

## Structural analysis of the charge transfer mechanism in the superconducting compounds $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$ .

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### Abstract

$\text{Pb}_2\text{Sr}_2\text{Ln}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  is one of the copper-based superconductors with high critical temperature. Undoped  $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$  is not a superconductor and becomes so when some of the trivalent Y cations are replaced by bivalent Ca cations.

Microprobe analysis and magnetic measurements have been carried out on several single crystals. The  $x_{\text{Ca}}$  values are found to be between 0 and 0.42, while  $T_C$  varies between 0 and 80 K. Structural determinations by X-ray diffraction (6 crystals) show that the introduction of calcium reduces the stress between the  $\text{CuO}_2$  and SrO layers. The Y substitution with Ca increases the valence of Cu(2) cations with no appreciable variation of the apical distance Cu(2)-O(1). The oxidation of substituted compounds is accompanied by the suppression of the superconducting state because of the movement of the O(1) atoms towards the  $\text{Pb}^{4+}$  cations and away from the Cu(2) ones. This mechanism of charge transfer is very different from that of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

### 1. Introduction

It is well known today that oxygen content is one of the most important crystallochemical parameters governing the physical properties of high  $T_C$  superconducting compounds such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . However, the oxygen stoichiometry is not the only parameter able to modify the physical properties in a superconducting compound. For example the superconductivity in  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  is created by the substitution of the trivalent Y cations by the divalent Ca ones.

Several critical temperatures were observed with different single crystals of  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  which were prepared in different conditions. This variation of  $T_C$  was interpreted by small variations of the molar fraction of the calcium in the structure. The aim of our work was to understand the structural evolution in  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  as a function of the Ca stoichiometry and the change of the superconducting properties.

The structures of  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  can be described as built of (AO) and (BO<sub>2</sub>) layers [1] arranged as to form either perovskite or NaCl blocks. The sequences for  $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+\delta}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$  are respectively as follows:

(CuO<sub>2</sub>)(Y)(CuO<sub>2</sub>)(SrO)(PbO)(CuO<sub>8</sub>)(PbO)(SrO)(CuO<sub>2</sub>)(Y)(CuO<sub>2</sub>)

and

(CuO<sub>2</sub>)(Y)(CuO<sub>2</sub>)(BaO)(CuO<sub>8</sub>)(BaO)(CuO<sub>2</sub>)(Y)(CuO<sub>2</sub>)

Besides the blocks (CuO<sub>2</sub>)(Y)(CuO<sub>2</sub>) a common feature between the two compounds is the presence of the oxygen deficient (Cu) layers.

The superconductivity can be created by increasing the average valency of the copper in the (CuO<sub>2</sub>)(Y)(CuO<sub>2</sub>) blocks. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , this is done by the introduction of extra oxygen atoms in the initially oxygen-depleted (Cu) layer. One part of the extra charges oxidize the monovalent Cu(1) cations to  $\text{Cu}^{2+}$ , the other part is transferred in the direction of the double-pyramidal blocks to oxidize a fraction of the  $\text{Cu}^{2+}$  to  $\text{Cu}^{3+}$ . The average valency of the copper becomes higher than 2+ and the superconductivity is created.

In  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$ , the charge transfer mechanism is very different. In its undoped state  $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+\delta}$  do not exhibit superconductivity and the introduction of extra oxygen atoms into the (Cu) layer do not create superconductivity. As reported in a previous publication [2] the extra charges are trapped by the  $\text{Cu}^{+1}$  and the  $\text{Pb}^{+2}$  cations, and are not transferred to the (CuO<sub>2</sub>) layer.

To induce superconductivity an element must be introduced in the yttrium layer of the double pyramidal structure in order to create extra positive charges (holes) that can be directly transferred to the neighbouring  $\text{Cu}^{2+}$  cations thus increasing their valency.

Here we report the effect of calcium substitution on the structure and the evolution of the copper valency.

## 2. Single crystal preparation and characterization

Single crystals of  $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$  were synthesized in a PbO-PbF<sub>2</sub> based flux with different Y/Ca ratios. The powder was heated above the fusion temperature to about 960 °C in a gas flow of 98-99 % N<sub>2</sub>, 1-2 % O<sub>2</sub>. More details are given in reference [3].

Six crystals taken from six different batches (261190, 220190, 010690, 120490, 220190, and 37D1E) with different T<sub>C</sub> were selected to be used in a detailed study of the structure using single crystal X-ray diffraction.

Microprobe analysis and a.c. magnetic measurements were carried out on other single crystals taken from the same batches as those selected above, assuming a homogeneity across all crystals in a given batch.

The superconducting transition temperatures of all the crystals used are shown in figure 1. The  $\chi$ -T curve shows that the T<sub>C</sub> (onset) are 0, 40, 40, 50, 65, and 80 K. The superconducting volume was estimated to be 100 % after the demagnetizing field corrections had been applied.

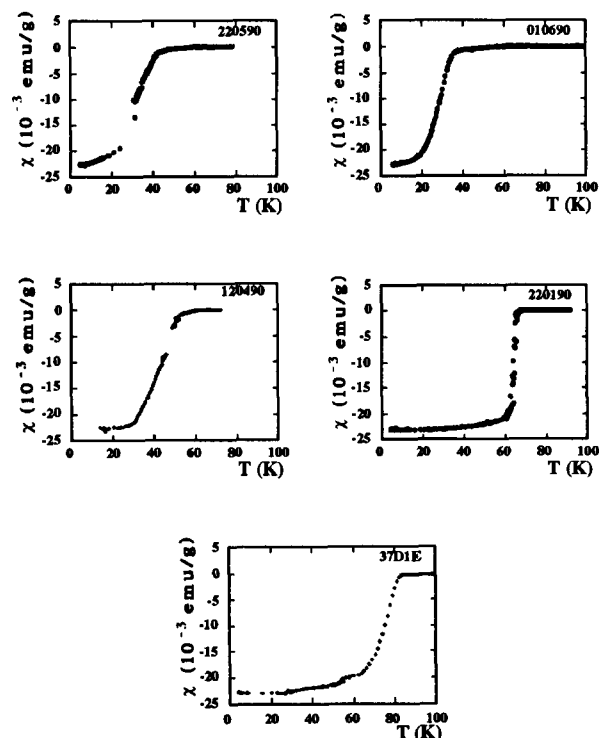


Figure 1. A.C. magnetic susceptibility showing the different critical temperatures of the chosen crystals. T<sub>C</sub> are found to be 40, 40, 50, 65, and 80 K. Crystals from batch reference 261190 are not superconducting.

Microprobe analysis was carried out at 15 KV with Cu<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, YSi<sub>1.77</sub>, CaSiO<sub>3</sub>, SrSO<sub>4</sub> and PbS as standards.

The chemical composition of the well-polished crystals was determined over 10 different points on the surface of each crystal. The measured composition in each point shows that the crystals are homogeneous. Pb and Sr values seem to be in agreement with the formula stoichiometry while the Ca and the Y values vary in a regular way as a function of the critical temperature.

Figure 2 shows graphically the relation between the Ca molar fraction and the critical temperature.

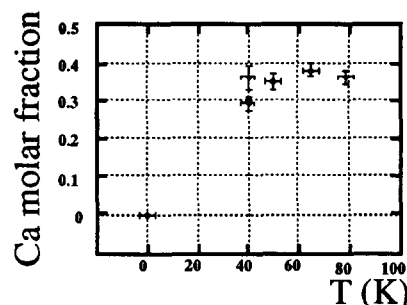


Figure 2. Molar fraction of calcium as a function of critical temperature.

## 3. X-ray data collection and structural refinement

In order to limit absorption effects, the crystals were shaped in form of spheres with diameters varying between 0.13 and 0.2 mm. The spherical crystals were then mounted on a Philips 4-circle diffractometer equipped with a short wavelength AgK<sub>α</sub> tube (0.56087 Å) selected with a monochromator of graphite.

The X-ray diffraction intensities have been collected at ambient temperature. A spherical zone in the reciprocal space was explored in order to calculate the average intensities of the equivalent reflections. These reflections were averaged in the Laue class (mmm). Structural refinements have been carried out with the MXD program [4]. The initial atomic parameters of the structure were those determined by the neutron single crystal diffraction study reported by Chaillout et al. [5]. In our refinements, we have tried other space groups without meaningful results. In fact, the only possible space groups seem to be Cmmm (Cava et al. [6,7]) and Pman [5]. X-ray diffraction data for all six crystals were refined in both space groups. The calculations resulted in lower values of the agreement factors R with Pman than Cmmm. It should be also noted that the temperature factor values of the different atoms, especially for the oxygen O(2) which is in the same layer as Pb cations, were very reasonable in space group Pman and that higher values were obtained in space group Cmmm.

## 4. Results and discussion

During the refinements, the occupancy parameters of all the oxygen atoms were fixed to unity. On the other hand, the occupancy of (Y,Ca) site was refined assuming

that  $p(Y) = 1-p(Ca)$ . The nominal and refined Y/Ca ratios are given in the following table (table 1), as well as the values determined by microprobe analysis. It can be easily seen that the final crystal composition has largely deviated from the nominal one of the melt. The two methods of analysis give very comparable results.

Table 1. Values of the Y/Ca ratio obtained from microprobe analysis and structural refinements. Nominal values are the Y/Ca ratios of the melt.

Crystal	Nominal ratio Y/Ca	Microprobe analysis Y/Ca	Refined ratio Y/Ca
261190	1/0	1/0	0.94/0.00
220590	0.2/0.8	0.71/0.29	0.71/0.29
010690	0.2/0.8	0.64/0.36	0.64/0.36
120490	0.3/0.7	0.65/0.35	0.66/0.34
220190	0.3/0.7	0.62/0.38	0.62/0.38
37D1E	0.3/0.7	0.64/0.36	0.58/0.42

Figure 3 shows the variation of the apical distance Cu(2)-O(1) (fig.3-a) and the average distance of Cu(2)-O(3) and Cu(2)-O(4) (fig.3-b) as a function of the Ca molar fraction.

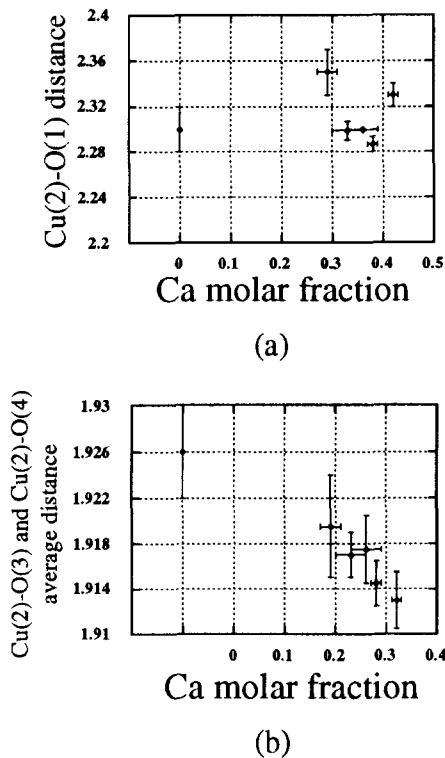


Figure 3. a- The apical distance Cu(2)-O(1), & b- The average distance of Cu(2)-O(3) and Cu(2)-O(4) as a function of the Ca molar fraction.

In good agreement with the neutron results [5] the small variation of the apical Cu(2)-O(1) distance does not seem to be significant. On the other hand, the average distance of Cu(2)-O(3) and Cu(2)-O(4) decreases in a regular way with the increase of the Ca value. These variations are consistent with the behavior of the a and b parameters when substituting trivalent yttrium cations by bivalent calcium cations [9].

Due to the substitution of the Y cations by the divalent Ca cations and the decrease of the distances between the copper Cu(2) and its first neighbors O(3) and O(4) (in the same layer), the average valency of the Cu(2) cations is increased.

The rise in the calculated Cu(2) and Sr valencies was first observed in the neutron diffraction experiments [5,8]. Using our data, we have determined the charge evolution of the Cu(2) and the Sr cations formal valencies as a function of the calcium stoichiometry (fig.4, table 2).

Strontium is known as a very stable chemical element with a valency equal to 2+. The initial value of the calculated strontium valency in the undoped compound  $Pb_2Sr_2YCu_3O_{8+\delta}$  is found to be 1.65(3) (see table 2) with an important deviation when compared to its real value. Doping with the Ca cations leads to a decrease

Table 2. Sr and Cu(2) calculated formal valencies.

Ref.	$T_c(K)$	$v(Sr)$	$v(Cu(2))$
261190	0	1.65(3)	2.239(6)
220590	40	1.67(4)	2.252(8)
010690	40	1.74(4)	2.289(5)
120490	50	1.73(3)	2.295(7)
220190	60	1.77(2)	2.310(4)
37D1E	80	1.80(2)	2.296(5)

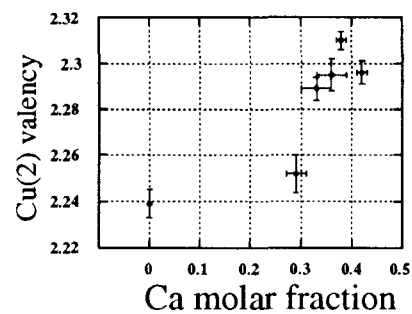


Figure 4. Change in copper Cu(2) valency as a function of the Ca molar fraction.

in the average distance Sr-O(1) (fig.5) and consequently an increase in the strontium valency which approaches its ideal value 2+. In reality, there is no gain in strontium valency and the observed charge evolution can be very reasonably explained by the relaxation of the stresses between the two neighbor layers (SrO) and (CuO<sub>2</sub>) existing in the yttrium compound [10]. This means that Cu(2) which is situated in one of those two layers is directly influenced by this phenomenon and the real

variation of the Cu(2) valency is so reduced by the diminution of stresses symmetric to those observed with the strontium. Thus, the augmentation of the Cu(2) valency is underestimated by the calculations using the Brown and Altermatt formula [11].

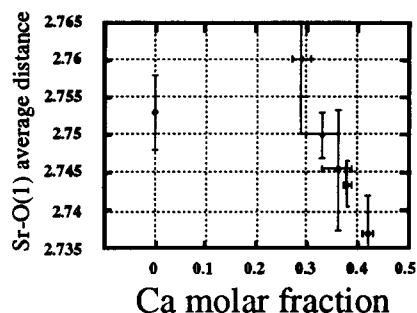


Figure 5. Average distance of Sr-O(1).

In theory, the charge equilibrium in the undoped yttrium compound leads to the following electronic configuration :  $Pb_2^{2+}Sr_2^{2+}Y^{3+}Cu_1^{1+}Cu_2^{2+}O_8^{2-}$ . Substituting 42 % of yttrium cations by calcium cations should result in an increase of the valency of the initially bivalent copper cations to an average value of 2.21 u.v. as calculated by Cava [6] from the chemical formula. This represents a gain in charges of (0.21+). In the undoped compound the formal calculated valency is 2.239 u.v., with 0.239 u.v. in excess compared to the ideal value. This valency increases to 2.296(5) u.v. (table 2) in the  $(Y_{0.58}Ca_{0.42})$  compound (crystal, batch 37D1E) with a gain of 0.057 u.v. This represents only a part of the total gain in copper valency. One can logically suppose that the second part is equal to the gain in the calculated strontium valency which is  $(1.80(2) - 1.65(3)) = 0.15$  u.v.). This value (0.15 u.v.) added to the first one (0.057 u.v.) gives exactly the same theoretical calculated gain (0.21 u.v.). Figure 6 shows the evolution of the copper valency gain calculated from the chemical formula and from the results of the structural refinements, taking into account the contribution of the stress relaxation in the structure.

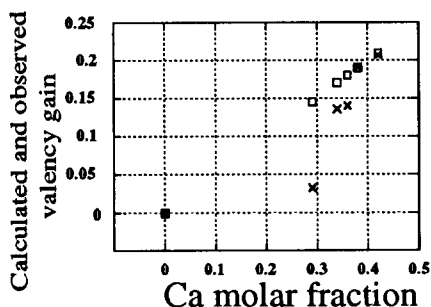


Figure 6. Ca refined molar fraction as a function of : a- calculated copper valency gain (from the chemical formula), (squares) & b- observed copper valency gain (from the structural refinements), (crosses).

As it can be seen in figure 6, the observed gain in the copper valency is in good agreement with the theoretical one.

In conclusion, the substitution of yttrium cations by calcium ones reduces the stresses between the neighbouring planes  $CuO_2$  and  $SrO$ . It has no effect on the position of the apical oxygen O(1) with respect to  $CuO_2$ , but induces an increase of the formal copper valency by narrowing the in plane oxygen-copper distances. This rise of valency corrected from the effect of stress relaxation in the structure is in good agreement with the theoretical value, calculated from the chemical formula, assuming that all the extra charges resulting from the substitution are transferred to the copper cations.

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