# Bond valence sum , hole density and irreversibility line in Ca substituted

# $YSrBaCu_{3-y}M_yO_{6+z}$ (M=Al,Fe,Co).

R. Suryanarayanan, L. Ouhammou, M. S. R. Rao, O. Gorochov, H. Pankowska, N. Le Nagard and A. Das.

Laboratoire de Physique des Solides de Bellevue, CNRS, 92195 Meudon, France.

## Abstract

Structural and superconducting properties of $Y_{1-x}Ca_xSrBaCu_{3-y}M_yO_{6+z}$ (M=Al,Fe,Co) are presented. For x =0, for all M, $T_c$ decreases as a function of y and insulating state is obtained for y=0.4 accompanied by a decrease in the carrier density (p ) and the Cu-O apical distance (d) . For x>0, superconductivity is restored (for y=0.4). A relation between x, $T_c$, p, d and bond valence sum of Cu2 is obtained. Further in the case of M=Co and y=0.3, an enhancement in the irreversibility line as determined by ac susceptibility measurements is observed.

## 1. Introduction

The structural and superconducting properties of $YBa_2Cu_3O_{6+z}$ as a function of substitution at different sites have been extensively studied [1]. Recently, several reports have appeared on the co-substitution of Ca at Y site and M(Al, Fe, Co) atoms at Cu site [2,3,4,5,6]. These studies have shown the remarkable changes in normal and superconducting properties that take place as a result of Ca substitution. For example, it was shown [7] that superconductivity could be restored with 10% of Ca in an otherwise insulating samples of $YSrBaCu_{2.6}M_{0.4}O_{6+z}$ (M=Al,Fe). Here, we show a relation between $T_c$, x(Ca), Cu-O apical distance (d) , bond valence sum (bvs) and the hole density inferred from Hall measurements in the title compound. Further, the effect of Ca on the irreversibility line on some of the samples is presented.

## 2. Experimental techniques

The polycrystalline samples were obtained by standard ceramic processing. All the samples discussed here were oxygen annealed for 3 days. The ac susceptibility was measured (1500 Hz) in an ac field of 0.1 Oe . The maximum temperature $T_p$ at which the imaginary part of the susceptibility occurs was measured as a function of dc fields. Resistivity and Hall constant, $R_H$ (10 mA, 10 kOe) were measured by ac techniques. Assuming a single band model, the hole density (p) was calculated from $p = 1/eR_H$.

## 3. Results and discussion

| x | y | $T_c$(K) | x | y | $T_c$(K) |
|---|---|---|---|---|---|
| 0 | 0 | 83 | 0 | 0.1 | 67 |
| 0.1 | 0.1 | 72 | 0.2 | 0.1 | 77 |
| 0.3 | 0.1 | 76 | 0.4 | 0.1 | 76 |
| 0 | 0.2 | 42 | 0.1 | 0.2 | 60 |
| 0.2 | 0.2 | 68 | 0.3 | 0.2 | 72 |
| 0.4 | 0.2 | 70 | 0 | 0.3 | 29 |
| 0.1 | 0.3 | 50 | 0.2 | 0.3 | 66 |
| 0.3 | 0.3 | 65 | 0 | 0.4 | 0 |
| 0.1 | 0.4 | 29 | 0.2 | 0.4 | 40 |
| 0.3 | 0.4 | 60 | | | |

Table 1. $T_c$ of $Y_{1-x}Ca_xSrBaCu_{3-y}Al_yO_{6+z}$ derived from susceptibility data.

The resistivity and susceptibility curves are published elsewhere [8]. Here, we discuss only

the summary of the data obtained. Table 1 gives the $T_c$ values of (Ca,Al) substituted samples determined from susceptibility data.The detailed X-ray studies of these samples discussed elsewhere [8] showed them to be single phase except for x >0.3. The orthorhombic to tetragonal transformation occured for y>0.1 and was not influenced by the presence of Ca.With increasing Al, both $T_c$ and p decreased and when Ca was cosubstituted both of them increased. Superconductivity was destroyed for y=0.4, when p reached a critical value of $1.5.10^{21}/cm^3$ and was restored with x(Ca)=0.1 with $T_c$ increasing from 0 to 29K. The increase in $T_c$ was accompanied by an increase in p. For all the samples given in Table 1, we determined p at 300K and found a relation between $T_c$ and p (fig.1). Such a relation was well established in the case of Sr susbtituted $La_2CuO_4$ [9]. We have also carried out Rietveld analyses on these samples and calculated in particular Cu1-O apical distance (d). As y increased (with x=0), there was a decrease in d (fig.2a) but when Ca was substituted (for a given y) d increased (Fig.2b).
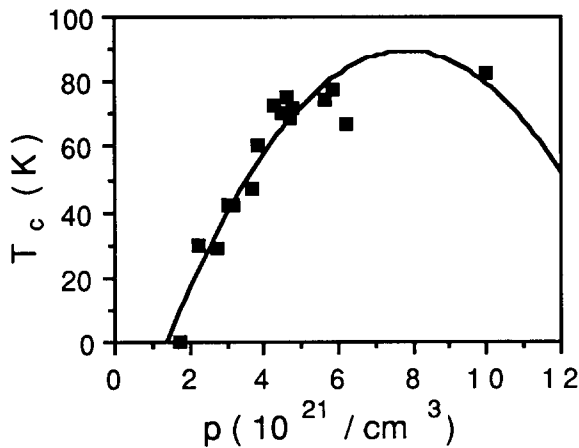
where $r_{ij}$ is the distance between the atom i and its surrounding atom j and $r_0$ is a empirically determined parameter. Assuming the oxidation state of +2 for Cu and -2 for O , we took $r_0$=1.679.
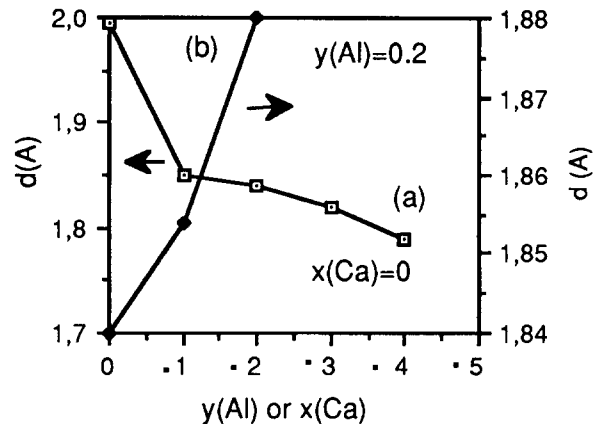


Fig. 2. $Cu_1$-O apical distance (d) as a function of (a) y(Al) with x(Ca)=0 , scale on the left and (b) x(Ca) with y(Al)=0.2, scale on the right.

In the case of strongly hybridized systems such as superconducting copper oxides,the bvs for the copper atoms should be taken to represent the total charge in the bond. One could then monitor the relative changes in bvs as a function of other parameters such as oxygen content [11] or substitution. The details of the calculations are given elsewhere [12]. We concentrate here only on the bvs of Cu(2). The bvs decreased as y (with x=0) increased indicating less positive charge in the Cu(2)-O plane which also agreed with our observation of a decrease in the measured hole density. For a given y, we observed steady increase of bvs as a function of Ca. This is shown in fig.3 for y=0.2 and y=0.4. It is clear that bvs scales approximately with $T_c$ and p.



Fig. 1. Hole density (p) measured at 300 K of (Ca,Al) samples (Table 1) as a function of $T_c$.

Another quantity that is useful to discuss is the bond valence sum (bvs). Brown and Altermatt [10] proposed that the valence of an atom i in a solid can be expressed by the following sum

$$V_i = \Sigma_j exp[(r_0 - r_{ij})/0.37]$$

The above data can be understood qualitatively as follows. It has been fairly well established that Al goes to the Cu1 chain sites[1]. Since the average valence of Cu 1 is less than 3, Al substitution will increase the oxygen content in the chains resulting in an increase in negative charge and the hole in the plane will

tend to reduce as was also explained by Cava et al [11] in their charge transfer model. Further, it was argued recently that within a class or subclass of cuprates the variation of the Cu-O bond valence sum could reflect a corresponding change in the hole density [13]. Our data show that $T_c$, p, d and bvs decreased as y , but increased as x. Partial substitution of Y by Ca injects holes into Cu-O layers as was also surmised earlier [14-16]. In particular, it was shown in

$Y_{1-x}Ca_xBa_2Cu_3O_{6+z}$, for z<0.4, superconductivity was induced for x>0.2 and that Ca did substitute for Y [15,16].
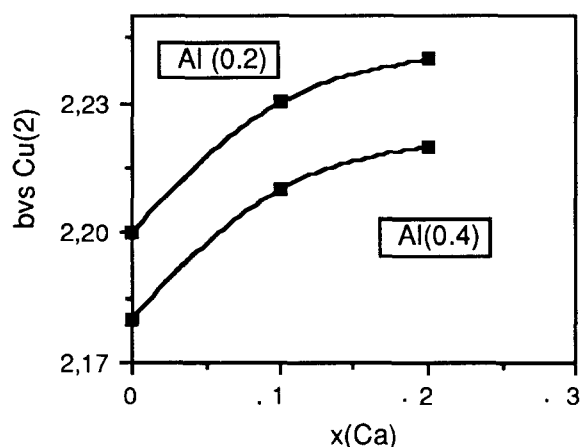
Ca.The rate of increase of $T_c$ with Ca dependend on the substituted M element. Whereas $T_c$ increased steadily with Ca for Al and Co, it decreased in the case of Fe after reaching a maximum value of about 30 K at around x=0.15 (fig.4). This decrease could result from several factors such as an increase in hole density beyond the optimum value, changes in structural parameters and pair breaking effect due to an increased occupation of Fe at the Cu2 planar sites. Further experiments are necessary to clarify this point.
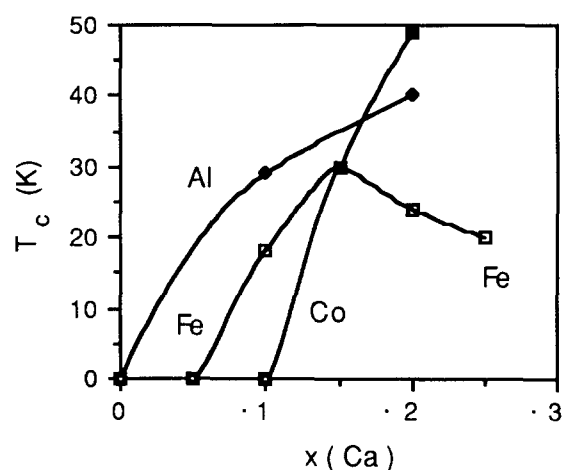


Fig. 3. Bond valence sum(bvs) of Cu(2) as a function of Ca concentration for Al=0.2 and 0.4.



Fig. 4. $T_c$ of 0.4 (Al, Fe, Co) samples as a function of x (Ca) concentration. The lines are drawn to guide the eyes.

Based on the above qualitative interpretation, we expect similar effects in Fe and Co substituted samples since Co and Fe (to some extent) are known to substitute the Cu chain sites [1]. Indeed, Ca was found to restore superconductivity in the otherwise insulating samples containing y =0.4 of Fe and Co. However, there were important differences. For example, we compare the $T_c$ values of Al,Fe and Co (y=0.4) as a function of Ca concentration in fig.4. All these samples were annealed at 450 C in flowing oxygen for 72 h and furnace cooled. For x=0, the oxygen content of these (Al and Fe) samples were between 6.98 to 7.05 which decreased to between 6.9 and 6.8 as a function of

In order to investigate if substitution of Ca brings about changes in the superconducting state, we have measured the imaginary susceptibility ( $\chi''$) of Co(0.3) samples as a function of T in different static magnetic fields H.Though the interpretation of $\chi''$ is not straightforward, several authors have pointed out [17] that under certain conditions, the peak observed at $T_p$ in such experiments reflect the intergranular critical current ($J_g$)and the T -H data could represent the irreversibility line (IL). All the samples studied were of similar size and shape.
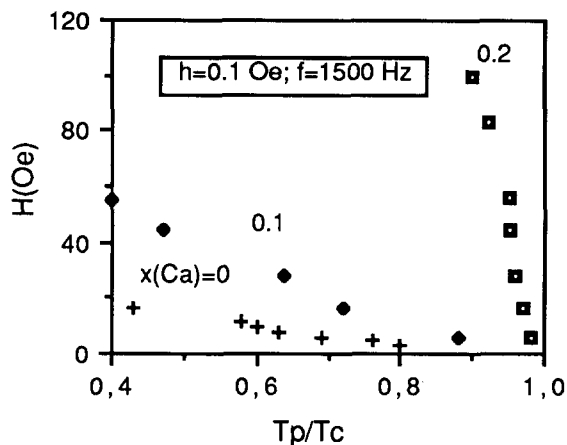
Fig. 5. $T_p/T_c$ as a function of applied dc field for Co(0.3) samples having different Ca concentrations.

H is plotted as a function of $t = T_p/T_c$ for x(Ca) = 0,0.1 and 0.2 (fig.5). A remarkable enhancement of the IL can be seen as a function of Ca. Following Müller et al[18], the data were anlysed using the relation $H=K(1-t)^n$. We obtained n =1.67(x=0), 1.37(x=0.1) and 1.74 (x=0.2). There was thus no correlation between x and the exponent n. However, the constant K steadily increased as x(Ca). In the limit of $T_p$ tending to zero, we obtained, from the above relation, H= H'= 45, 100 and 7100 Oe respectively for x=0, 0.1 and 0.2. If one interprets the appearance of $T_p$ as due to $J_g$ then one could possibly say that $J_g$ vanishes at higher fields H' when Ca concentration increased from 0 to 0.2. In the absence of a detailed microstructural study, we would like to attribute this increased pinning to a reduction in oxygen disorder and an increase in the electron mean free path. The latter could also explain a reduction in the normal state resistivity by a factor of 15 when x increased from 0 to 0.2 [5].

## 4. Conclusions

Remarkable effects of Ca on the structural and superconducting properties of $Y_{1-x}Ca_xSrBaCu_{3-y}M_yO_{6+z}$ (M=Al,Fe,Co) were observed. In particular, superconductivity was restored in the otherwise insulating samples with y=0.4 for all M when x>0.1. A relation was established between $T_c$, hole density,Cu-O apical distance and the bond valence sum of Cu2. The variation of $T_c$ with x in the case of (0.4) Fe samples which is different from that in the case of Al and Co samples, could be due to some Fe going to Cu planar sites. An enhancement in the irreversibility line was found as a result of Ca substitution. The compounds studied here and the data presented should be useful to test several models based on charge transfer, bi-polaron, magnetic interactions, phase separation etc.

## References

1 For a detailed discussion and additional references see B. Raveau, C. Michel, M. Hervieu and D. Grout, Crystal Chemistry of High -$T_c$ Superconducting Copper Oxides, Springer, Berlin, 1991

2 R. Suryanarayanan et al. Physica C 185-189 (1991) 463

3 Y Zhao et al. Physica C 179 (1991) 207.

4 M. G. Smith et al. J. A. P. 69 (1991) 4894.

5 R. Suryanarayanan et al. Physica C 199 (1992) 37.

6 E. Suard et al. Physica C 200 (1992) 43

7 R. Suryanarayanan et al. Solid State Comm. 81 (1992) 593

8 R. Suryanarayanan et al in High Temperature superconductors, (eds) J. Pouch, S. A. Alterowitz and R. R. Romanowsky, Transtech Publications, Switzerland, 1992.

9 Y. Tokura et al. Phys. Rev. 38B (1988) 7156

10 I. D. Brown and D. Altermatt, Acta Crystallogr. B41 (1985) 244.

11 R. J. Cava et al. Physica C 165 (1990) 419.

12 L.Ouhammou, Ph.D Thesis, Paris University, 1992 (unpublished)

13 M. H. Whangbo and C. C. Torardi, Science 249 (1990) 1143.

14 A. Manthiram et al. J. Solid State Chem. 73 (1988) 278.

15 J. B. Parise et al. MRS Proc. San Diego, 156 (1989) 105.

16 R. S. Liu et al. Solid State Comm. 86 (1990) 334

17 For an extensive discussion and additional references, see, S. Senoussi, J. de Physique III (France) 2 (1992) 1041

18 K. A. Müller et al. Phys. Rev. Lett. 58 (1987) 408