

ON THE SELECTIVE COPPER SUBSTITUTION  
WITH  $Zn^{2+}$  AND  $Ni^{2+}$  IONS IN LSCO CUPRATES

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Direct proof of the role of the  $CuO_2$  planes in the occurrence of the high temperature superconductivity in cuprates is got experimentally from the investigation of the behaviour of the critical temperature  $T_c$  under gradual substitution of the in plane  $Cu^{2+}$  ions by divalent metal ions  $M^{2+}$ . In the present paper, functional dependencies  $T_c = T_c(y)$  on the  $y$  content of M ion are inferred from the existing experimental evidence on  $La_{1.85}Sr_{0.15}Cu_{1-y}M_yO_4$  (LSCO) for  $M^{2+}$  denoting either  $Zn^{2+}$  or  $Ni^{2+}$ . Data processing and analysis point, in both cases, to a sharp linear decrease of  $T_c$  under the increase of  $y$ , with an M ion dependent slope. The result substantiates the basic hypothesis of the two-dimensional two-band Hubbard model of searching the origins of the high- $T_c$  superconductivity in cuprates inside individual  $CuO_2$  planes.

*Key words*: Cuprates, high temperature superconductivity, copper substitution, effective Hubbard model.

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## 1. INTRODUCTION

The effective two-dimensional two-band Hubbard model ([1]–[6] and references therein) starts from the fundamental assumption that the high temperature superconductivity in cuprates originates in the interactions occurring inside the individual  $CuO_2$  planes of the existing layered perovskite structures. On the other side, claims concerning the occurrence of an alternative, phonon-based high- $T_c$  mechanism, were vigorously advocated (see, *e.g.*, [7]–[9]). The universal feature of the cuprates of exhibiting within their crystalline structures at least one  $CuO_2$  unit per elementary cell, together with the accumulated experimental evidence probing the sharp decrease of the transition temperature  $T_c$  under increasing copper substitution inside the  $CuO_2$  planes by divalent metal ions  $M^{2+}$ , are strong arguments in favour of the Hubbard model approach.

## 2. A THREE-STEP STUDY PROGRAM

However, in view of the lack of a bird's-eye-view survey of the copper substitution and the occurrence of contradictory results coming from different groups of authors, we have embarked on a three-step program aiming at reaching an increased reliability of the conclusions drawn from the available experimental evidence.

*Step 1, Data collection:* Grouping together the available data concerning the variation of  $T_c$  in various cuprates under copper substitution by divalent  $\text{M}^{2+}$  metal ions with Shannon's crystal ionic radii [10] close to that of  $\text{Cu}^{2+}$ . A distinct data set collects the  $T_c$  data reported in the literature at various copper substitution levels  $y_k$  by a specific  $\text{M}^{2+}$  ion in a given cuprate, at a characteristic doping level  $x$  defining the charge reservoir status.

*Step 2, Data processing:* From the available  $\{T_{c,l}(y_k) \mid l = 1, 2, \dots, L(k)\}$  evidence, we derive a unique value as the arithmetic average

$$\bar{T}_c(y_k) = L^{-1} \sum_{l=1}^L T_{c,l}(y_k), \quad L = L(k). \quad (1)$$

Concerning  $\bar{T}_c(y_0 = 0)$  in the absence of the substituting  $\text{M}^{2+}$  ion, we decided to take the average (1) over *all* existing  $T_c$  data for a given cuprate, at a characteristic doping level  $x$ .

*Step 3, Least squares fit (LSQF) analysis:* The resulting set

$$\{\bar{T}_c(y_k) \mid k = 0, 1, \dots, K\} \quad (2)$$

is subject to a weighted LSQF analysis using the Hamming termination criterion which assumes [11] that the optimal degree of the fitting polynomial is reached when the distribution of the residuals gets stochastic (for implementation details, see [12]).

## 3. PURPOSE AND SCOPE OF THE PAPER

This is a preliminary report on the  $\text{Cu}^{2+}$  substitution in the optimally doped LSCO cuprate  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  by either  $\text{Zn}^{2+}$  or  $\text{Ni}^{2+}$  ions [13]–[26] resulting in the generic LSCMO formula  $\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-y}\text{M}_y\text{O}_4$ .

As emphasized by various authors, in spite of the lower  $T_c$  value, the characteristic feature of the LSCO cuprates of showing a single  $\text{CuO}_2$  unit per elementary cell enhances the data reliability since the  $\text{M}^{2+}$  ions are expected to migrate uniquely toward the  $\text{Cu}^{2+}$  sites inside the  $\text{CuO}_2$  planes during the sample preparation. Apart from diffraction studies devoted to the accurate definition of the crystallographic positions occupied by the  $\text{M}^{2+}$  ions of interest inside the lattice, the comparison of the Shannon's crystal ionic radii [10] of the various LSCMO ions enhances this conclusion. Indeed, the  $\text{Ni}^{2+}$  radius (83 pm) and the  $\text{Zn}^{2+}$  radius (88 pm) are close to the

$\text{Cu}^{2+}$  ionic radius (87 pm) while being significantly different from the  $\text{Cu}^{3+}$  radius (68 pm),  $\text{O}^{2-}$  radius (126 pm),  $\text{La}^{3+}$  radius (117.2 pm) and the  $\text{Sr}^{2+}$  radius (132 pm). Therefore,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  substitute indeed the  $\text{Cu}^{2+}$  ions inside the crystal.

#### 4. NUMERICAL RESULTS AND THEIR DISCUSSION

Within the fourteen references [13]–[26] we have identified nine data sets pertaining to  $\text{Zn}^{2+}$  substitutions [15]–[21], [23], [24] and eleven to  $\text{Ni}^{2+}$  [13], [14], [16], [18]–[22], [24]–[26]. We have strictly followed the rule of retaining for scrutiny really independent from each other data sets. As an instance, from the  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  data sets of [23], only the first one was retained. As it concerns the  $\text{Ni}^{2+}$  data, the larger set of reference [25] entered the present discussion.

Among the twenty available values in [13]–[26] at  $y = 0$ , fourteen were found to be distinct from each other, hence the average  $\bar{T}_c(0)$  was computed from (1) using this larger set instead of considering the  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  sets separately.

We notice the unwanted feature of some data sets namely, the occurrence of different  $T_c(y = 0)$  values, in a same paper, investigating several  $\text{M}^{2+}$  substitutions (for instance, in [16], each of the six reported  $\text{M}^{2+}$  substitutions started with its own  $T_c(y = 0)$ , see also [17]). In such cases, we have had nothing to do than to include the different  $T_c(y = 0)$  inputs of a same reference as distinct contributions to (1).

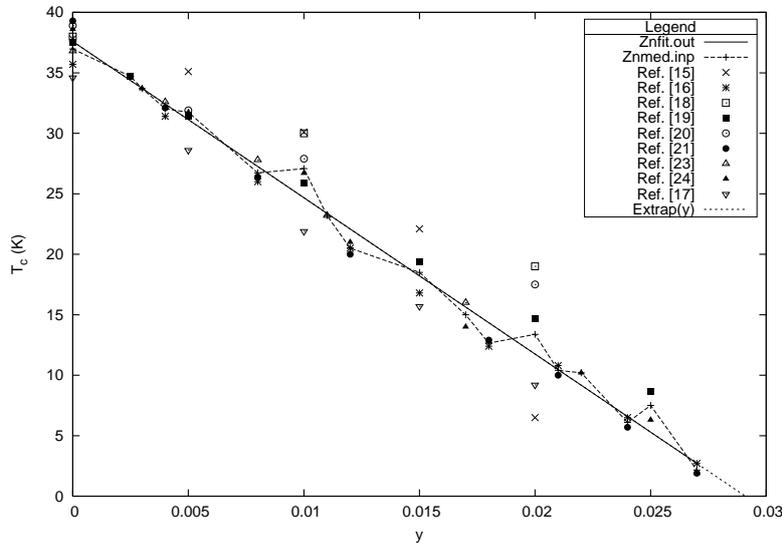


Fig. 1 –  $T_c$  versus the fraction  $y$  of  $\text{Zn}^{2+}$  ions substituting  $\text{Cu}^{2+}$  in  $\text{CuO}_2$  planes.

The forty six  $T_c$  values on  $\text{Zn}^{2+}$  substitutions reported in the abovementioned nine studies addressed seventeen  $\text{Zn}^{2+}$  concentrations  $y_k \neq 0$ . The resulting seven-

teen averages  $\bar{T}_c(y_k \neq 0)$  provided, together with  $\bar{T}_c(y_0 = 0)$ , the eighteen value data set serving as input to the LSQF analysis mentioned at Step 3 above.

In the case of  $\text{Ni}^{2+}$ , the reported forty eight values addressed fifteen  $\text{Ni}^{2+}$  concentrations  $y_k \neq 0$ , hence in a sixteen value data set serving as input to the LSQF analysis. In both cases, the resulting statistics significantly exceeds the ones reported in each of the references [13]–[26] taken separately.

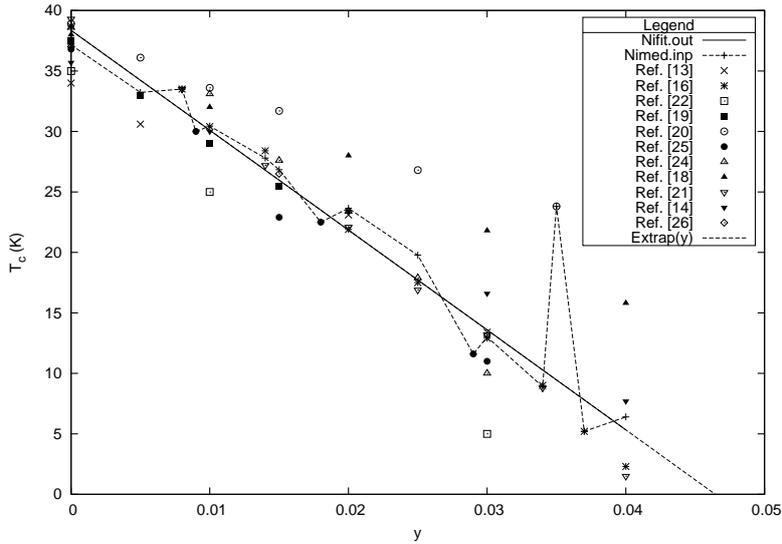


Fig. 2 – Same as Fig. 1 but for  $\text{Ni}^{2+}$  substitution.

Outputs of the LSQF analyzes are reported in Fig. 1 and Fig. 2. In both figures, the inputs  $\bar{T}_c(y_k)$  are joined by interrupted lines to guide the eye. The raw data entering the averages (1) are plotted as well, as separate points.

The outputs of LSQF analyzes are plotted by solid lines. In both cases sharp *linear* decreases of  $T_c$  with the increase of the fraction  $y$  of the  $\text{M}^{2+}$  ion of interest are obtained. The negative slopes of the two linear dependencies are  $\text{M}^{2+}$  ion dependent:  $-1291.85$  under  $\text{Zn}^{2+}$  substitutions and  $-825.8$  under  $\text{Ni}^{2+}$  substitutions. The fit values  $T_c(y_0 = 0)$  agree with each other within one degree Kelvin ( $37.59\text{ K}$  for  $\text{Zn}^{2+}$  and  $38.36\text{ K}$  for  $\text{Ni}^{2+}$ ) and are larger than the input value ( $36.97\text{ K}$ ).

The extrapolations of the fit curves toward lower  $T_c$  (dotted lines in figures 1 and 2) provide the critical  $y_c$  substitution concentrations at which  $T_c$  vanishes. From Fig. 1 it results  $y_c = 0.029$  for  $\text{Zn}^{2+}$ , while from Fig. 2,  $y_c = 0.0464$  for  $\text{Ni}^{2+}$ .

The conclusion following from the present LSQF analysis on the sharp linear decrease of  $T_c$  under increase of the  $y$  fraction of  $\text{Zn}^{2+}$  ions is supported by the overwhelming part of the conducted separate studies, hence an overall consensus

exists on this topic.

The situation is different in the case of  $\text{Ni}^{2+}$  substitution for  $\text{Cu}^{2+}$  inside the  $\text{CuO}_2$  planes in LSCO. Here the opinions are almost equally divided between the idea of a linear and a non-linear (concave) decrease of  $T_c$  under the increase of the  $y$  fraction of  $\text{Ni}^{2+}$  ions. The result of the present LSQF analysis which uses on equal footing inputs provided by eleven independent of each other studies, corroborates the idea of the linear decrease. Two hints follow. First, the effects coming from diluted  $\text{Ni}^{2+}$  ions inside a  $\text{CuO}_2$  plane are uncorrelated with each other. Second, the origins of the  $T_c$  decrease should be similar for both the  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  substitution ions.

## 5. CONCLUSIONS

The application of the described three-step procedure to the scrutiny of the copper substitution by either  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  in LSCO resulted in significantly improved statistics, hence in increased reliability of the derived conclusions as compared to those following from particular, fewer data, reports.

The results of the study substantiate one of the basic hypotheses of the two-dimensional two-band Hubbard model namely, that the high temperature superconductivity in cuprates originates in the interactions inside individual  $\text{CuO}_2$  planes.

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