Improving Statistics in the Study of Copper Substitution with Metal Ions in Cuprates

Gh. Adam[1,2], S. Adam[1,2], A. Oprea[1,2]
e-mail: adamg@jinr.ru, [1]Laboratory of Information Technologies, JINR, Dubna
[2]IFIN-HH, Magurele – Bucharest, 077125, Romania

A three-step study program. 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 metal ions characterized by ionic radii close to that of Cu^{2+}. The available references discuss this topic based on experimental data obtained by their specific groups of authors.

In view of the lack of a bird's-eye-view survey on the copper substitution and of 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 [1].

Step 1, Data collection: Grouping together the available data concerning the variation of T_c in various cuprates under copper substitution by divalent M^{2+} metal ions with Shannon's crystal ionic radii [2] close to that of 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 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 $\{T_{c,l}(y_k)\,|\,l = 1, 2, \cdots, L(k)\}$ evidence, we derive a unique value as the arithmetic average

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

Concerning $\bar{T}_c(y_0 = 0)$ in the absence of the substituting 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

$$\{\bar{T}_c(y_k)\,|\,k = 0, 1, \cdots, K\} \qquad (2)$$

is subject to a weighted LSQF analysis using the Hamming termination criterion which assumes [3] that the optimal degree of the fitting polynomial is reached when the distribution of the residuals gets stochastic (for implementation details, see [4]).

Present investigation. This is a preliminary report on the Cu^{2+} substitution in the optimally doped LSCO cuprate $La_{1.85}Sr_{0.15}CuO_4$ by either Zn^{2+} or Ni^{2+} ions [5]–[18] resulting in the generic LSCMO formula $La_{1.85}Sr_{0.15}Cu_{1-y}M_yO_4$.

As emphasized by various authors, in spite of the lower T_c value, the characteristic feature of the LSCO cuprates of showing a single CuO_2 unit per elementary cell enhances the data reliability since the M^{2+} ions are expected to migrate uniquely toward the Cu^{2+} sites inside the CuO_2 planes during the sample preparation. Apart from diffraction studies devoted to the accurate definition of the crystallographic positions occupied by the M^{2+} ions of interest inside the lattice, the comparison of the Shannon's crystal ionic radii [2] of the various LSCMO ions enhances this conclusion. Indeed, the Ni^{2+} radius (83 pm) and the Zn^{2+} radius (88 pm) are close to the Cu^{2+} ionic radius (87 pm) while being significantly different from the Cu^{3+} radius (68 pm), O^{2-} radius (126 pm), La^{3+} radius (117.2 pm) and the Sr^{2+} radius (132 pm). Therefore, Ni^{2+} and Zn^{2+} substitute indeed the Cu^{2+} ions inside the crystal.

Numerical results and discussion. Within the fourteen references [5]–[18] we have identified nine data sets pertaining to Zn^{2+} substitutions [7]–[13], [15], [16] and eleven to Ni^{2+} [5], [6], [8], [10]–[14], [16]–[18]. We have strictly followed the rule of retaining for scrutiny really independent from each other data sets. As an instance, from the Zn^{2+} and Ni^{2+} data sets of [15], only the first one was retained. As it concerns the Ni^{2+} data, the larger set of reference [17] entered the present discussion.

Among the twenty available values in [5]–[18] 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 Zn^{2+} and 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 M^{2+} substitutions (for instance, in [8], each of the six reported M^{2+} substitutions started with its own $T_c(y = 0)$, see also [9]). 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). The forty six T_c values on Zn^{2+} substitutions reported in the abovementioned nine studies addressed seventeen Zn^{2+} concentrations $y_k \neq 0$.

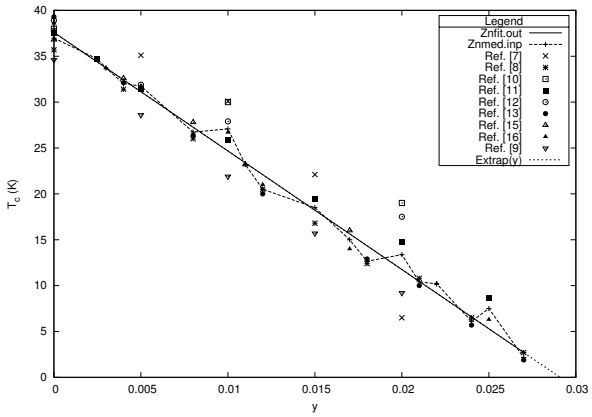

Figure 1: T_c versus the fraction y of Zn^{2+} ions substituting Cu^{2+} in CuO_2 planes.

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

In the case of Ni^{2+}, the reported forty eight values addressed fifteen 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 [5]–[18] taken separately. Outputs

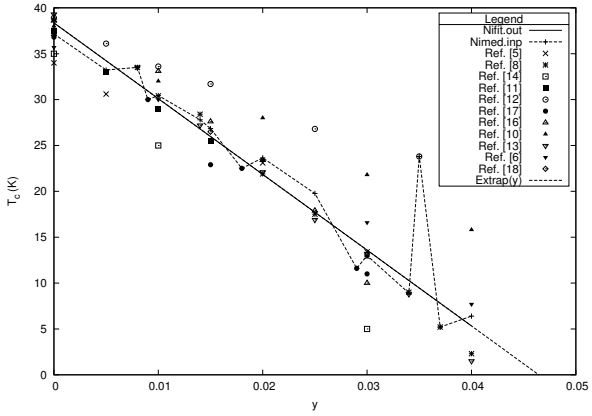

Figure 2: Same as Fig. 1 but for Ni^{2+} substitution.

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 M^{2+} ion of interest are obtained. The negative slopes of the two linear dependencies are M^{2+} ion dependent: -1291.85 under Zn^{2+} substitutions and -825.8 under Ni^{2+} substitutions. The fit values $T_c(y_0 = 0)$ agree with each other within one degree Kelvin (37.59 K for Zn^{2+} and 38.36 K for Ni^{2+}) and are larger than the input value (36.97 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 Zn^{2+}, while from Fig. 2, $y_c = 0.0464$ for 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 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 Ni^{2+} substitution for Cu^{2+} inside the 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 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 Ni^{2+} ions inside a CuO_2 plane are uncorrelated with each other. Second, the origins of the T_c decrease should be similar for both the Zn^{2+} and Ni^{2+} substitution ions.

Conclusions. The application of the described three-step procedure to the scrutiny of the copper substitution by either Zn^{2+} and 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 ([19]–[24] and references therein) namely, that the high temperature superconductivity in cuprates originates in the interactions inside individual CuO_2 planes of the existing layered perovskite structures.

Acknowledgments. Part of the results were presented at the MMCP 2013 International Conference, JINR-Dubna, July 8–12, 2013. Work was done within the JINR research topic 05-6-1060-2005/2013. Partial financial support from the Romania-JINR Cooperation Programs, JINR Orders 80/18.02.2013, p.18; 81/18.02.2013, p.68, 69; 82/18.02.2013, p.27, 28, is acknowledged.

References

[1] *Oprea A., Adam S., Adam Gh.*, On the selective copper substitution with Zn^{2+} and Ni^{2+} ions in LSCO cuprates. // Submitted to publication.

[2] *Shannon R.D.*, Revised effective ion radii and systematic studies of interatomic distances in halides and chalcogenides. // Acta Cryst. A. 1976. V.32 P.751.

[3] *Hamming R.W.* Numerical methods for scientists and engineers. Second Ed. New York (NY), USA: Dover, 1986. Part II. Chap. 27.

[4] *Adam Gh., et al.* Performance assessment of the SIMFAP parallel cluster at IFIN-HH Bucharest. // Rom. Journ. Phys. 2008. V.53 P.665.

[5] *Kang W., et al.* Effects of Ni-to-Cu substitution on the properties of the high-T_c superconductor $La_{1.85}Sr_{0.15}CuO_{4-y}$. // Phys. Rev. B. 1988. V.37 P.5132.

[6] *Fujishita H., Sato M.*, Comparison of the normal state properties between the superconducting and the nonsuperconducting metallic phases in $La_{2-y}Sr_yCu_{1-x}Ni_xO_4$. // Sol. St. Comm. 1989. V.72 P.529.

[7] *Xiao Gang, et al.* Correlation between superconductivity and normal-state properties in the $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$ system. // Phys. Rev. B. 1989. V.39 P.315.

[8] *Xiao Gang, et al.* Magnetic pair-breaking effects: Moment formation and critical doping level in superconducting $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$ systems (A=Fe, Co, Ni, Zn, Ga, Al). // Phys. Rev. B. 1990. V.42 P.8752.

[9] *Harashina H., et. al.*, Cu-site doping effects, transport and magnetic properties of high-T_c oxides and their hole concentration dependence. // Physica C 1993. V. 212 P. 142.

[10] *Gaojie Xu, et al.* Two dimensional hole localization induced by Zn, Ni, and Mg dopings in Cu sites in $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_y$. // Journal of Superconductivity 1997. V. 10 P. 13.

[11] *Nakano T. et al.* Contrasting Ni- and Zn-substitution effects on magnetic properties and superconductivity in $La_{2-x}Sr_xCuO_4$. // Phys. Rev.B. 1998. V.58 P.5831.

[12] *Zaleski A.J., Klamut J.*, Influence of Ni and Zn substitution on anisotropy of the penetration depth in $La_{1.85}Sr_{0.15}CuO_4$. // Phys. Rev. B. 1999. V. 59 P.14023.

[13] *Liu G.D., Zhao Z.X., Che G.C.*, A possible mechanism for the effect of impurities in the CuO_2 plane of high T_c superconductors. // Solid State Comm. 1999. V. 109 P.495.

[14] *Haskel D. et al.*, Ni-induced local distortions in $La_{1.85}Sr_{0.15}Cu_{1-y}Ni_yO_4$ and their relevance to T_c suppression: An angular-resolved XAFS study. // Phys. Rev. B. 2001. V.64 P.104510 (10 pp.).

[15] *Kofu M., Kimura H., Hirota K.*, Zn and Ni doping effects on the low-energy spin excitations in $La_{1.85}Sr_{0.15}CuO_4$. // Phys. Rev. B. 2005. V.72 P.064502 (12 pp.).

[16] *Dong A.F. et al.*, Structural change and superconductivity in $La_{1.85-2x}Sr_{2x+0.15}Cu_{1-x}Ru_xO_4$ and $La_{1.85}Sr_{0.15}Cu_{1-x}Ru_xO_4$ systems. // Supercond. Sci. Technol. 2006. V.19 P.206.

[17] *Matsuura M., et. al.*, Ni-substitution effects on the spin dynamics and superconductivity in $La_{1.85}Sr_{0.15}CuO_4$. // Phys. Rev. B. 2012. V.86 P.134529 (8 pp.).

[18] *Kurosawa T., et. al.*, Ni-impurity effects on the superconducting gap of $La_{2-x}Sr_xCuO_4$ studied from the magnetic field and temperature dependence of the electronic specific heat. // Phys. Rev. B. 2012. V.85 P.134522 (7 pp.).

[19] *Plakida N.M.* High-Temperature Cuprates Superconductors. Experiment, Theory, and Applications. Berlin, Heidelberg: Springer, 2010. 570pp. Chap. 7.

[20] *Plakida N.M., Hayn R., Richard J.-L.*, Two-band singlet-hole model for the copper-oxide plane. // Phys. Rev. B. 1995. V.51 P.16599.

[21] *Plakida N.M., Anton L., Adam S., Adam Gh.*, Exchange and spin-fluctuation mechanisms of superconductivity in cuprates. // Zh. Eksp. Teor. Fiz. 2003. V. 124. P. 367. [JETP. 2003. V. 97. P. 331].

[22] *Adam Gh., Adam S.*, Rigorous derivation of the mean-field Green functions of the two-band Hubbard model of superconductivity. // J. Phys. A.: Math. Theor. 2007. V. 40. P. 11205.

[23] *Adam Gh., Adam S.*, Generalized mean field energy spectrum of the modified two-band Hubbard model in cuprates. // Rom. Journ. Phys. 2010. V. 55. P. 481.

[24] *Plakida N.M., Oudovenko V.S.*, On the theory of superconductivity in the extended Hubbard model: Spin-fluctuation pairing. // Eur. Phys. J. B. March 2013. V. 86:115 (15pp.).