# Combinative energy between two structural blocks and its correlation with superconductivity in Bi and Hg superconducting systems

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The influence of the interaction between two structural blocks on superconductivity was studied by calculating the cohesive energy in Bi-system superconductors, $Bi_2Sr_2CuO_y$ (2201), $Bi_2Sr_2CaCu_2O_y$ (2212), and the $Bi_2Sr_2Ca_2Cu_3O_y$ (2223) phases, and Hg-system superconductors, $HgBa_2CuO_y$ (1201), $HgBa_2CaCu_2O_y$ (1212), $HgBa_2Ca_2Cu_3O_y$ (1223), $HgBa_2Ca_3Cu_4O_y$ (1234), and $HgBa_2Ca_4Cu_5O_y$ (1245), respectively. We developed a program to calculate the combinative energy between Cu-O planes and remaining parts, and between blocks in the superconductors. The result indicates that if we consider the cell as two blocks combined together, a close relationship among the combinative energy between the two blocks, the value of $T_c$, and the number of the Cu-O planes in the Bi- and Hg-system superconductors is established. The result gives an interesting way to understand the change of the value of $T_c$ as the number of the Cu-O planes. In contrast, the combinative energy between the Cu-O planes and the remains obtained from the method separating all the Cu-O planes from the cell and leaving some discrete remaining parts does not show any relationship with the value of $T_c$. This means that considering the cell as the two blocks is more reasonable, and the interaction between the two blocks plays an important role in superconductivity.

## I. INTRODUCTION

Because high-$T_c$ superconductors demonstrate strong two-dimensional characteristics, the coupling along the *c* direction in the crystals is of great importance, and this characteristic has been studied extensively.[1] In most of these studies, the high-$T_c$ superconductors are regarded as a multilayer with superconducting and nonsuperconducting layers, and the coupling between the superconducting layers is considered. However, the role of different layers to superconductivity is not very clear. As is well known, there are many layers along the *c* direction in the high-$T_c$ superconductors. If we consider the coupling between each plane, it will be difficult to deal with this problem; however, if we can divide these layers into a few blocks reasonably based on the structural characters and experimental facts, the problem will become easy. The aim of this study is based on this consideration.

A lot of work has been done on understanding superconductivity from different methods. Among those researches, to study the relationship between cohesive energy and superconductivity is important. Billesbach and Hardy[2] calculated the lattice instability using a rigid-ion model. Torrance and Metzger[3] studied the effect of Madelung energy on the hole conductivity in high-$T_c$ superconductors. Muroi and Street[4] calculated the cohesive energy as a function of different Cu-O planes, and found the cohesive energy had correlation with the hole concentration in the Cu-O planes. Zhang *et al.*[5] used the cohesive energy to explain the change of $T_c$ of Y-doped superconductors successfully. Ohta and Maekawa[6] studied the Madelung energy of Pb-system superconductors, and found some relations between the energy and carrier concentration. Mizuno, Tohyama, and Maekawa[7] found some relationship between the Madelung energy and carrier in La-system superconductor. Mueller[8] reviewed that the study of Madelung energy was of great importance to high-$T_c$ superconductivity. Although much work has been done on this aspect, quantitative relationship between the cohesive energy and superconductivity has not been established within our knowledge. We developed a program to calculate the cohesive energy of different Bi- and Hg-system superconductors. When treating the cell as two blocks, perovskite where the Cu-O plane is located and rock salt, it is found that the combinative energy between the two blocks is closely related with the value of $T_c$. This result supports our point of view that the interaction between the two blocks is very important to superconductivity.

## II. MODEL

According to the classical theory of crystals, the cohesive energy $E_n$ is made up of Madelung energy, repulsive energy of ions, and electron affinity energy,

$$E_n = E_m + E_r + E_a, \tag{1}$$

which can be derived by the following formula:

$$E_m = 1/2\alpha\Sigma e_i e_j / r_{ij}, \tag{2}$$

$$E_r = a e^{-r/\rho}, \tag{3}$$

 

TABLE I. Comparison of the calculations with experimental results (Refs. 13 and 14).

| Substance | $U$ (calc.) Kcal/mol | $U$(exp) Kcal/mol | Difference (Kcal/mol) |
|---|---|---|---|
| CsCl | 152.9 | 155.1 | 2.2 |
| LiCl | 207.8 | 198.1 | 9.7 |
| TlCl | 170.5 | 170.9 | 0.4 |
| CsBr | 146.05 | 148.6 | 2.55 |
| $CaTiO_3$ | 8569 | 8561 | 8 |
| CuCl | 221.43 | 226.3 | 4.87 |

$$E_a = \Sigma\Sigma\varepsilon_{ij}\,. \tag{4}$$

Here $E_m$, $E_r$, and $E_a$ represent the Madelung energy, repulsive energy, and electron affinity, respectively. $e_i$, $e_j$ are the electric charges of different atoms in cell, $\varepsilon_{ij}$ is the $j$th ionization energy of the $j$th atoms in cell, $r$ the distance between the positive and negative ions, and a, $\propto$ the coefficients. We discard the electron affinity energy, because once the atom becomes ion, the ion has a closed outer shell then, and the electron affinity energy will not strongly affect other electrons or vacancies any more. We use ionic model to simplify this problem. Some authors[2–8] have demonstrated that the ionic model can be used to deal with the high-temperature superconductors. According to Pauling's rule,[9] it is reasonable to consider that the Bi-system superconductors are ionic compounds. But, obviously, they have some covalent character. In the Cu-O plane, Cu3$d$ and O2$p$ orbits hybridize, giving carriers. In order to compensate for the deficiency of the ionic model for the Bi system, we directly put some holes on the Cu-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 on the Cu-O plane. In this way, the covalence is approximately considered, which makes the calculation more precise and the model more reasonable.

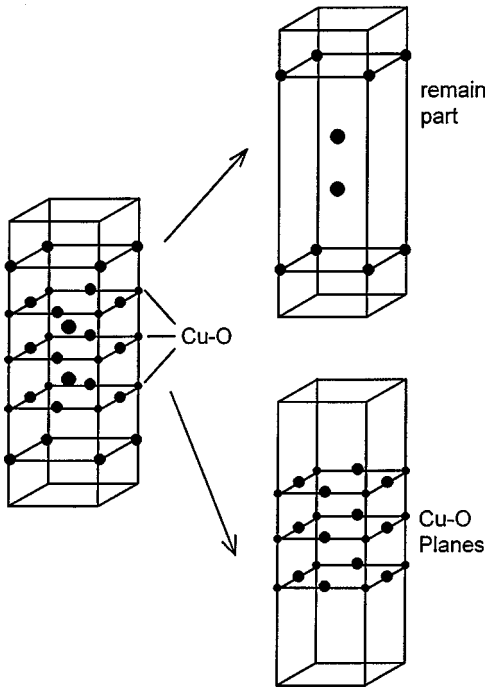


FIG. 1. First method to disassemble the cell. The Cu-O planes are divided into independent planes.

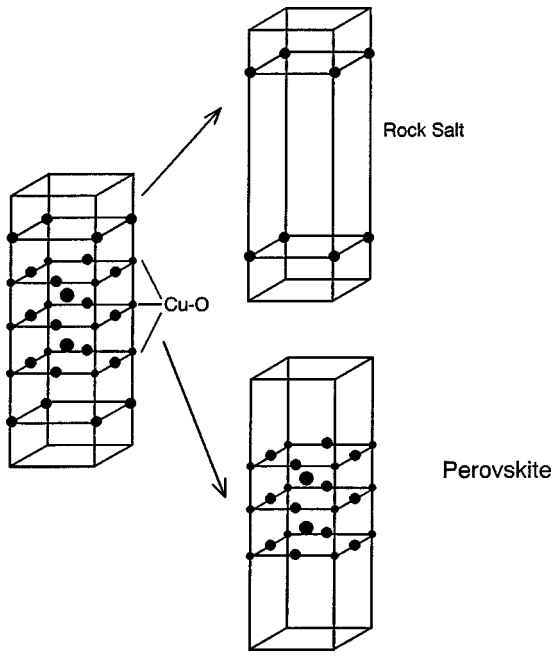


FIG. 2. Second method to disassemble the cell. The structure is divided into two blocks.

To calculate the Madelung energy, we use the standard Evjen[10] method. In this way, the distribution of charges in a cell is balanced and the summation is highly convergent. In the calculation of the repulsive energy we use a Bohr approximation. To test the accuracy of this program we calculated several samples and found that the calculated results matched the experimental results very well (see Table I). We believe that the program is reliable.

Besides the calculation of the cohesive energy of whole cell, the energy of the different parts in a single cell was calculated for the consideration of the interaction of the different blocks mentioned above. To calculate of the energy between the different parts in a single cell (hereafter, in order to differentiate it from the cohesive energy of whole cell, it is called combinative energy), there are two ways. The first way is to separate all the Cu-O planes out of the cell and leave the remains. This method is demonstrated by Fig. 1. In this way, all the Cu-O planes are considered equally. All the Cu-O planes are separated from the cell into independent plane, leaving some discrete remaining parts. After calculat-

TABLE II. The total cohesive energy of the cell ($E_n$), the cohesive energy of the Cu-O plane and remains ($E_{cu}$:$E_{re}$), and the combinative energy ($E_{ce}$) between per Cu-O plane and the remains in the Bi system calculated by the first method.

| Superconductors Bi system | $E_n$ (eV) | $E_{cu}$:$E_{re}$ (eV) | $E_{ce}$ (eV) | $T_c$ (K) |
|---|---|---|---|---|
| Bi2201 | 276.58 | 45.50 : 184.25 | 46.83 | 10 |
| Bi2212 | 327.22 | 68.02 : 182.65 | 38.28 | 80 |
| Bi2223 | 423.84 | 97.29 : 172.45 | 51.37 | 110 |

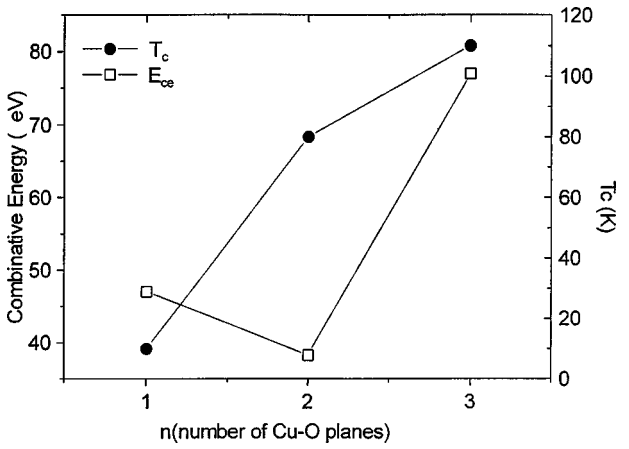


FIG. 3. The combinative energy (calculated by the first method) and the value of $T_c$ in the Bi system. There is no corresponding relationship between the energy and the value of $T_c$.

ing, we get the average combinative energy between each Cu-O plane and the remains. The combinative energy indicates the strength of interaction between each Cu-O plane and its adjacent planes.

Another way is to treat the cell as two different blocks, so-called perovskite and rock salt, instead of some independent planes. Figure 2 demonstrates this process. Unlike the first method, in this way the perovskite and rock salt block are considered as a ''packaged unit.'' Then the combinative energy calculated will mainly indicate the interaction between the two blocks in the cell. In fact, we do find something interesting in this way, which does not appear in the first method. The structural parameters used in the calculations for the Bi-system superconductors are from Ref. 11, and for the Hg system from Ref. 12.

### III. CALCULATING RESULTS AND DISCUSSIONS

With the first methods described in the model we calculated the cohesive and combinative energies of the Bi-system superconductors. Table II is the calculated results of the different Bi-system superconductors: $Bi_2Sr_2CuO_y$, (2201), $Bi_2Sr_2CaCu_2O_y$, (2212) and the $Bi_2Sr_2Ca_2Cu_3O_y$ (2223) phases, respectively. The table lists the total cohesive energy of the cell of the different phases, the cohesive energy of the Cu-O planes and remains, and the combinative energy of per Cu-O plane and the remains. The relationship among them is the total cohesive energy=the cohesive energy of the Cu-O planes and remains $+N$ (number of the Cu-O planes)$\times$the combinative energy. The relationship among the combinative

TABLE III. The total cohesive energy of the cell ($E_n$), the cohesive energy of the perovskite block and the rock salt ($E_{pe}:E_r$), and the combinative energy ($E_{ce}$) between the perovskite block and the rock salt in the Bi system calculated by the second method.

| Superconductors Bi system | $E_n$ (eV) | $E_{pe}:E_{re}$ (eV) | $E_{ce}$ (eV) | $T_c$ (K) |
|---|---|---|---|---|
| Bi2201 | 276.58 | 45.50 : 184.25 | 46.83 | 10 |
| Bi2212 | 327.22 | 120.89 : 177.70 | 28.63 | 80 |
| Bi2223 | 423.84 | 212.61 : 186.55 | 24.68 | 110 |

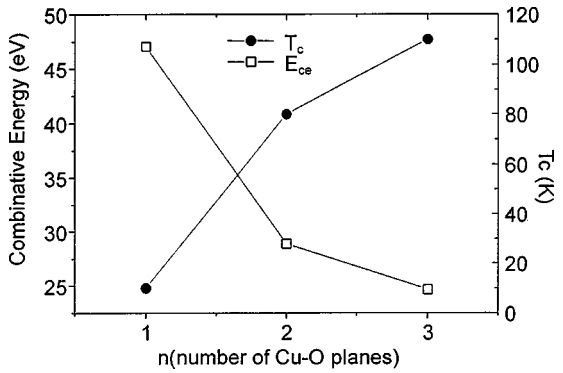


FIG. 4. The combinative energy (calculated by the second method) and the value of $T_c$ in the Bi system. There exists a close relationship between the energy and the value of $T_c$.

energy, the value of $T_c$, and the number of the Cu-O planes in the Bi-system superconductors is illustrated in Fig. 3.

From the data listed in Table II and Fig. 3 we can see that there is no obvious correlation among the cohesive energy, combinative energy, value of $T_c$, and the number of the Cu-O planes. The combinative energy for the 2201 phase is 46.83 eV, the 2212 phase 38.28 eV, and the 2223 phase 51.37 eV. We cannot find any regular pattern among these parameters.

The second method shows different result from the first one. We also calculated the same parameters as we did on the first model. The results are listed in Table III. The relationship among these parameters is the total cohesive energy=the cohesive energies of the perovskite and rock salt blocks+the combination energy between the two blocks. Figure 4 illustrates the relationship among the combinative energy between the two blocks, the value of $T_c$, and the number of the Cu-O planes in the Bi system. Clearly, there exists an obvious correlation between the combinative energy and the value of $T_c$. As the value of $T_c$ gets the maximum in the three Cu-O planes, the combinative energy between the two blocks gets the minimum. The value of $T_c$ and combinative energy demonstrate very good correspondence. Besides calculating the combinative energy in different phases, the combinative energy in one phase with different

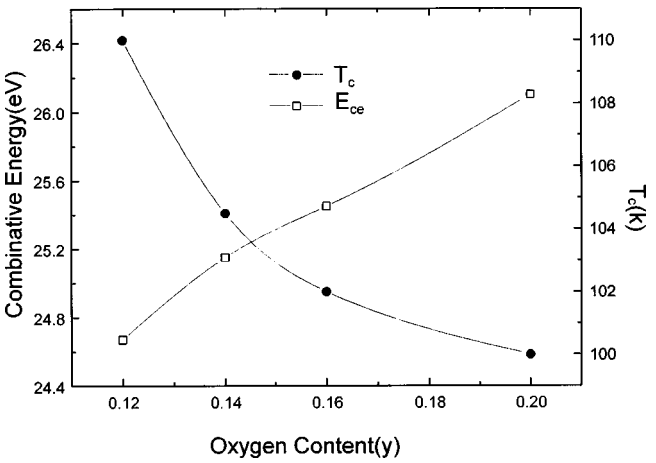


FIG. 5. The combinative energy $E_{ce}$ (calculated by the second method) and the value of $T_c$ in the 2223 phase with different oxygen content ($y$).

TABLE IV. The total cohesive energy of the cell ($E_n$), the cohesive energy of the Cu-O plane and remains ($E_{cu}$:$E_{re}$), and the combinative energy ($E_{ce}$) between per Cu-O plane and the remains in the Hg system calculated by the first method.

| Superconductors | $E_n$ (eV) | $E_{cu}$:$E_{re}$ (eV) | $E_{ce}$ (eV) | $T_c$ (Refs. 12,15) (K) |
|---|---|---|---|---|
| Hg1201 | 162.84 | 59.810 : 83.063 | 19.97 | 94 |
| Hg1212 | 249.82 | 96.376 : 77.648 | 37.90 | 128 |
| Hg1223 | 339.87 | 133.380 : 55.883 | 50.20 | 133 |
| Hg1234 | 426.71 | 153.910 : 26.575 | 61.57 | 123 |
| Hg1245 | 514.41 | 199.060 : −6.986 | 65.07 | 110 |

oxygen content was also calculated. Figure 5 shows the relationship among the combinative energy, $T_c$, and the oxygen content in the 2223 ($Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{10+y}$) phase with different oxygen content. As the $T_c$ increases, the combinative energy decreases. There also exists a good corresponding relationship.

The second method considers the cell as two relatively independent blocks. The combinative energy between those blocks mainly represents the strength of the interaction between the blocks. It seems that the interaction of these blocks, perovskite and rock salt, plays an important role in the superconductivity. This result also demonstrates that the high-$T_c$ superconductor is naturally inhomogeneous, even in energy distribution, and supplies some important clues for understanding the mechanism of the high-$T_c$ superconductivity.

In order to confirm our calculation and the correlation among the value of $T_c$, combinative energy between the two blocks, and the number of the Cu-O planes, the parameters described above were further calculated for the Hg-system superconductors by the two different methods. The Hg system has five superconducting phases, $HgBa_2CuO_y$ (1201), $HgBa_2CaCu_2O_y$(1212), $HgBa_2Ca_2Cu_3O_y$, (1223) $HgBa_2Ca_3Cu_4O_y$, (1234) and $HgBa_2Ca_4Cu_5O_y$(1245). The relationship between the value of $T_c$ and the number of the Cu-O planes shows a clear domeship. If the correlation as that in the Bi system exists in the Hg system, it will be more reliable and important.

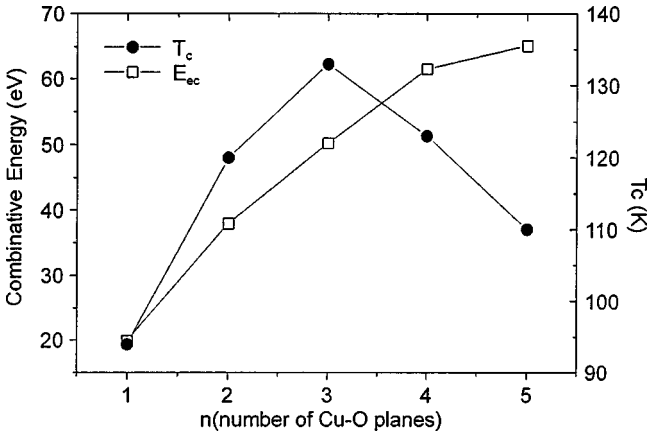


FIG. 6. The combinative energy (calculated by the first method) and the value of $T_c$ in the Hg system. There is no corresponding relationship between the energy and the value of $T_c$.

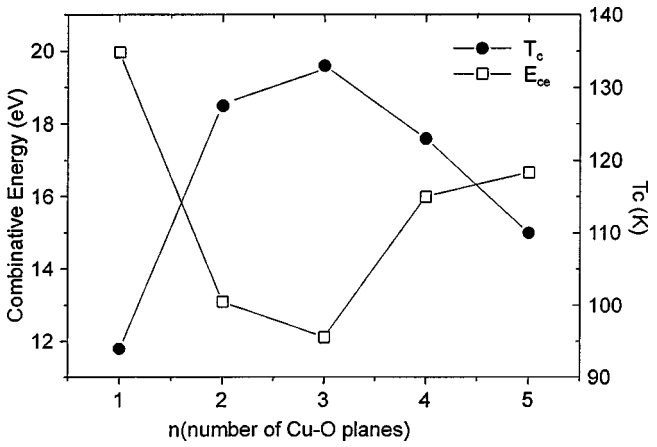


FIG. 7. The combinative energy (calculated by the second method) and the value of $T_c$ in the Hg system. There exists a close relationship between the energy and the value of $T_c$.

Table IV lists the parameters calculated by the first method and Fig. 6 illustrates them. Generally, the cohesive energy increases with the increase of atoms in one cell. The total cohesive energy increases with the increase of the Cu-O planes in the Hg-system superconductors, but it has no correlation with the value of $T_c$. In the Hg system, as the increase of the Cu-O planes, the value of $T_c$ gets a maximum (~133 K) in the 1223 phase, i.e., the number of the Cu-O plane is 3. Then it decreases with the increase of more Cu-O planes. For the 1234 and 1245 phases, they have more than three Cu-O planes, but the value of the $T_c$ of them is not over 133 K (see Table V). So far, there has not been a satisfying answer for the change of the value of $T_c$ as the number of the Cu-O planes. The following results may give a possible way to understand it. The cohesive energy of the Cu-O planes and remains also do not show correlation with the value of $T_c$. In Table IV the cohesive energy of the remains for the 1245 phase is negative. That means the suggested structure does not existence. These results may show that dividing the Cu-O planes into some independent plane is not reasonable and destroys some key factor in the cell.

The second method shows different result from the first one. We also calculated the same parameters as we did on the first model. The results are listed in Table V. Figure 7 illustrates the relationship among the combinative energy between the two blocks, the value of $T_c$, and the number of the Cu-O planes in the Hg system. Clearly, there exists an obvi-

TABLE V. The total cohesive energy of the cell ($E_n$), the cohesive energy of the perovskite block and the rock salt ($E_{pe}$:$E_{re}$), and the combinative energy ($E_{ce}$) between the perovskite block and the rock salt in the Hg system calculated by the second method.

| Superconductors | $E_n$ (eV) | $E_{pe}$:$E_{re}$ (eV) | $E_{ce}$ (eV) | $T_c$ (K) |
|---|---|---|---|---|
| Hg1201 | 162.84 | 59.803 : 83.063 | 19.97 | 94 |
| Hg1212 | 249.82 | 149.980 : 86.740 | 13.09 | 128 |
| Hg1223 | 339.87 | 238.080 : 89.677 | 12.11 | 133 |
| Hg1234 | 426.71 | 324.510 : 89.444 | 12.83 | 123 |
| Hg1245 | 517.41 | 411.160 : 89.575 | 16.67 | 110 |

ous correlation between the combinative energy and the value of $T_c$. As the value of $T_c$ gets the maximum in the three Cu-O planes, the combinative energy between the two blocks gets the minimum. The value of $T_c$ and combinative energy demonstrate very good correspondence.

In summary, by calculating the combinative energy between the two different blocks, and considering the correlation between the combinative energy and the value of $T_c$, we suggest that the interaction between the two structural blocks have a close correlation with the superconductivity.

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[1] For example, R. Kleiner, F. Steinmeyer, G. Kunkel, and P. Muller, Phys. Rev. Lett. **68**, 2394 (1992); Y. Zhao, G. D. Gu, G. R. Russel, N. Nakamura, S. Tajima, J. G. Wei, K. Uehara, and N. Koshizuka, Phys. Rev. B **51**, 3134 (1995).

[2] D. P. Billesbach and J. R. Hardy, Phys. Rev. B **39**, 202 (1989).

[3] J. B. Torrance and R. M. Metzger, Phys. Rev. B **63**, 1515 (1989).

[4] M. Muroi and R. Street, Physica C **248**, 290 (1995).

[5] H. Zhang, Y. Zhao, X. Y. Zhou, and Q. R. Zhang, Phys. Rev. B **42**, 2253 (1990).

[6] Y. Ohta and S. Maekawa, Phys. Rev. B **41**, 6524 (1990).

[7] Y. Mizuno, T. Tohyama, and S. Maekawa, Physica C **282**, 991 (1997).

[8] K. A. Mueller, Physica C **185**, 3 (1991).

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

[10] H. M. Evjen, Phys. Rev. **39**, 675 (1932).

[11] C. C. Toraidi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flippen, V. Chowdhry, and A. W. Sleight, Phys. Rev. B **38**, 225 (1988); H. Maeda, Y. Tanaka, M. Fukutumi, and T. Asano, Jpn. J. Appl. Phys., Part 2 **27**, L209 (1988); J. M. Tarascon, W. R. McKinnon, P. Barboux, D. M. Hwang, B. G. Bayley, L. H. Greene, G. W. Hull, Y. LePage, N. Stoffel, and M. Giroud, Phys. Rev. B **38**, 8885 (1988).

[12] H. Schwer, K. Conder, E. Kopnin, G. I. Meujer, R. Molinski, and J. Karpinski, Physica C **282**, 901 (1997).

[13] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill, New York, 1940).

[14] F. S. Galasso, *Structure, Properties and Preparation of Perovskite-type Compounds* (Pergamon, New York, 1969).

[15] G. B. Peacock, I. Gamesun, M. Slaski, J. J. Capponi, and P. P. Edwards, Physica C **289**, 153 (1997).