J. Edu. & Sci., Vol. (22), No. (1) 2009

The Effect of Ionic Substitution on the E.P. of $La_{2-x}Sr_xCuO_4$ Superconductor using Madelung Method

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Received 18 / 04 / 2007 **Accepted** 03 / 10 / 2007

المستخلص

درس تأثير استبدال الأيون Sr^{+2} بدلاً من La^{+3} في المركب $La_{2-x}Sr_xCuO_4$ ولقد لوحظ ازدياد في الطاقة الكامنة بزيادة تركيز السنترونتيوم مع تغير مفاجئ عند التراكيز القلية وهذا يعني تغيراً طورياً في التركيب البلوري. إن ازدياد T_c مع ازدياد التركيز والملاحظ سابقا ربط هنا مع ازدياد الطاقة الكامنة . و وجدت علاقة بينهما $T_c = 90.227 - 6.604E - 1.545E^2$ ، إن هذا الازدياد يعود إلى ظهور الثقوب بفعل الفرق بين تكافؤ (La&Sr)، والذي يقود إلى تقلص البلورة بفعل انخفاض التنافر بين ذرات (Sr&Cu) والذي له نفس تأثير الضغط الهيدروستاتيكي والذي يؤدي إلى ازدياد T_c. وعندما تكون $x \rangle 0.15$ تظهر الفجوات والتي تقوم بحجب المجال الكهروستاتيكي. مما يودي إلى تناقص قيمة T_c .

Abstract

The effect of substitution of the ion Sr^{+2} instead of La^{+3} in the superconductor $La_{2-x}Sr_xCuO_4$ was studied, an increase in electrostatic potential energy E. P. (E) with increase of Sr % was noticed, and a step change in P. E. when Sr is added is noticed indicating a phase change occurrence in the crystal structure .Increase of T_c, with the increase of Sr, noticed earlier, is linked with increase of E.P. and a relation between E.P. and T_c is found $T_c = 90.227 - 6.604E - 1.545E^2$, the increase of T_c is due the creation of holes by valance difference between La & Sr, which also leads to collapse of crystal by reduction of repulsion between Sr & Cu atoms this have the same effect as the application of pressure on the crystal, which increases T_c also. For x >0.15, T_c decreases due to the appearance of vacancies which may have screening effect of the electrostatic field.

Introduction

After the discovery of the High Temperature Superconductors HTSC (Bednorz & Muller, 1986), these compounds have received great importance, since (Wu et al, 1987) was succeeded to synthesize the superconductor $YBa_2Cu_3O_7$ (YBCO) (T_c=95 K). 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 temperatures was synthesized, like Bi-Sr-Ca-Cu-O (BSCCO), and Ba-Sr-Ca-Cu-O (BSCCO) (Sharp, 1990). Higher critical temperature was recorded like that of the compound Hg-Ba-Ca-Cu-O (HBCCO) with the critical temperature 135 K (Chu, 2002).

The CuO compounds are insulators. By substituting for certain atoms in the unit cell, these materials are made to behave as metals and may become superconductors. The transition temperature depend strongly on the density of states at the Fermi level, that parameter in turn is strongly affected by doping of the initial ceramics with other atoms of different valance to provide extra electrons (Or holes) which are then available for participation in Superconductivity (Chu, 2002).

The practice of doping has along history in the field of semiconductors, and similar efforts applied to HTSC. A tremendous quantity of substitution have been tried to improve mechanical, magnetic or transport properties of these materials. The Fermi level is badly distorted from a simple spherical shape by the anisotropy in HTSC(Pickett,1989).

Superconductivity observed in La_2CuO_4 system when La is partially substituted by Ba then forming the compound $La_{2-x}Ba_xCuO_4$ the value of T_C reaches maximum value when x = 0.15 . Substitution by divalent ions $M = Ba^{2+}, Sr^{2+}, Cu^{2+}$ Leads to the appearance of superconductivity for $0.05 < x < 0.3$ in $La_{2-x}M_xCuO_{4-y}$ (Takagi et al, 1989).

The aim of this research is to study the effect of ionic substitution of Sr ion in the compound $La_{2-x}Sr_xCuO_{4-y}$ on the electrostatic potential energy and its relation to the critical temperature T_c.

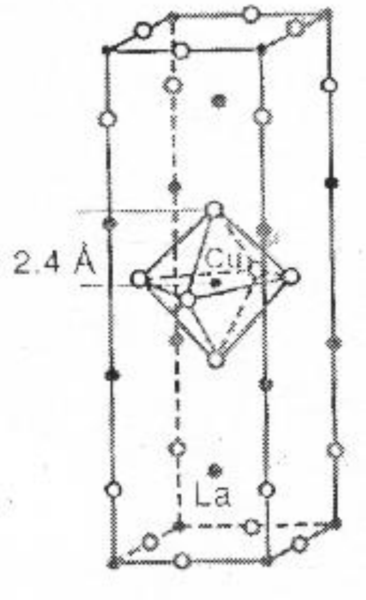

Fig.1: the crystal structure of La-Sr-Cu-O, octahedral structure surrounding the Cu ion (Sharp, 1990)

The crystal structure

The structure of the Superconducting phase was identified as a derivative of the layered pervoskite and shown in figures 1 and 2 .Fig. shows CuO_2 layers which consist of octahedrally coordinated Cu, with Cu-O length of 1.9 A in the a-b plane and 2.4A in c direction .Also the Cu atom occur at (000) and (½, ½ , ½) lattice sites in the unit cell, similar to the body centered structure. The substituted Sr Ion occupy a fraction of La ion and the difference in valance bring about a increase in the number of holes. Superconductors with hole conduction are called P-type similar to that followed in semiconductors. Since La^{3+}, Sr^{2+} are large ions the compound formed have the formula A_2BO_4, unlike the pervoskite which has the ABO_3. If however, a slice of the pervoskite structure of thickness one unit cells taken fig. 2. Thus it has a stoichiometry A_2 BO_4. If these units are displaced relative to one another they formed a tetragonal structure with c = 3a. Where a is the length of the cell edge of the pervoskite building bricks. In this structure the x of the copper atoms, must be in the oxidation state (3+), in order to compensate for the presence of the Sr atoms (Sharp, 1990).

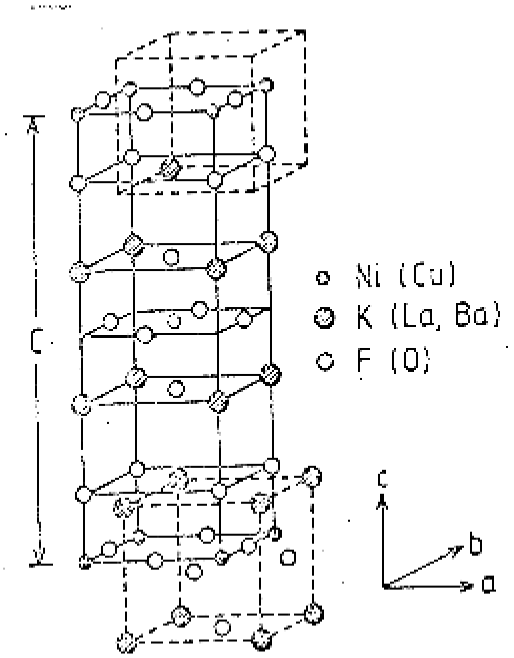

Fig.2: derivation of the A_2BO_4 structure from three pervoskite units (Sharp, 1990).

Theory

One of the important properties of the HTSC are their ionic bonds (Wright & Butler,1990). As shown in fig.2 Cu ion are coordinated to six 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 Sr substitution. If we try to compute the electrical potential energy E.P., which as we think: is an important parameter that greatly affects charge distribution inside the crystal, especially when we try to understand the effect of doping on the properties of the superconductor, because it affect the charge balance by the introduction of the new ion, with different valances. to calculate the E.P. we use Madelung method (Torrance & Metzger, 1989) where the electrical potential energy between a reference ion and the other ions of the crystal is considered. This energy is calculated as follows (Kittel, 2005).

$$E = \frac{-q^2}{4\pi\varepsilon_o R}\alpha \qquad \text{...} \quad (1)$$

q, α are the charge and the Madelung constant (MC) which expresses the geometrical structure of the crystal. R is the nearest neighbor distance from the reference ion. The MC can be calculated on the basis of the position of the ions and their share in the charge of the crystal therefore:

$$\alpha = R\sum_j \frac{(\pm)}{r_j} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

R are the nearest neighbors distance and r_j the distance of the j ion from the reference ion.

For our crystal La_2CuO_4, and as shown in figures 1 & 2. If we consider Cu as reference ion, therefor we have four oxygen ions in the CuO plane with distance 1.9 A, two other O ions at the epics of the of the octahedral with distance 2.4 A from Cu ion, and 8 La with distance $R\sqrt{3}$. On the above basis the MC for our crystal without doping is:

$$\alpha = \left[\frac{V_{OP}N_{OP}/4}{1} + \frac{V_{OE}N_{OE}}{1.263} - \frac{V_{La}N_{La}/8}{\sqrt{3}}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

V_{OP} & N_{OP} …etc are the valance and number of the neighboring ions. The subscripts OP, OE, stands for the plane and the epics ions, the same are for the subscript of the La ion, and the electrostatic energy electron volt (eV) is

$$E = -0.843 \left[\frac{V_{OP}N_{OP}/4}{1} + \frac{V_{OE}N_{OE}}{1.263} - \frac{V_{La}N_{La}/8}{\sqrt{3}}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

in order to consider the effect of doping with Sr^{2+} on the electrostatic energy some changes in eq.4 must be done especially on the term of La ions .

$$E = -0.843 \left[\frac{V_{OP}N_{OP}/4}{1} + \frac{V_{OE}N_{OE}}{1.263} - \frac{V_{La}N_{La}/7}{\sqrt{3}}(1-x) - \frac{V_{Sr}N_{Sr}}{\sqrt{3}}(x)\right] \qquad \ldots\ldots \quad (5)$$

The value of x represent the percent of the substitution of Sr^{2+} instead of the ion La^{3+}.

Results and Discussion

To find the effect of substitution of the Sr ion instead La ion we apply the above procedure in the theoretical part . By applying equations 3 and 4 we can calculate the MC after substituting for the valances , distances ,number of ion considering Cu as a reference ion .So we have for MC.

$$\alpha = \left[8 + \frac{8}{1.263} - \frac{6}{\sqrt{3}}\right]$$

and the electrostatic energy is equal to in electron volt (eV).

$$E = 0.843 \left[8 + \frac{8}{1.263} - \frac{6}{\sqrt{3}}\right] \quad \text{eV}$$

$$E = -9.149eV$$

after calculating the energy in non doped crystals, we use eq.5 to calculate the effect of substitution with Sr on the electrostatic energy of the doped crystals . The result of this calculations are shown in figure 3 and also in table 1.

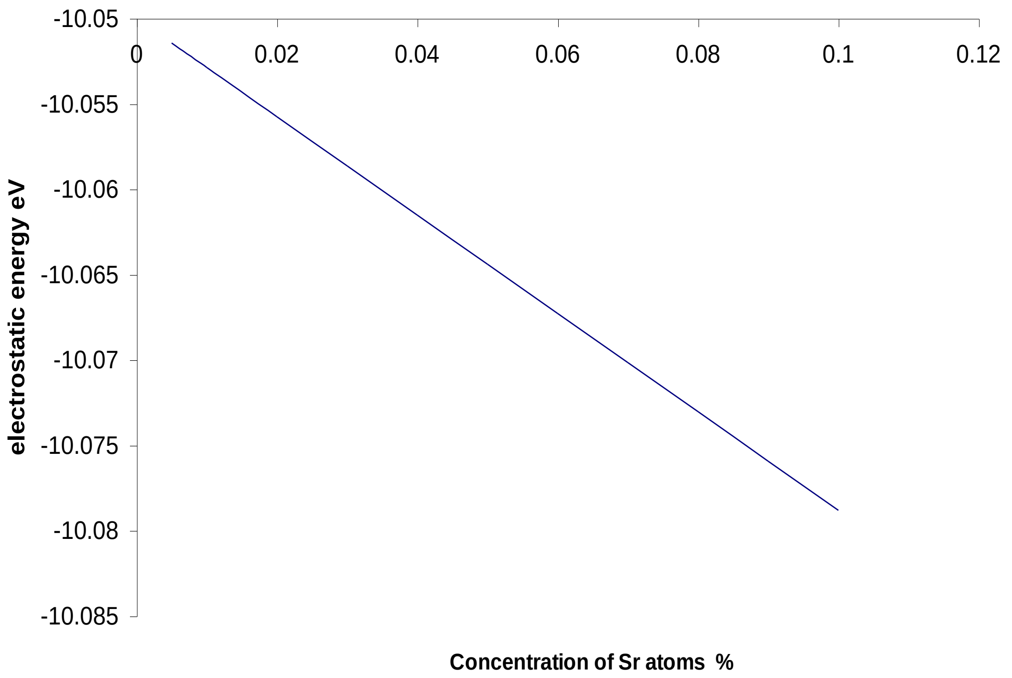

Figure 3 : The dependence of E.P. on the concentration of Sr in the crystal .

It is clear that there is an increase in the potential energy by the introduction of Sr. This increase will change the binding energy of the crystal, this effect represent a good result, because it show us an increase in the potential energy due to the increase in Sr concentration. As seen from figure 3, we start with the concentration 0.01 and not from 0 concentration which represent un substituted La_2CuO_4 crystal. This figure is such drawn to show clearly the effect of changing the concentration of Sr on the E.P. which appear clearly in fig.3. The figure 4 is like figure 3, but we have been started from the 0 concentration, this figure show a sudden change in the potential by the transformation from the compound La-Cu-O to the compound La-Sr-Cu-O.

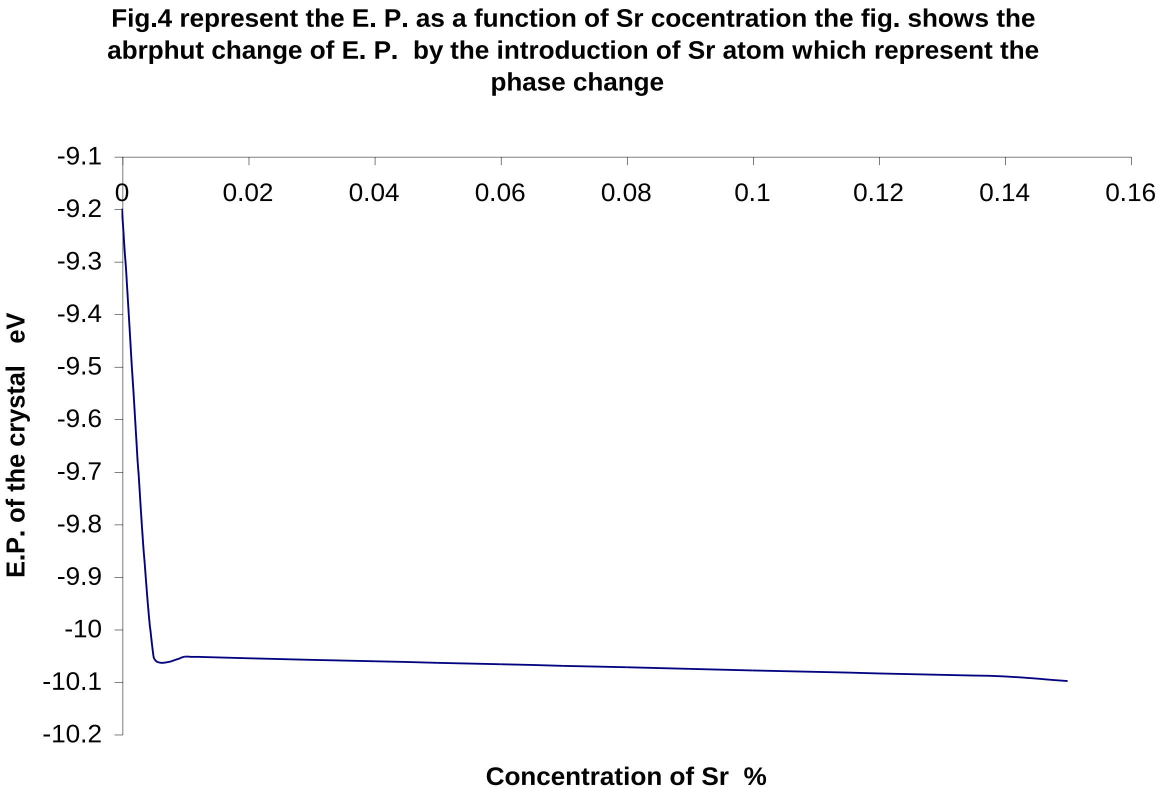

Figure 4 : Represent the E.P. as a function of Sr concentration the figure shows abrupt change of E.P. by the introduction of Sr atom which reveal the phase change.

As shown in the above figure that: the introduction of the Sr ion lead to abrupt change in the potential energy, which is an expression of the second order phase transition, which means that we have a structural change in the crystal (Cyrot, Pavuna, 2004). This second order phase transformation is a characteristic property of high temperature superconductors. thus our treatment of the dependence of the concentration on the E. P. brings us to show the phase transformation which must be occurred in order that a normal material will be transformed into superconducting material. This means that our treatment of the superconductivity using the electrostatic potential is a valid approach to handle part of the superconducting problems, thus electrostatic potentials shared in the process of superconductivity as one of the important factors. the abrupt change in the E. P. dose not lead to the appearance of superconductivity directly as we will see from the next figure, because there are other factors which plays also major roles like the electronic configuration inside the crystal spin effects (Maki et al, 2002), (Pickett, 1989).

If we compare the effect of the increase of the potential with the increase of the concentration of Sr with the study of (Takagi et al, 1989) where they showed that there an increase in T_c with increasing Sr concentration, their results is shown in the upper half of figure 5 :

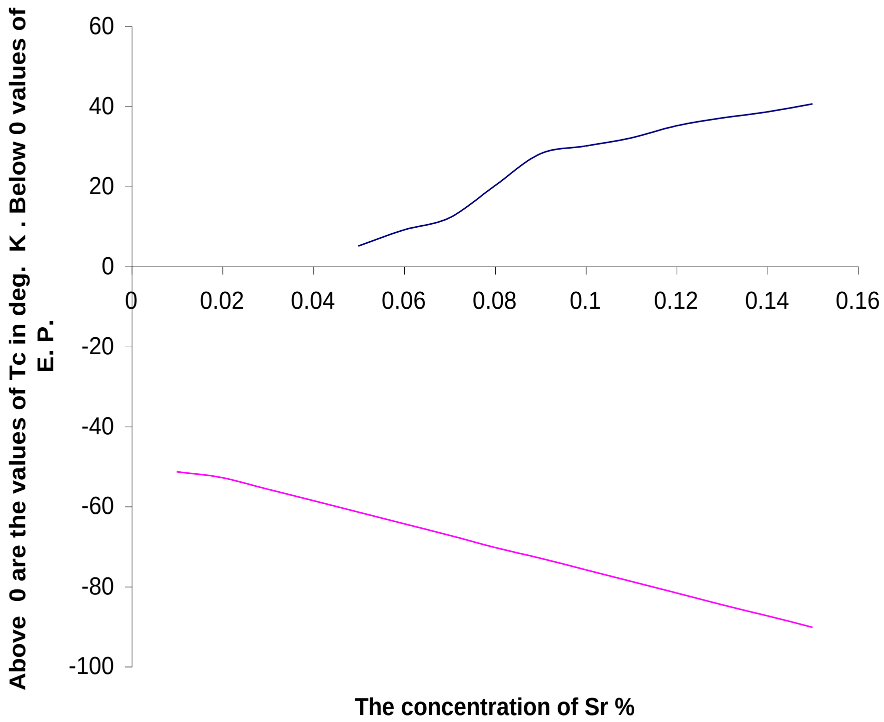

Figure 5: The dependence of both T_c and E.P. on the concentration of Sr the results of T_c are from (Takagi et al, 1989).

With our result of the dependence of E. P. on the concentration of Sr. Figure 5 is drawn such as that it demonstrate this comparison. In this figure T_c values were from the study of (Takagi et al, 1989). The values of T_c is started from the concentration 0.05. The values of the E. P. was from figure 3. this graph was drawn to show the changes in the transition temperature with that of E. P. every value y on the line can give the real value of E. P. by the transformation factor (y/100-10). as it is shown in the fig. 5 there is a good relation between the two variables within the range shown. This is a good result. This also prove the that increase in the E. P. plays a big role in affecting the superconductivity, and its most important factor T_c.

In order to find a correlation between the E. P. and T_c, let us consider that the relation between them having the following polynomial:

$$T_c = a_1 + a_2 E + a_3 E^2 \qquad \text{.. (6)}$$

where E represent the E. P. for any concentration of Sr.

The next table represent the values of E and T_c for each concentration of the Sr atoms.

Table 1: the values of the potential energy and the transition temperature as a function of the concentration of Sr (values of the transition temperature are from (Takagi et al, 1989).

Concentration of Sr %	*E eV*	*T_c in degrees K*
1	- 10.0514	0
2	-10.0529	0
3	-10.0558	0
4	-10.0586	0
5	-10.0615	5
6	-10.0644	9
7	-10.0673	12
6	-10.0703	20
9	-10.0730	28
10	-10.0759	30
11	-10.0788	32
12	-10.0817	35
13	-10.0846	37
14	-10.0874	38.5
15	-10.0903	40.5

From the above table we will find the (a‘s)coefficient as follows (Sokolnikoff and Redheeffer,1966):

Let $E = x$; Then

$$4a_1 + \left(\sum_{i=1}^{15} x_i\right)a_2 + \left(\sum_{i=1}^{15} x_i^2\right)a_3 = \sum_{i=1}^{15} y_i \qquad \text{.............................. (7)}$$

$$\left(\sum_{i=1}^{15} x_i\right)a_1 + \left(\sum_{i=1}^{15} x_i^2\right)a_2 + \left(\sum_{i=1}^{15} x_i^3\right)a_3 = \sum_{i=1}^{15} x_i y_i \qquad \text{...................... (8)}$$

$$\left(\sum_{i=1}^{15} x_i^2\right)a_1 + \left(\sum_{i=1}^{15} x_i^3\right)a_2 + \left(\sum_{i=1}^{15} x_i^4\right)a_3 = \sum_{i=1}^{15} x_i^2 y_i \qquad \text{.................... (9)}$$

to solve the above equations we must found the values of the summations in them. The following table is contains the values of the summations for variables ($x_i, x_i^2, x_i^3, x_i^4, x_i y_i, x_i^2 y_i$) for the corresponding values in table 1.

table 2 : The different statistical parameters needed to find the values of the constants (a_1, a_2, a_3, a_4) in the polynomial equation 6 .

$V = x_i$	T_c	x_i^2	x_i^3	x_i^4	$x_i y_i$	$x_i^2 y_i$
-10.0514	0	101.0306	-1015.5	10207.19	0	0
-10.0529	0	101.0608	-1015.95	10213.28	0	0
-10.0558	0	101.1191	-1016.83	10225.08	0	0
-10.0586	0	101.1754	-1017.68	10236.47	0	0
-10.0615	5	101.2338	-1018.56	10248.28	-50.3075	506.1689
-10.0644	9	101.2921	-1019.44	10260.1	-90.5796	911.6293
-10.0673	12	101.3505	-1020.33	10271.93	-120.808	1216.206
-10.0703	20	101.4109	-1021.24	10284.18	-201.406	2028.219
-10.073	28	101.4653	-1022.06	10295.21	-282.044	2841.029
-10.0759	30	101.5238	-1022.94	10307.07	-302.277	3045.713
-10.0788	32	101.5822	-1023.83	10318.95	-322.522	3250.631
-10.0817	35	101.6407	-1024.71	10330.83	-352.86	3557.424
-10.0846	37	101.6992	-1025.6	10342.72	-373.13	3762.869
-10.0874	38.5	101.7556	-1026.45	10354.21	-388.365	3917.592
-10.0901	40.5	101.8106	-1027.28	10365.4	-408.65	4123.33

From the above table: summations of the different statistical parameters ($x_i, x_i^2, x_i^3, x_i^4, x_i y_i, x_i^2 y_i$) used in the equations 7 , 8 and 9 can be found, then after substitution of these summations in the former equations. we got three equations. Solving them simultaneously we got the values of a_1, a_2, a_3 : the polynomial will be :

$$T_c = 90.227 - 6.604E - 1.545E^2 \quad \text{…………………………………….. (10)}$$

Thus we reach to the conclusion of establishment of the most important superconducting parameter T_c and the electrical *P. E.* of the crystal, This, as we consider, may be a very little brick in the search to establishment of a theory of high temperature superconducting. Even though this relation is limited for the concentrations of Sr up to 15 % but its validity comes from the right and essential basis of it (electrical interaction between ions of the superconducting crystal). Another reason for its validity that superconductivity depends on many essential variables (electrical, electronic, spin, magnetic of the holes and electrons ..etc) another effect may appear (Pickett,1989), which we will try to consider in our coming studies .Also good superconductors are fabricated within such range of Sr concentrations. finally in the lack of a general accepted theory of the high temperature superconducting, The attempts of this paper may help (however little) in the way to build a theory, like a river formed from little brooks.

In order to explain the dependence of both Tc and the E. P. on the concentration of Sr and to explain also the relation established between them we will try to explain this on two basis:

1- Increase of the concentration of holes by the increase of Sr concentration this increase of holes is attributed to the difference in valance between the Sr atom and the La atom (Chu ,2002).
2- Increase of the pressure increases the transition temperature which is a well established behavior of the superconductors (Huber, and Liverman 1990).

The appearance of electrons and holes in the superconductor by the process of substitution is similar to the appearance of them in the semiconductors (Kittle, 2005). The addition of neutral atoms with different valance from that already existing will lead to the appearance of holes or electrons due to the difference in their valances. If the valance of the La atom is V_{La} and that of Sr atom is V_{Sr}. Thus if we have a sample with N crystals then the number of holes n_h appeared is:

$$n_h = \frac{c}{100} \times (V_{la} - V_{Sr}) N \qquad \text{(11)}$$

c is the concentration of Sr. Here Sr ion have valance (+2) and La ion have valance (+3). Thus each substitution by one atom will bring to the solid one hole. In next figure the dependence of the number of holes created on the concentration of Sr atoms.

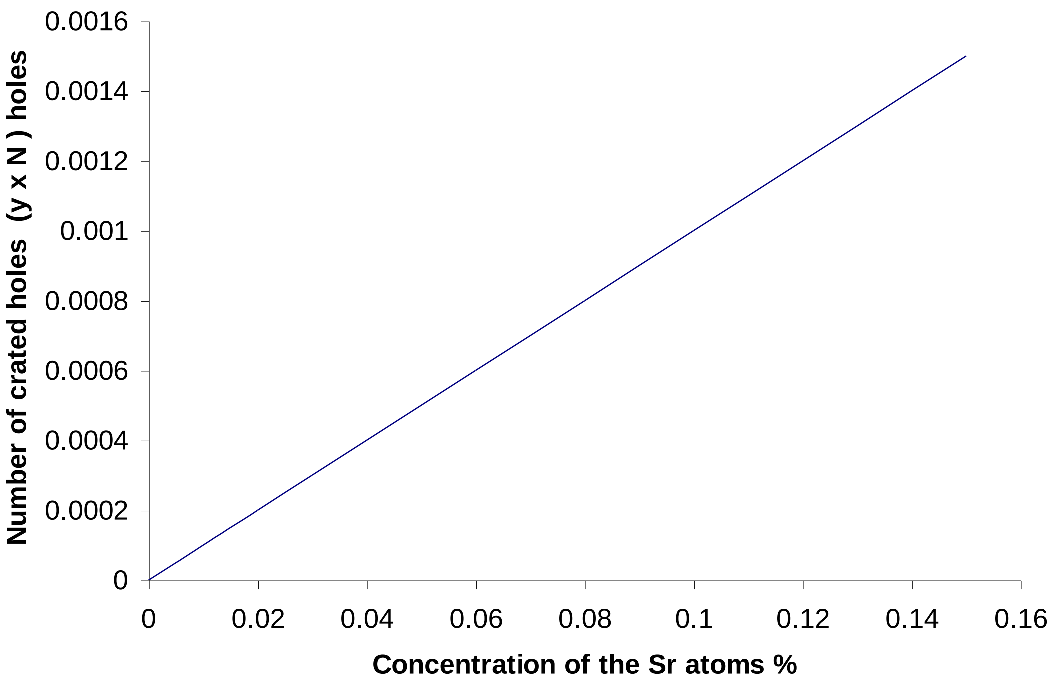

Figure 6 : The dependence of the number of created holes on the concentration of the Sr atoms in a sample with N crystals .

In the above figure the readings on the Y-axis must be multiplied by N to find the number of created holes, the figure show us that the concentration of holes increases linearly with increasing Sr concentration. This increase of holes by the substitution by Sr will enhance the formation of the Cooper pairs this will lead as a result to the increase of T_c (Kondo,1990).

On the other side the. increase of potential energy will have an effect like that of pressure application (Chu and Woollam, 1977). This process is demonstrated in figure 7, which compare the effect of the hydrostatic pressure which as a result leads to the collapse of the crystal (the figure was drawn in two dimensions for simplicity and the effect can be imagined better returning to figs. 1 & 2) by the substitution with the Sr ion as shown in the [a] & [b] drawings in the figure. For the [c] & [d] drawings collapse of the same crystal is due to the decrease of the electrostatic repulsion due to the decrease off the positive charge of the central ion by one. Thus substitution by Sr is equivalent to the application of the hydrostatic pressure (Rabinowitz,&McMullen 1997). It was proved experimentally (Sadewasser & Schilling, 1999) that the hydrostatic pressure leads to increase of T_c (Khosroabadi et al, 2002). This ensures our conclusion that the substitution by Sr as a result leads to increase of T_c.

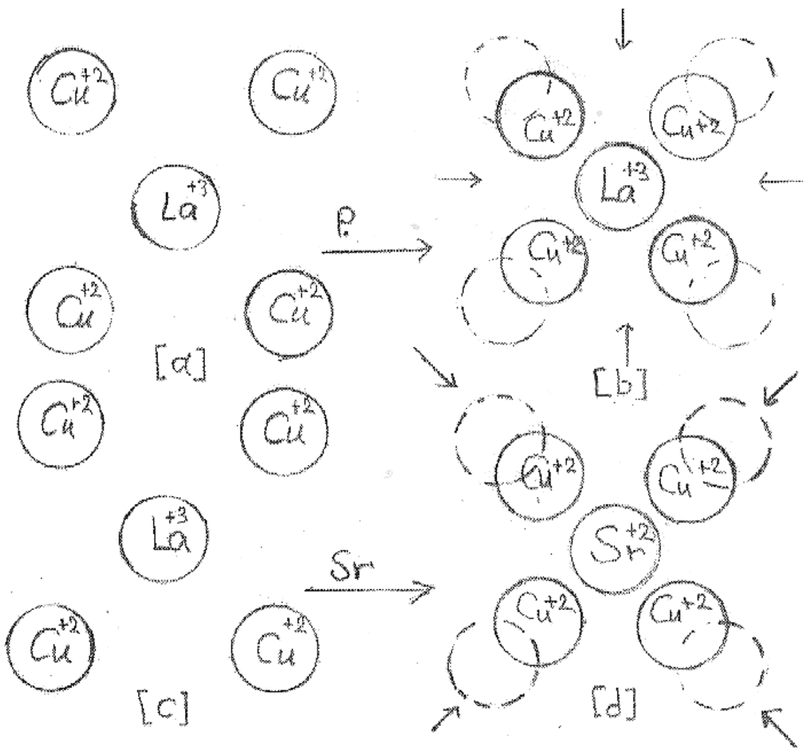

Figure 7 : Comparison of the effect of the pressure P. [b] on the crystal of La_2CuO_4 [a] and that of the substitution by the Sr ion. Since the substitution of Sr^{+2} [d] instead of La^{+3} in the crystal La_2CuO_4 [c] decreases electrical repulsion, this have effect like the application of pressure.

According to (Takagi et al, 1989), there must be a continuous increase of T_c, after x=0.15, T_c decreases due to the appearance of vacancies. We can explain our result also on the same basis that the appearance of vacancies will make screening effect, this will gradually decrease the potential energy, thus decreases T_c. increasing concentration of Sr above 0.15 leading to appearance of vacancies. The appearance of a vacant site have two effects: 1^{st} of them is screening effect of the electric field and decrease it, the 2^{nd} is acting as a traps for the holes, This as a result may decreases critical temperature. Other more complicated reasons may also leads to such decrease in T_c because they affect superconductivity in general like electrons distributions (Kondo, 1989), and type of orbitals of the carriers if it is of S or P types (Maki et al, 2002).

Conclusion

1) Substitution of the ion Sr^{+2} in the superconductor $La_{2-x}Sr_xCuO_4$ increases electrostatic potential energy this effect increases with increase of Sr. This comes from reduction of repulsive force by reduction of the charge on the new ion.

2) A relation is established between the increase of electrostatic potential energy and the transition temperature.

3) Increase of the transition temperature is due to the increase of holes by the decrease of one positive charge due to the substitution.

4) Increase of the transition temperature is also due to the effect of collapse of the crystal due to reduction of repulsive force. Thus substitution by Sr is equivalent to the application of the hydrostatic pressure which increases the transition temperature.

5) Substitution of the ion Sr^{+2} in the superconductor $La_{2-x}Sr_xCuO_4$ leads to a step increase in the electrostatic potential energy, which is a sign of the occurrence of a phase change, which in turn a necessary condition for superconductivity to occur.

6) increasing concentration of Sr above 0.15 leading to appearance of vacancies which decreases the transition temperature.

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