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The Effect of Substitution on the Critical Temperature in the Superconducting Compound $Y_{1-x-y}Ca_yPr_xBa_2Cu_3O_7$

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ABSTRACT

Substitution mechanism have great effects on superconducting properties of HTSC. In this research a method is proposed to calculate the electrostatic energy for the high temperature superconductor in case of single and double ion simultaneous substitution with different oxidation state and studying the effect of changes in this energy by this substitution. For YBCO the substitution of Ca ion (+2e) instead Y ion (+3e) decreases the electrostatic energy, and this effect increases with increasing concentration of Ca. Whereas the substitution of Pr ion (+4e) instead Y ion (+3e) increases the electrostatic energy, and this effect increases with increasing concentration of Pr. The simultaneous substitution of the ion Pr (+4e) for concentration (0,05, 0.1,0.15 and 0.2) with increasing the concentration of Ca from (0 to 0.1) for each Pr concentration shows increase in the electrostatic energy, but shows decrease with increasing Ca.The decrease of the electrostatic energy is due is due to increase the free hole which leads to increase the transition temperature T_c whereas the increase of the electrostatic energy is due to decrease in the free hole which leads to decrease T_c .

تأثير التعويض على درجة الحرارة الحرجة في المركب الفائق التوصيل

الملخص

إن عملية الإبدال لها تأثيرات كبيرة على خواص التوصيل الفائق للمركبات الفائقة التوصيل ذات الدرجة الحرارية العالية HTSC في هذا البحث اقترحت طريقة لحساب الطاقة الكهروستاتيكية للمركبات HTSC في حالة إبدال ذرة واحدة أو ذرتين في نفس الوقت ذوات جهد تأكسد مختلف ودراسة تأثير ذلك على الطاقة الكهروستاتيكية. لمركبات YBCO فإن إبدال أيون الكالسيوم ذو التكافؤ الثنائي الموجب محل الايتريوم ذو التكافؤ الثلاثي الموجب يقلل الطاقة الكهروستاتيكية وهذا التأثير يزداد بزيادة تركيز الكالسيوم . فيما يؤدي التبديل بأيون البراسوديوم Pr إلى زيادة الطاقة الكهروستاتيكية وهذا التأثير يزداد بزيادة تركيز أيون البراسوديوم ويودي الإبدال المتزامن للأيون بنسب (0.05 , 0.1 , 0.15, 0.2) إلى ازدياد الطاقة الكهروستاتيكية مع تناقصها مع تغيير تركيز أيون الكالسيوم (من 0 إلى 0.1). إن

زيادة الطاقة الكهروستاتيكية تعود إلى ازدياد عدد الفجوات , والتي تودي إلى ازدياد درجة حرارة التحول T_c . بيد أن نقصان الطاقة الكهروستاتيكية يعود إلى نقصان عدد الفجوات , والتي تودي إلى نقصان درجة حرارة التحول T_c.

INTRODUCTION

After the discovery of the High Temperature Superconductors (HTSC) in 1986 by (Bednorz and Muller, 1986), these compounds have received great importance. Especially after (Wu et al., 1987) was succeeded to synthesize the superconductor $YBa_2Cu_3O_7$ (YBCO).And since then HTSC have moved into realm of practical application because they are mostly superconducting above the boiling point of liquid nitrogen (77 K) which is cheaper and has much greater cooling capacity than liquid helium, thus refrigeration cost was decreased by thousand time. The newly discovered materials are CuO based ceramics that remain Superconducting near 100 K. Soon after this discovery many other Superconducting compounds with higher critical temperature was synthesized (Meada et al, 1988), (Schilling, 1993) .

Substitution of the ion Sr^{2+} instead of Ba^{2+} results in a higher T_c in the compound LaBaCuO. The substitution mechanism and the increase of pressure can both leads to higher transition temperatures and these properties is of fundamental importance for understanding HTSC, and points the way to the synthesis of oxide superconductors with higher T_c . The increase of T_c observed by pressure led to replace La^{3+} by Y^{3+} leading to a first superconductor with T_c higher than the boiling point of liquid N_2 (77 K) (Chu, 2004). The compound synthesized was $YBa_2Cu_3O_{7-8}$ with a T_c of 92 K .For this nice properties it is the most widely studied of the HTSC oxides (Jorgensen et al., 1991). Its superconducting properties such as T_c , the maximum current density that it can carry ,and the maximum strength of magnetic field that it could expel via the Meissner effect (H_c) are all highly sensitive to crystal structure and crystal quality of the YBCO. Many studies shows a close relation between the ionic substitution and T_c in YBCO (Neumeier et al., 1989)and other HTSC compounds (Takagi et al., 1989).

The aim of this study is to investigate the role of two types of substitutions , Ca^{2+} and Pr^{4+} on the electrostatic energy of the YBCO crystal due to their effect on the transition temperature of the superconductor YBCO, the study depends on model of the crystal structure in which positions of the many atoms forming this big crystal are linked to certain sites Cu(1), O(1), O(2), …etc. This model consider ionic forces as the main forces between its constituents in the complex copper oxide crystal.

Theory

In order to find the effect of the substitution on the electrostatic energy , a model of crystal structure must be considered which shows the positions of the different atoms in the crystal , because the crystal is anisotropic one and as we will see from the models two of the CuO planes are distorted. However this anisotropy and distortion complicate the calculation as we will see, fortunately it brings high temperature superconductivity for these compounds (Jorgensen et al., 1991).

Models of crystal structure of $YBa_2Cu_3O_7$

The Crystal structure of $YBa_2Cu_3O_7$ is usually represented as in fig.1 of three units of pervoskite of structure ABO_3. Three unit cells of the pervoskite are expected to contain three A atoms with coordination number 12 and three B atoms with coordination number 6 (octahedral) and nine oxygen atoms. The unit cell shown in fig.1 ,however, contains only seven oxygen atoms ,inevitably reducing the coordination numbers around the yttrium and barium atoms in the A-sites and the copper atoms in the B–sites .The cubic symmetry is also destroyed and the unit cell is shown orthorhombic, a not equal to b and c = 3b . (Sharp ,1990).

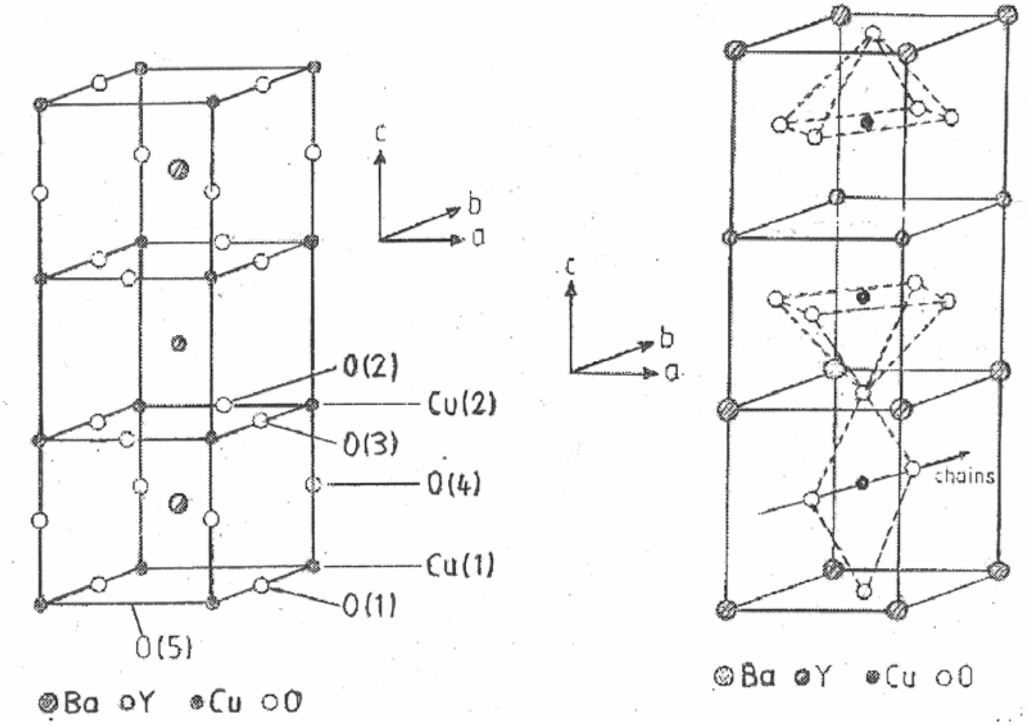

Fig. 1: Models of the crystal structure of YBCO with Cu atoms at the corners (left drawing) , and with Ba atoms at corners (right drawing) (Sharp , 1990)

There is ordering of Ba and Y atoms on the a-sites, such that the center of each triple atoms is occupied by Y with Ba atoms above and bellow. One of the missing O atoms has been removed from the plane around the Y atom, reducing its coordination number from 12 to 8. The other O atom is omitted from the O(5) site in the top and bottom planes of the unit cell, leaving the Ba atom in distorted ten fold coordination fig.2 The copper atoms occupy the B-sites. Inevitably the loss of O atoms affect the coordination of the Cu atoms this is clear from fig .1 (right drawing) where two of the Cu atoms those in the Cu(2) are coordinated to five oxygen atoms in the form of a square pyramid (one pointing up and one pointing down), while the other copper atom are coordinated to four oxygen atom in a square planar configuration. Whereas the square planar site is reasonably symmetrical with two Cu-O bonds of 1.95 A and two of 1.83 A, the five coordinate site is distorted with one Cu-O bond (2.28 A) significantly longer than the other four (1.95 A).

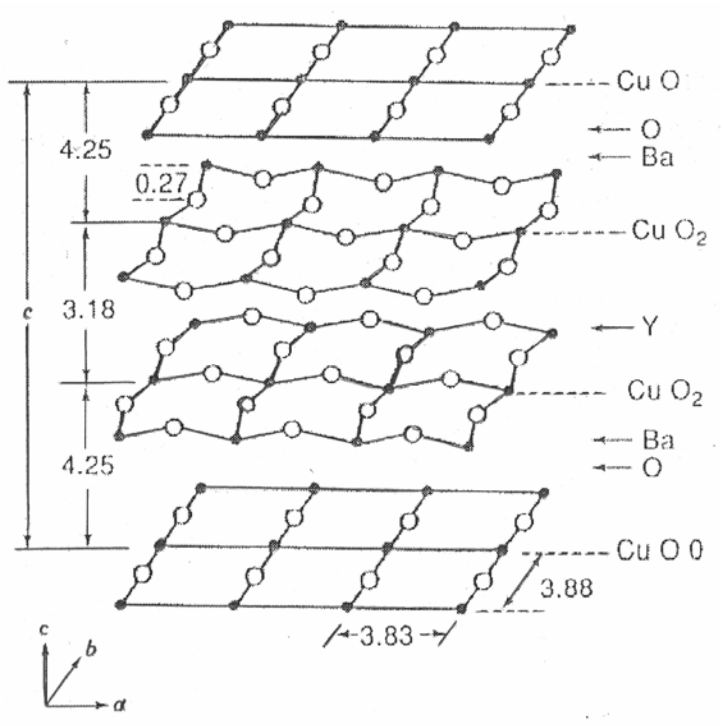

Fig. 2: Layered drawing of YBCO crystal structure showing the distortion in the CuO layer. (Poole et al., 1995)

Crystal electrostatic energy without substitution

One of the important properties of the HTSC are their ionic bonds (Wright and Butler .,1990) .As shown in fig.1(right drawing) Cu ion are coordinated to 5 oxygen ions as first nearest neighbors, and 8 La ions as second nearest neighbors. First of all we try to calculate the binding energy for the pure crystal i.e. without Ca and Pr substitution . If we try to compute the electrostatic energy (E),which as we think: is an important parameter that greatly affects charge distribution inside the crystal, especially when we try to understand the effect substitution on the properties of the superconductor , because it affect the charge balance by the introduction of the new ion ,with different valances sizes. To calculate the electrostatic energy E for the crystal we use the following relation.

$$E = \frac{1}{4\pi\varepsilon_o} \sum_{1}^{i} \frac{Qq_i}{r} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Q, q_i, r are the charge of the reference ion, the charge of the ion i and the distance between them respectively. Madelung method (Kittel ,2005) was not followed strictly because of the anisotropy and the distortion of this crystal as shown in the figures .So we have to modify (equation 1) to account for the (three types of ions present in the crystal i.e. Cu ,O , Ba) ,thus

$$E = \frac{1}{4\pi\varepsilon_o} \left(\sum_{1}^{m} \frac{Qq_{Cu}}{r_{Y-Cu}} + \sum_{1}^{n} \frac{Qq_O}{r_{Y-O}} + \sum_{1}^{l} \frac{Q_{Ba}}{r_{Y-Ba}} \right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (2)$$

$r_{Y-Cu}, r_{Y-O}, r_{Y-Ba}$ stands for the distances of the atoms Cu , O , Ba from the reference atom Y, m,n,l are numbers of the former atoms in the crystal respectively. Still another modification must be entered accounting for special situations of the O(1) ,O(2) and Cu(1) …etc atoms as seen in fig.1 . For this reason another figure was drawn pointing to the different situation of this atoms as shown in fig.3 . and we have at first to find values of the r :

$$r_{Y-Cu(2)} = \sqrt{r_1^2 + r_2^2 + r_3^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$r_{Y-O(2)} = \sqrt{r_2^2 + (r_3 - 0.27)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$r_{Y-O(3)} = \sqrt{r_1^2 + \left(r_3 - 0.27\right)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$r_{Y-O(4)} = \sqrt{r_1^2 + r_2^2 + (r_3 + r_4)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

$$r_{Y-O(1)} = \sqrt{r_1^2 + (r_3 + r_4 + r_5)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

$$r_{Y-Cu(1)} = \sqrt{r_1^2 + r^2{}_2 + (r_3 + r_4 + r_5)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$r_{y-Ba} = r_3 + r_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

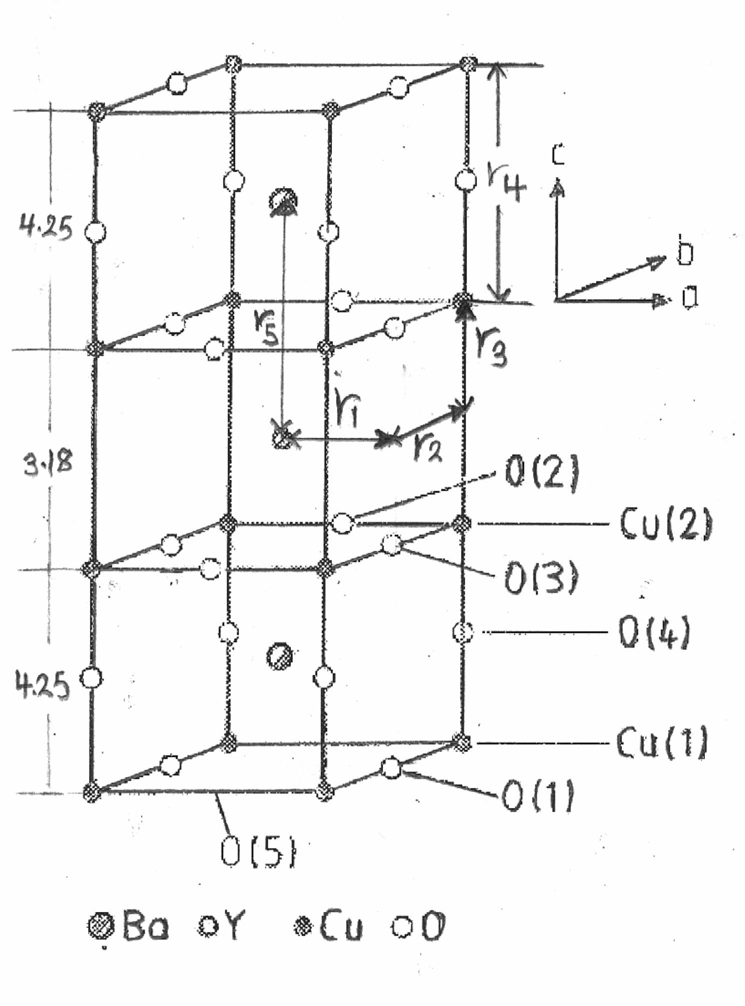

Fig. 3 : The crystal structure showing the essential distances (r_1 , r_2 ,…..etc) needed to calculate the inter-atomic distances.

The corresponding electrostatic energy are

$$E_{Y-Cu(2)}=\frac{1}{4\pi\varepsilon_o}\times 2\times\sum_{1}^{4}\frac{1}{8}\frac{(+3e)(+2e)}{r_{Y-Cu(2)}} \qquad \ldots\ldots\ldots\ldots(10)$$

$$E_{Y-O(2)}=\frac{1}{4\pi\varepsilon_o}\times 2\times\sum_{1}^{2}\frac{1}{4}\frac{(+3e)(-2e)}{r_{Y-O(2)}} \qquad \ldots\ldots\ldots\ldots(11)$$

$$E_{Y-O(3)}=\frac{1}{4\pi\varepsilon_o}\times 2\times\sum_{1}^{2}\frac{1}{4}\frac{(+3e)(-2e)}{r_{Y-O(3)}} \qquad \ldots\ldots\ldots\ldots(12)$$

$$E_{Y-O(1)}=\frac{1}{4\pi\varepsilon_o}\times 2\times\sum_{1}^{2}\frac{1}{4}\frac{(+3e)(-2e)}{r_{Y-O(1)}} \qquad \ldots\ldots\ldots\ldots(13)$$

$$E_{Y-O(4)}=\frac{1}{4\pi\varepsilon_o}\times 2\times\sum_{1}^{4}\frac{1}{4}\frac{(+3e)(-2e)}{r_{Y-O(4)}} \qquad \ldots\ldots\ldots\ldots(14)$$

$$E_{Y-Cu(1)}=\frac{1}{4\pi\varepsilon_o}\times 2\times\sum_{1}^{4}\frac{1}{8}\frac{(+3e)(+2e)}{r_{Y-Cu(1)}} \qquad \ldots\ldots\ldots\ldots(15)$$

$$E_{Y-Ba}=\frac{1}{4\pi\varepsilon_o}\sum_{1}^{2}\frac{(+3e)(+2e)}{r_{Y-Ba}} \qquad \ldots\ldots\ldots\ldots(16)$$

thus the total energy ET_Y for YBCO crystal without substitution is :

$$ET_Y=E_{Y-Cu(2)}+E_{Y-O(2)}+E_{Y-O(3)}+E_{Y-O(4)}+E_{Y-Cu(2)}+E_{Y-Cu(1)}+E_{Y-Ba} \qquad \ldots.(17)$$

by calculating the values of (r) using equations 3 to 9, then substituting the results into their corresponding equations i.e. 10 to 16, and by substituting the results in equation 18 the total electrostatic energy without substitution can be found.

Crystal Electrostatic Energy With Substitution

a - Substitution by Ca

When Substituting Y^{3+} by the Ca^{2+} we must consider two essential changes

1 – The change in the charge of the ions will be from (+3e) to (+2e) .

2 - The difference in radius of the ions from (0.94 A) for Y^{3+} ion to (0.99 A) for Ca^{2+} ion.

So we have to correct all the equations (3 to 16).Correction of charge is done by changing the charge from(+3e) to (+2e) .

In order to correct the change in the radii by the substitution with Ca atom we must correct(r_1, r_2, r_3, r_5)to ($r_1+0.05, r+0.05_2, r_3+0.05, r_5+0.05$)

And thus the total electrostatic energy when Substituting Y^{3+} by the Ca^{2+} completely ET_{Ca}

$$ET_{Ca}=E_{Ca-Cu(2)}+E_{Ca-O(2)}+E_{Ca-O(3)}+E_{Ca-O(4)}+E_{Ca-Cu(2)}+E_{Y-Cu(1)}+E_{Ca-Ba} \ldots.(18)$$

Thus the total electrostatic energy with substitution with Ca

$ET_{Y(1-x),Ca(x)}$

$$ET_{Y(1-x),Ca(x)}=ET_Y(1-x)-E_{Ca}x \qquad \ldots\ldots\ldots\ldots(19)$$

Thus the total electrostatic energy with substitution with Pr $ET_{Y(1-y),\Pr(x)}$

$$ET_{Y(1-y),\Pr(y)} = ET_Y(1-y) - E_{\Pr}\, y \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

b - Substitution by Ca and Pr

The steps followed in the previous section to calculate the total energy when substituting by Ca must be followed putting in mind that radius of Pr ion is (1.01 A) and its charge is (+4e)

And thus the total electrostatic energy when Substituting Y^{3+} by the Pr^{4+} completely $ET_{\Pr}$

$$ET_{\Pr} = E_{\Pr-Cu(2)} + E_{\Pr-O(2)} + E_{\Pr-O(3)} + E_{\Pr-O(4)} + E_{\Pr-Cu(2)} + E_{\Pr-Cu(1)} + E_{\Pr-Ba} \;\ldots(21)$$

Thus the total electrostatic energy with substitution with Ca and Pr $ET_{Y(1-x-y),Ca(x),\Pr(y)}$

$$ET_{Y(1-x-y),Ca(x),\Pr(y)} = (ET_Y(1-y) - ET_{\Pr}\, y)(1-x) - E_{Ca}\, x \quad \ldots\ldots\ldots\ldots\ldots\ldots (22)$$

Results and Discussion

According to the equations (3 to 9) we can calculate the distances of the ions from the reference ion if the values (r_1,r_2, …) is known . This are found from the reference (Wright and Butler .,1990)

Table 1 : values of the main atomic distances shown in fig 4 needed to determine the values of inter-atomic distances in table 2 .

Reference atom	r_1 **A**	r_2 **A**	r_3 **A**	r_4 **A**	r_5 **A**
Y	1.91	1.94	1.59	4.25	3.41
Ca	1.96	1.99	1.64	4.25	3.46
Pr	1.98	2.01	1.66	4.25	3.48

Table 2 : Inter-atomic distances between the reference atoms C (Y, Ca , Pr) and the other atoms in the crystal

Reference ion(C)	$r_{C-Cu(1)}$	$r_{C-O(2)}$	$r_{C-O(3)}$	$r_{C-O(4)}$	$r_{C-O(1)}$	$r_{C-Cu(2)}$	r_{C-Ba}
Y = 1	3.152	2.346	2.321	4.921	6.144	6.443	3.41
Ca = 1	3.660	2.415	2.391	5.002	6.207	6.518	3.46
Pr = 1	3.273	2.443	2.419	5.034	6.232	6.548	3.48

To find the electrostatic energy for the YBCO crystal equations 10 to 16 was applied using results of table 2 , from these values of the inter-atomic distances, the values of the electrostatic energy for the un substituted YBCO (first raw in table 3). Then the same procedure was followed for finding the electrostatic energy when atoms of Ca and Pr are substituted completely (2nd and 3rd in table 3) . The dependence of E on the concentration

Table 3: electrostatic energy between central reference ion and the main ions in the crystal

Reference ion (c)	$E_{C-Cu(1)}$	$E_{C-O(2)}$	$E_{C-O(3)}$	$E_{C-O(4)}$	$E_{C-O(1)}$	$E_{C-Cu(2)}$	E_{C-Ba}
Y=1	-17.127	23.013	23.258	21.944	8.788	-12.571	-31.671
Ca=1	-9.835	14.9003	15.054	14.393	5.7993	-8.2838	-20.809
Pr=1	-21.994	29.462	29.761	28.600	11.551	-14.658	-41.379

The total energy for each type of ions can be found by summing the values of each row.

The dependence of E on the concentration of the substituted ion Ca can be found by applying equation 18 and repeating the procedure in table 1, 2 and 3 for each concentration. The results are shown in fig 4

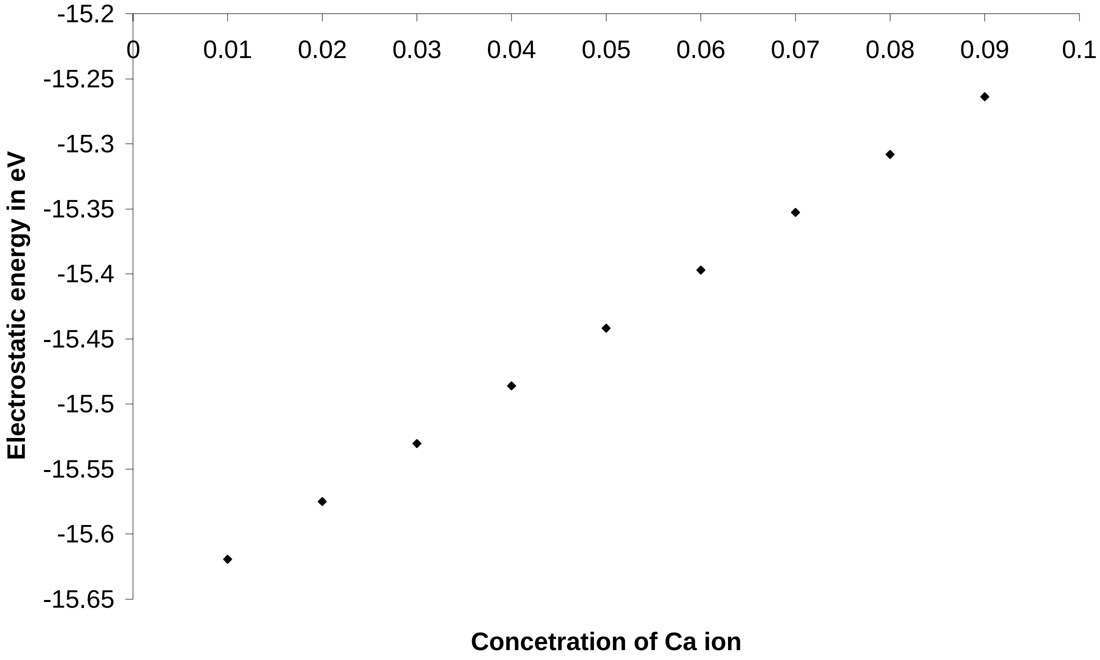

Fig. 4 : the dependence of the electrostatic energy on the concentration of Ca.

The change in the electrostatic energy is negative, this give us good indication about our model, because this energy is the energy needed to support the crystal structure. With the introduction of Ca this negative potential decreases linearly .Because Ca has (+2e) charge and the original Y ion have (+3e) charge This gives an important conclusion that substitution by Ca brings more holes near the Fermi level to be candidates to form Cooper pairs, which as a result increases the transition temperature T_c this conclusion supports the experimental results(Neumeier et al.,1989) about the increase of T_c within this range. In order to confirm this result another additional substitution of Pr atoms with ionic charge in this case (+4e) which in this case greater than that of Y ion (+3). The dependence of E on the concentration of the substituted ion Pr can be found by applying equation (21) and repeating the procedure in table 1, 2 and 3 for each concentration .

The results are shown in fig 5. As shown the result is opposite to that of the case of substitution with Ca . This happens because of the decrease of holes near the Fermi level and as a result the formation of Cooper pairs, which as a result decreases the transition temperature T_c this conclusion is support the experimental results (Neumeier et al., 1989)about the increase of T_c within this range.

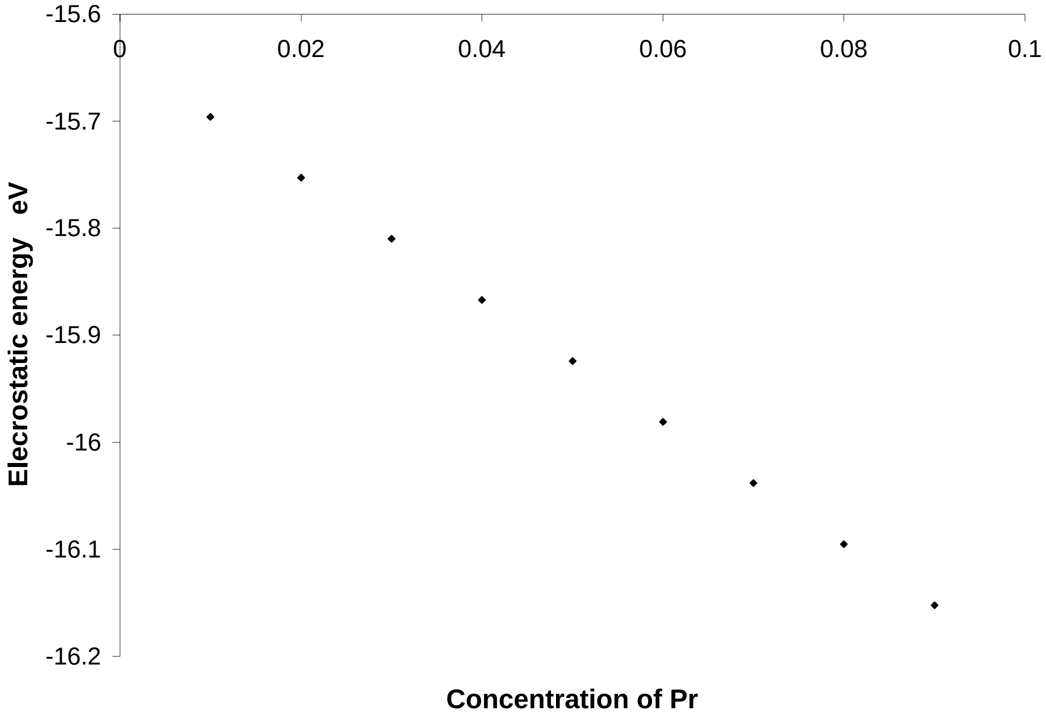

Fig. 5: the dependence of the electrostatic energy on the concentration of Pr .

A study of the simultaneous effects of both substitutions with Pr and Ca atoms to study the effect of that substitution on the electrostatic energy was done with Pr concentration (0 ,0.05,0.1,0.15 and 0.2) when concentration of Ca changes from (0 to 0.1). The method which suggested in this research was able to do such a job and the results is shown in fig.6.

Substitution with Pr with charge (+4e) will increase the negative potential of the crystal.With increasing the concentration of Pr from (0 to 0.2) the curves in fig.6 shows that : the potential energy increases for all values of Ca concentration. For the same Pr concentration the potential decreases with increasing Ca concentration , this as we have been said formerly that is an indication of increase of positive holes, Whereas the increase of Pr (+4e) will decrease the number of holes as a result of the decrease of holes which is predominant here and decrease of T_c occurs as it is confirmed by experiments. The calculation of electrostatic energy was limited substitution by Ca in the range (0 to 0.1) because T_c increases within this range and reach its maximum value at concentration of Ca about 0.1, increasing the concentration above this value decreases the transition temperature due to the formation of oxygen vacancies (Takagi et al., 1989).

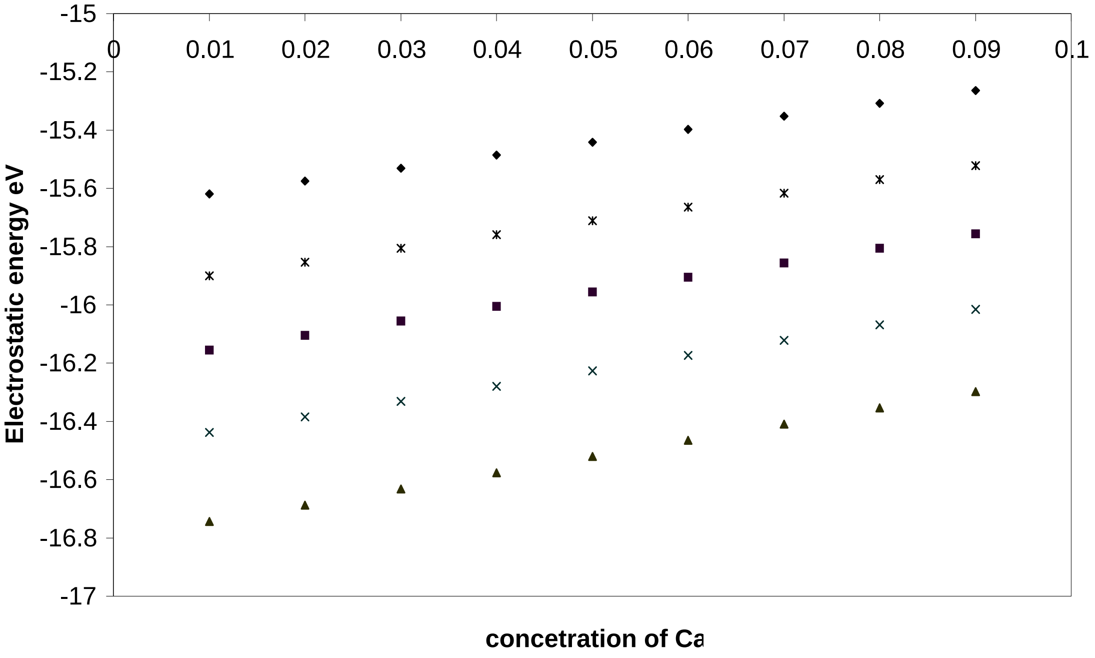

Fig. 6: the dependence of the electrostatic energy on the concentration of Ca for different values of substitution with Pr (0,0.05,0.1,0.15,& 0.2) from the upper curve to the lower curve respectively .

CONCLUSIONS

1 – A method was proposed to calculate the electrostatic energy for the high temperature superconductor in case of single and double ion simultaneous substitution with different oxidation state and studying the effect of changes in this energy by this substitution.

2 – For YBCO the substitution of Ca ion (+2e) instead Y ion (+3e) decreases the electrostatic energy , and this effect increases with increasing concentration of Ca.

3 - For YBCO the substitution of Pr ion (+4e) instead Y ion (+3e) increases the electrostatic energy , and this effect increases with increasing concentration of Pr.

4 - The simultaneous substitution of the ion Pr (+4e) for concentration (0,05, 0.1,0.15 and 0.2) with increasing the concentration of Ca from (0 to 0.1) is the sum of two effects.

5 – The decrease of the electrostatic energy is due is due to increase the free holes, which leads to increase T_c whereas the increase of the electrostatic energy is due to decrease in the free hole which leads to decrease T_c .

REFERENCES

Bednorz, J.G., Muller, K.A., 1986, Possible high-T_c superconductivity in the Ba-La-Cu-O system, Z. Phys. B. ,V.64, PP.186- 193.

Chu, C.W., 2004, Materials and physics of high temperature superconductors ,Hong Kong university press, 411 P.

Jorgensen, J.D, D.G., Hinks, P.G., Radaelli, Shiyou Pei, P. Lightfoot, B., Dabrowski, C. U., Segre,and B.A., Hunter, 1991 ,Defects, defect ordering ,structural coherence and superconductivity in the 123 copper oxides, Physica C 184, PP. 85 – 189.

Kittel, C., 2005, Introduction to Solid State Physics. 8th edit., John Wiley and Sons, 680p.

Meada, H.; Y. Tanaka, F. Fukutomi, T. Asano, 1988, Anew High-Tc oxide superconductor without rare earth element ,Jpn . J. Appl. , Phys., V. 27: P.L209 .

Neumeier , J.J. ,M.B .Maple and I. k. Schulers ,1989 ,Hole filling and Pair breaking by Praseodymium ion in Yttrium Barium copper oxide , Phys. Rev. Lett. ,V.63, 2516 P .

Pool, C.P., H.A. Farach, and R.J. Creswick, 1995, High Temperature superconductivity : Ca Academic , pp.182- 191. In "Engineering Superconductivity edited by, Peter, J.L. 2000, Wiley –Interscience , New York .

Sharp, J.H., Structural Chemistry of mixed oxides superconductors, Br. Ceram. Trans., J. 1990 ,V. 89 ,No. 1, PP.1-7 .

Schilling, A., 1993, Superconductivity rising temperature attributed to a mercury containing compound , Nature ,V.363 ,P.56 .

Takagi, H., 1989, Electron doped High – T_c superconductors, Phys. Rev. B.,V. 40 2254P. Wright , N.F. and Butler W. H. ,1990, Ionic model for the stability of the Y – Ba – Cu High-Temperature Superconductors ,Phys. Rev. Vol.42, No. 7,PP .4219 - 4227.

Wu, M. K., Ashburn , J.R. , Torn ,C.J. , Superconductivity at 93 K in a new mixed phase Y-Ba-Cu-O compound system at ambient pressure , Phys. Rev. Lett., 1987,V. 58, No 9, PP. pp.908-910 .