EUROPHYSICS LETTERS 15 June 1987

Europhys. Lett., 3 (12), pp. 1309-1314 (1987)

High-T_c Superconductivity in La-Ba-Cu-O and Y-Ba-Cu-O Compounds.

I. KIRSCHNER (*), J. BÁNKUTI (*), M. GÁL (**), K. TORKOS (**), K. G. SÓLYMOS (***) and G. HORVÁTH (*)

(*) *Department for Low Temperature Physics, Roland Eötvös University, 1088 Budapest, Puskin u.* 5-7, *Hungary*

(**) *Department of General and Inorganic Chemistry, Roland Eötvös University, 1088 Budapest, Muzeum krt.* 6-8, *Hungary*

(***) *Department of Petrology and Geochemistry, Roland Eötvös University, 1088 Budapest, Muzeum krt.* 4/a, *Hungary*

(received 21 April 1987; accepted 6 May 1987)

PACS. 74.70. – Superconducting materials.
PACS. 74.70N – Dirty superconductors.

Abstract. – A high-critical-temperature superconducting transition in multiple-phase La-Ba-Cu-O and Y-Ba-Cu-O systems has been found with the aid of electrical and magnetic measurements. The possible causes of superconductivity is also considered. Among them the change of Fermi-surface topology is the most appreciated.

During the last year investigations of Bednorz and Müller [1] opened a new direction in the field of superconductivity, when they observed a critical temperature in La-Ba-Cu-O above 30 K. In their opinion the nature of superconductivity is either percolative or fluctuative in double perovskite layers.

The later experiments accomplished by Chu [2], Cava [3], Wu *et al.* [4], Hor *et al.* [5] and Uchida *et al.* [6] show that the evaluation of the superconducting measurements is rather complicated due to the different and ambiguous possible reasons of superconductivity in single-phase and multiple-phase samples of La-Ba-Cu-O and Y-Ba-Cu-O.

Analysing earlier and recent experiments [7, 8] and moreover some theoretical investigations [9-11], the following probable superconducting interactions can be proposed: 1) interfacial effects in mixed phases, 2) concentration fluctuations in tetragonal K_2NiF_4-type phase or in cubic $CaTiO_3$-type perovskite, 3) bulk superconductivity of the ordinary electron-phonon interaction, 4) interfaces between metals and insulators or between metals and semiconductors, 5) ferroelectricity, 6) unidentified phases, 7) mixed and variable valence, 8) lattice instability, 9) Peierls-instability and a strong phonon coupling to the conduction electrons and 10) soft phonon contribution to a large electron-phonon interaction.

In order to avoid the uncertainty concerning the working samples a well-considered preparation technique and a systematic analytical investigation were elaborated. The aim of our experiments was to find the possible highest-T_c superconductors among La-Ba-Cu-O and Y-Ba-Cu-O compounds.

Because of this, the optimum value of ionic radii, of the substitution of lanthanides with alkaline earths and that of the ratio of lanthanides plus alkaline earths to the copper were taken into account during the preparation process.

Two kinds of La-based and two kinds of Y-based oxide systems have been found to be successful in this respect, namely $(La_{1.6}Ba_{0.4})CuO_{4-\delta}$ as La(1) samples, $(La_{0.8}Ba_{0.2})Cu_{4-\delta}$ as La(2) ones, $(Y_{1.2}Ba_{0.8})CuO_{4-\delta}$ as Y(1) samples and $(Y_{0.6}Ba_{0.2})CuO_{4-\delta}$ as Y(2) ones. They were prepared by solid-state reactions from pure Merck's chemicals of La_2O_3, $BaCO_3$, CuO for La(1) samples, La_2O_3, $Ba(NO_3)_2$, $Cu(NO_3)_2 3H_2O$ for La(2) ones and Y_2O_3, BaCO and CuO for both kinds of Y-samples. The weighing quantities were chosen so that the molar ratio of metallic components was La:Ba:Cu = 1.6:0.4:1, La:Ba:Cu = 0.8:0.2:1, Y:Ba:Cu = 1.2:0.8:1 or Y:Ba:Cu = 0.6:0.2:1, respectively. It is very important that the ratios concerning Cu are as follows: (La + Ba):Cu = 2:1 for La(1), and 1:1 for La(2) samples, (Y + Ba):Cu = 2:1 for Y(1) and 0.8:1 for Y(2) samples.

These mixtures were pulverized and homogenized in agate mortars. Thermogravimetry analysis of the powders was performed in the temperature range of (500 ÷ 1500) °C with the aim to obtain the optimal temperature for solid-state reaction. On the basis of thermogravimetric measurements the heat treatment was accomplished at 900 °C for La-samples and 925 °C for Y-samples during 14 hours at ambient atmosphere in quartz crucibles. The furnaces were heated gradually over 3 hours.

Powder X-ray diffraction patterns (Siemens D-500) on reacted and pulverized mixtures unambiguously demonstrate the existence of microcrystalline structure and the absence of amorphous phases.

The powders were then pressed into pellets of 13 mm diameter and 1 mm thickness of 20 kbar pressure and sintered once more.

The photographs taken by a scanning electron microscope (Jeol JXA-50A) on the pellets show that samples consist of a medley of different crystalline shapes. According to a rough estimation, about 85 vol.% of cigar, 15vol.% of pancake and 5vol.% of cube form a La(1) sample (fig. 1). The pictures of a La(2) sample show a more homogeneous structure (fig. 2) and the edges being rounded. It hints at the possibility, that the lower ratio of (La + Ba):Cu is more favourable for the parameters of superconductivity, which is supported by the later experiments.

Similar results were obtained by analysing photographs taken on Y(1) and Y(2) samples (fig. 3 and 4). As is shown, different crystalline shapes appear again in the pellets. Comparing the more sintered picture of the kind (2) sample to the measured superconducting electrical and magnetic data, it seems to be more hopeful from the point of view of high-T_c superconductivity.

The dependence of resistance on temperature was measured by a conventional four-point technique in La-samples, where the electrical leads were attached to the periphery of the samples in a right-angle formation by silver paste. On the other hand, in the case of Y-samples a six-probe arrangement was used based on evaporated gold contacts to which the leads were soldered by silver paste. The purpose of this complicated measuring structure was to eliminate the self-resistivity of the contacts and to point out the contingent inhomogeneity and anisotropy of the samples. Because of this aim, all contact-pairs were used for measurement of voltage signals. During the electrical experiments 1 mA measuring current was used. Temperature was indicated by Lake Shore Cryotronics Ge-sensors (GR-200 A-1000) and controlled by Pt-resistor thermometers (NBS 391 and 207187). The magnetic field was produced by a superconducting magnet and measured by Hall-probes (LSC LGHA-321).

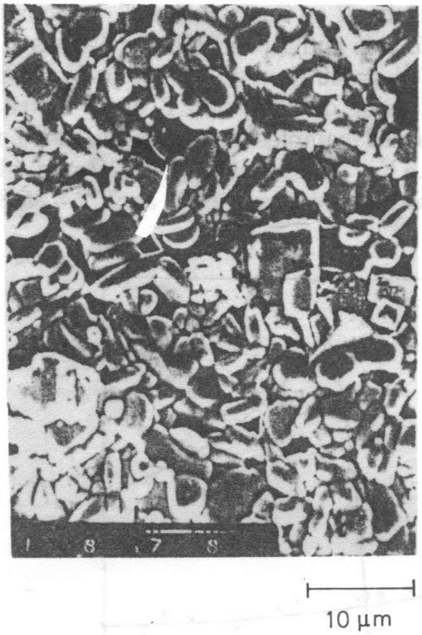

Fig. 1.

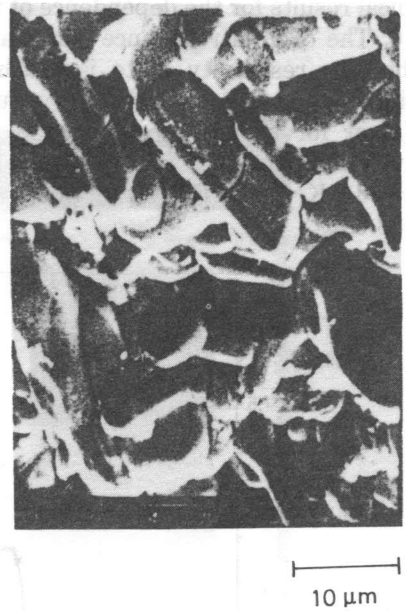

Fig. 2.

Fig. 1. – SEM photograph on a kind (1) La-based sample ($M = 1500$).
Fig. 2. – SEM photograph on a kind (2) La-based sample ($M = 1500$).

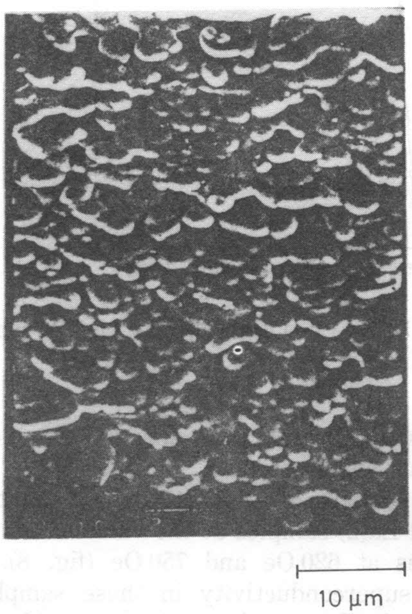

Fig. 3.

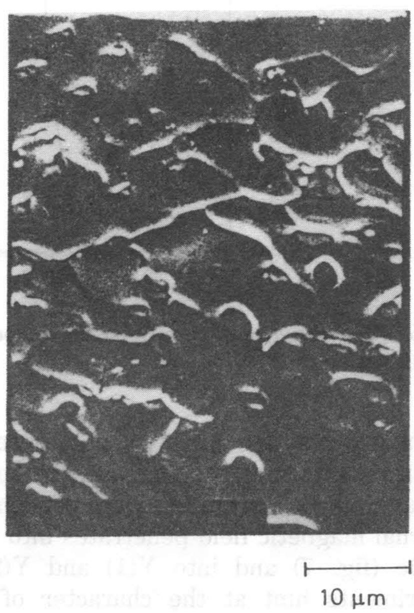

Fig. 4.

Fig. 3. – SEM photograph on a kind (1) Y-based sample ($M = 1500$).
Fig. 4. – SEM photograph on a kind (2) Y-based sample ($M = 1500$).

Typical results for the dependence of the resistivity R on temperature T are shown in fig. 5 and 6. The drop of resistance starts at $T_0^{(1)} = 51.2$ K and $T_0^{(2)} = 56$ K for La-based oxides and the zero-resistivity state is reached at $T_{R=0}^{(1)} = 49$ K and $T_{R=0}^{(2)} = 53$ K. Using the midpoint method, the critical temperature has a value of $T_c^{(1)} = 50.2$ K or $T_c^{(2)} = 54.5$ K for kind (1) or for kind (2), respectively. The Y-based samples have similar slope for the resistivity-temperature curves and $T_0^{(1)} = 90.5$ K, $T_{R=0}^{(1)} = 80.8$ K, $T_0^{(2)} = 94.4$ K and $T_{R=0}^{(2)} = 83.2$ K. From these the values of critical temperature result as $T_c^{(1)} = 85.8$ K and $T_c^{(2)} = 88.6$ K.

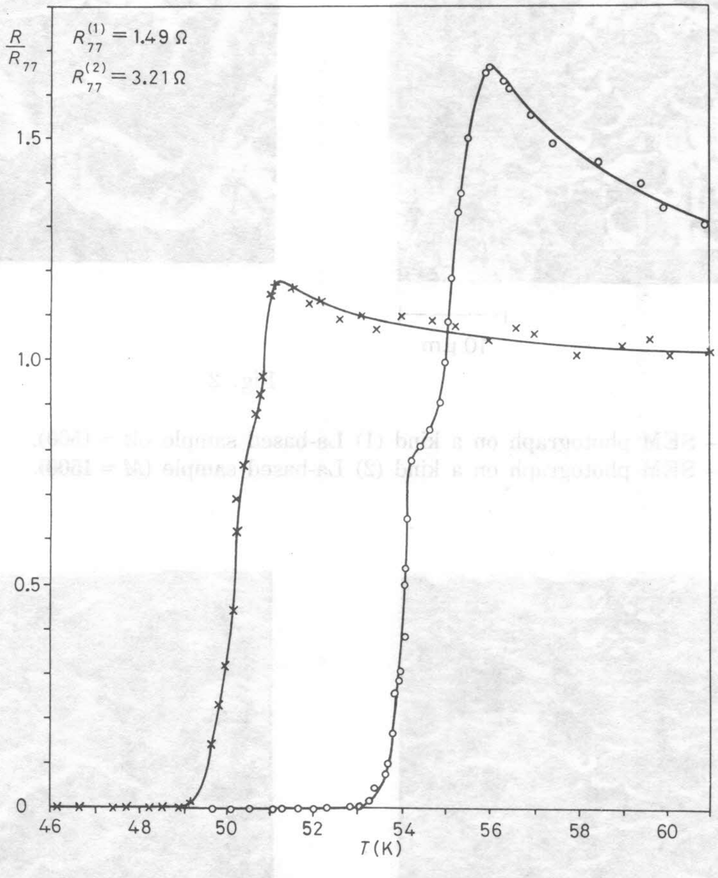

Fig. 5. – Dependence of resistivity on temperature of La-Ba-Cu-O compounds; × kind (1) samples, ○ kind (2) samples.

The six-contact arrangement permitted us to prove with the aid of electrical measurements that the samples are homogeneous and isotropic.

Magnetic measurements were perfomed at temperature of 4.2 K. It can be stated that the external magnetic field penetrates into La(1) and La(2) samples at the value of 300 Oe and 370 Oe (fig. 7) and into Y(1) and Y(2) samples at 620 Oe and 750 Oe (fig. 8). These experiments hint at the character of type-II superconductivity in these samples and demonstrate that about 10 vol.% or 13 vol.% for the La-samples and at least 18 vol.% or 23 vol.% for the Y-ones are in Meissner's state at this temperature.

As stated in our earlier investigations [12-14], type-I superconductivity goes over into type-II on the effect of additive material content. This phase transition is a consequence of

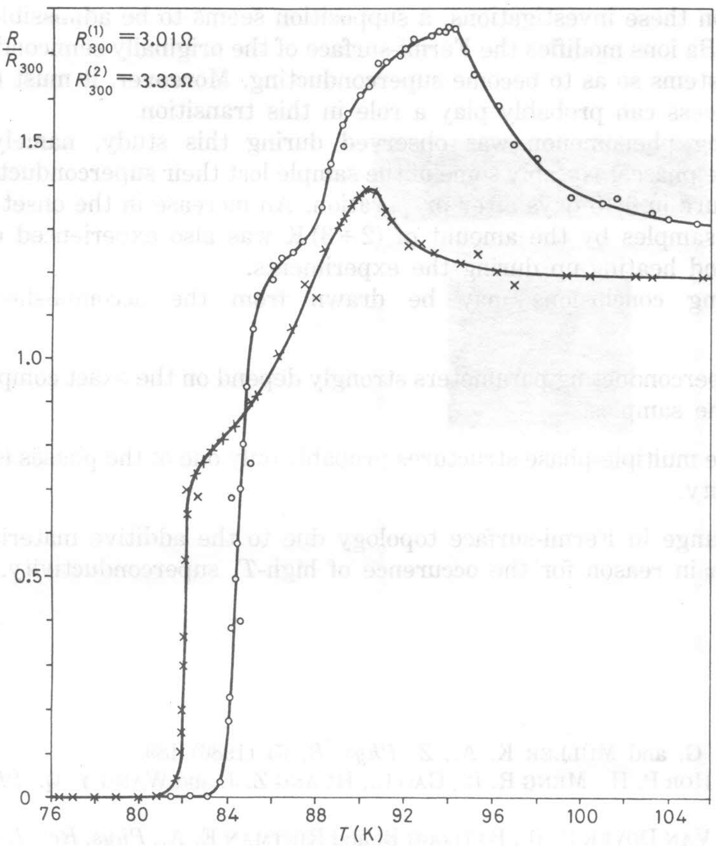

Fig. 6. – Dependence of resistivity on temperature of Y-Ba-Cu-O compounds; notations as in fig. 5.

the change in Fermi-surface topology due to the Lifshitz-singularity. It was also shown that type-II superconductivity can be transformed into normal state by an increase of the concentration of alloying material. This is percolationlike process.

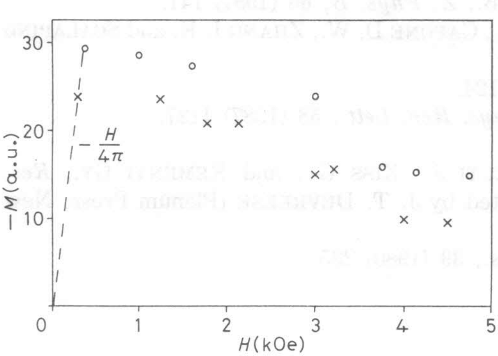

Fig. 7.

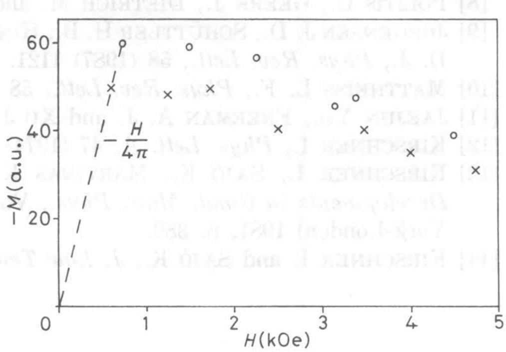

Fig. 8.

Fig. 7. – A magnetic moment-magnetic field relation at 4.2 K in La-based samples; notations as in fig. 5.

Fig. 8. – A magnetic moment-magnetic field relation at 4.2 K in Y-based samples; notations as in fig. 5.

Depending on these investigations, a supposition seems to be admissible, by which the contribution of Ba ions modifies the Fermi-surface of the originally semiconducting La-Cu-O and Y-Cu-O systems so as to become superconducting. Moreover, it must be noted, that a percolation process can probably play a role in this transition.

An interesing phenomenon was observed during this study, namely the temporal instability of the phases. Notably some of the sample lost their superconducting character at room temperature in 6-15 days after preparation. An increase in the onset temperature of some Y-based samples by the amount of $(2 \div 3)$ K was also experienced on the effect of cooling-down and heating-up during the experiments.

The following conclusions may be drawn from the accomplished experimental investigations:

1) The superconducting parameters strongly depend on the exact composition and heat treatment of the samples.

2) In these multiple-phase structures probably only one of the phases is responsible for superconductivity.

3) The change in Fermi-surface topology due to the additive material of Ba can be taken as the main reason for the occurence of high-T_c superconductivity.

REFERENCES

[1] BEDNORZ J. G. and MÜLLER K. A., *Z. Phys. B*, **64** (1986) 189.
[2] CHU C. W., HOR P. H., MENG R. L., GAO L., HUANG Z. J. and WANG Y. Q., *Phys. Rev. Lett.*, **58** (1987) 405.
[3] CAVA R. J., VAN DOVER R. B., BATLOGG B. and RIETMAN E. A., *Phys. Rev. Lett.*, **58** (1987) 408.
[4] WU M. K., ASHBURN J. R., TORNG C. J., HOR P. H., MENG L., GAO L., HUANG Z. J., WANG Y. Q. and CHU C. W., *Phys. Rev. Lett.*, **58** (1987) 908.
[5] HOR P. H., GAO L., MENG R. L., HUANG Z. J., WANG Y. Q., FORSTER K., VASSILIOUS J., CHU C. W., WU M. K., ASHBURN J. R. and TORNG C. J., *Phys. Rev. Lett.*, **58** (1987) 911.
[6] UCHIDA S., TAKAGI H., KITAZAWA K. and TANAKA S., *Jpn. J. Appl. Phys.*, **26** (1987) L-1.
[7] BEDNORZ J. G., TAKASHI M. and MÜLLER K. A., *Europhys. Lett.*, **3** (1987) 379.
[8] POLITIS C., GEERK J., DIETRICH M. and OBST B., *Z. Phys. B*, **66** (1987) 141.
[9] JORGENSEN J. D., SCHÜTTLER H. B., HINKS D. G., CAPONE D. W., ZHANG I. K. and SCALAPINO D. J., *Phys. Rev. Lett.*, **58** (1987) 1121.
[10] MATTHEISS L. F., *Phys. Rev. Lett.*, **58** (1987) 1124.
[11] JAEJUN YU., FREEMAN A. J. and XU J. H., *Phys. Rev. Lett.*, **58** (1987) 1127.
[12] KIRSCHNER I., *Phys. Lett. A*, **47** (1974) 139.
[13] KIRSCHNER I., SAJÓ K., MARTINÁS K., BÁNKUTI J., KISS GY. and REMÉNYI GY., *Rec. Developments in Cond. Matt. Phys.*, Vol. 4, edited by J. T. DEVREESE (Plenum Press, New York-London) 1981, p. 389.
[14] KIRSCHNER I. and SAJÓ K., *J. Low Temp. Phys.*, **39** (1980) 235.