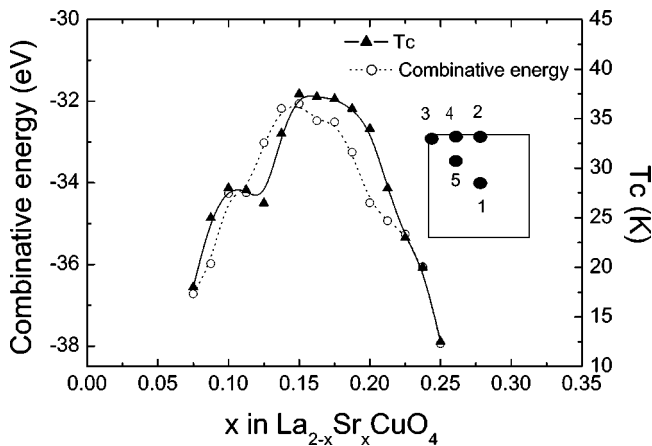


FIG. 3. The combinative energy (circles) and the value of T_c (triangles) vs x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with holes at position 1 (0.5,0.5) in the CuO_2 planes.

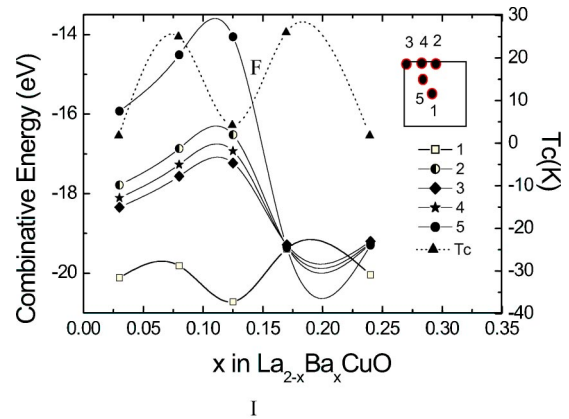


FIG. 4. The combinative energy and the value of T_c (triangles) vs x in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with holes at different positions: 1 (0.5,0.5), 2 (0.5,0), 3 (0,0), 4 (0.25,0), and 5 (0.25,0.25) in the CuO_2 planes as shown above.

when holes are at other positions. The curves related to other positions are similar to each other to some extent. This indicates that the position of the holes also affects the combinative energy between the two blocks, thus influencing the superconductivity of these systems. In the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the combinative energy between the two blocks and the T_c value has the closest relationship when holes are at position 1 as displayed in Fig. 5. From the curves in Figs. 4 and 5, it is evident that position 1 is favorable for the superconductivity in both systems. To show this more directly, the curves of the combinative energy versus the holes position are plotted in Figs. 6 and 7. It suggests that position 1 is the most sensitive position among the five positions within the CuO_2 plane. Although there is little chance of finding real holes there according to the calculation result of Mattheiss,¹⁸ the results of our calculation suggest that the effective charge center might be there.

Also, as it was found that an additional feature influencing T_c is the Cu-O-Cu bond angle within a CuO_2 plane.¹⁹ Because of the angle of Cu-O-Cu bond, position 1 may be a reasonable place for charges to exist. From Fig. 4, we have also noticed that there are several special positions in the

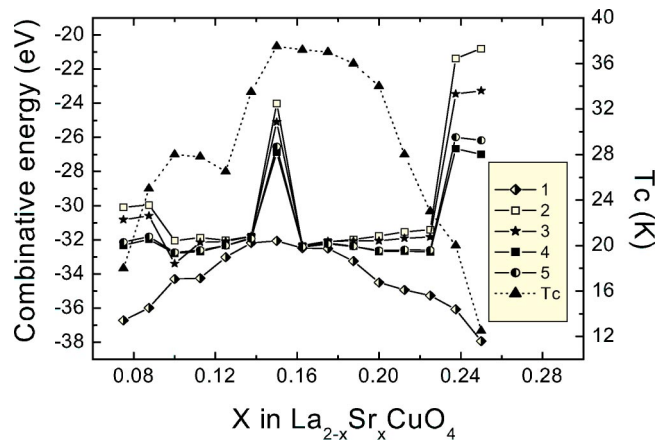


FIG. 5. The combinative energy and the value of T_c (triangles) vs x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with holes at different positions.

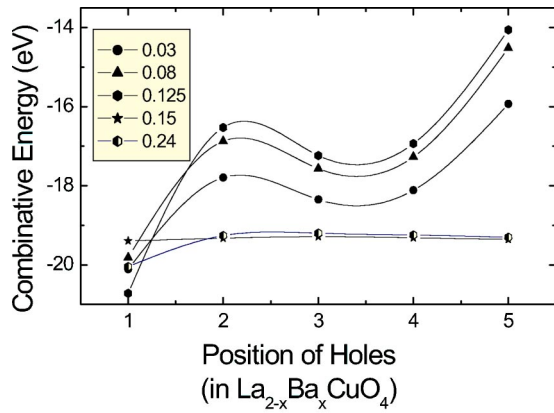


FIG. 6. The combinative energy vs the position of the holes in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with different Ba content.

curves of the combinative energy versus the Ba content. The first one is at $x = 1/8$ where there is a depression of the combinative energy as well as T_c when the holes are at position 1. But the combinative energy has an opposite tendency when the holes are at other positions. This might be closely related to the 1/8 anomaly, which seems common to other high- T_c superconductors containing the CuO_2 plane, such as the La-214 (Refs. 15 and 16), Bi-2212 (Refs. 17 and 20), and Y-123 (Refs. 21–23) systems. In the overdoped regime of this system, all positions seem to be equivalent for the case that the combinative energy varies little when holes are at different positions. This is similar to that in the overdoped Y-123 system.²⁴ As to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, we can see from Fig. 5 that all positions tend to be equivalent in the narrow range from $x = 0.125$ to $x = 0.1375$ and also at $x = 0.2125$ for the case that the combinative energy between two blocks varies little when the holes are at different positions. But at other positions, however, it is evident that there is an energy difference among different positions. This phenomenon is even obvious in the underdoped region where the material turns

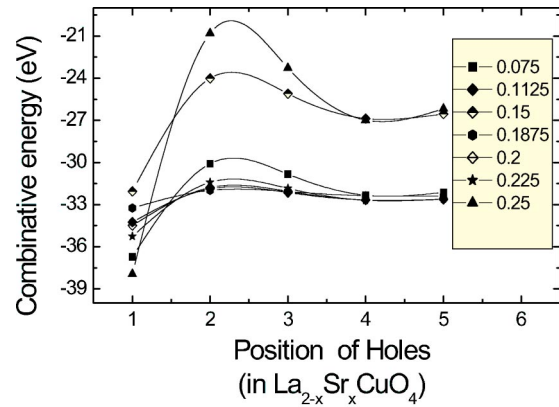


FIG. 7. The combinative energy vs the position of the holes in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with different Sr content.

superconducting and in the overdoped region where the superconductivity is disappearing. According to the theory of the stripe phase, as a hole moves from one position to another, it causes a fluctuation of the stripe and energy. Hence, the difference of the energy of these positions might hint at something important to the nature of the connection between the superconductivity and charged stripe. In an experiment, Hunt *et al.*²⁵ found that there exist slowly fluctuating, quasi-static charge stripes around $1/16 < x < 1/8$. This might be related to the small energy difference among the different positions within the CuO_2 planes as the results of our calculation show. As the difference between the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ system and the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system, it might result from the different properties of barium and strontium and needs further study.

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