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# SUPPRESSION OF SUPERCONDUCTING FLUCTUATIONS IN THE ELECTRICAL CONDUCTIVITY IN OXYGEN UNDERDOPED AND OXYGEN OVERDOPED $Bi_2Sr_2CaCu_2O_8$ SINGLE CRYSTALS

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**Dedicated to Professor Boran Leontić on the occasion of his 70$^{\mathrm{th}}$ birthday**

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The *ab* plane resistivity of the same single crystals of $Bi_2Sr_2CaCu_2O_8$ at different oxygen stoichiometries has been measured. As the oxygen content is lowered, the crystals become underdoped and the transition temperature ($T_c$) falls off from 85 to 58 K. Increasing the oxygen concentration causes the crystals to become overdoped and the $T_c$ falls off again. The contribution to the electrical conductivity from superconducting fluctuations above $T_c$ falls off drastically as oxygen concentration deviates from the optimum. We argue that the data may be consistent with a relatively large Maki – Thompson contribution, which falls off sharply both in the underdoped and overdoped regions – probably because of pair breaking.

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## 1. Introduction

High transition temperatures ($T_c$) in cuprate superconductors have much smaller values of the coherence length and lower carrier densities than most conventional superconductors, as well as an anisotropic layer structure. Because of these properties, fluctuation effects [1, 2] are more important and have been studied both above and below $T_c$ and in applied magnetic fields by many research groups [3–11]. Over the last few years [12] it has become clear that several families of cuprate superconductors exhibit a parabolic curve of $T_c$ versus hole concentration ($p$) similar to that originally established for $La_{2-x}Sr_xCuO_{8-\delta}$. Superconductivity only exists over a rather limited range of $p$ and disappears both for "underdoped" and "overdoped" samples. This behaviour may provide a critical test for different theoretical mechanisms and it is clearly of interest to understand how the fluctuation effects change with doping.

The two-layer superconductor $Bi_2Sr_2CaCu_2O_{8-\delta}$ (hereafter BISCO) is the only system where one can tune the $T_c$ from the underdoped to the overdoped side merely by changing the oxygen concentration $\delta$. These samples are much more homogeneous than reduced $T_c$ samples obtained by other means, and the high quality crystalline form permits one to study subtle effects such as the excess conductivity ($\sigma'$) above $T_c$ due to superconducting fluctuations.

In this paper we report some data for the $ab$ ($CuO_2$) plane conductivity of single crystals of BISCO. The contribution to the electrical conductivity from superconducting fluctuations above $T_c$ falls off drastically as oxygen concentration deviates from the optimum, both on the underdoped and overdoped sides. We argue that the data may be consistent with a relatively large Maki – Thompson contribution which falls off sharply both in the underdoped and overdoped regions – probably because of pair breaking.

## 2. Experimental

Thin, uniform platelets approximately 2 mm $\times$ 1 mm and 2 – 10 $\mu m$ thick were cleaved from larger crystals. Electrical contacts were made by using Dupont 6838 fire-on silver epoxy. As in the other studies [14, 15], the oxygen content was varied by annealing in a small quartz tube for 1 – 2 hrs at 745 °C at various oxygen partial pressures and quenching the tube in water. In this way $T_c$ could be reduced from 85 K to 50 – 60 K in a reliable and reversible manner. However, it was difficult to obtain still lower values of $T_c$ because of irreversible changes to the crystals. The hole doping level was varied in the same crystal, with the same electrical contacts, by varying the oxygen depletion $y$.

The overdoping under high oxygen pressure was performed in a home designed cell [16]. Several flakes of BISCO were put into the high pressure vessel which was filled with liquid oxygen, sealed and heated up to 450 °C. After two days of heat treatment the vessel was quenched in water, and during the opening the released oxygen gas was measured in order to precisely calculate the pressure during the doping procedure. The highest oxygen pressure at the doping temperature was 4.4 kbar. The platelets for resistivity measurements were cleaved from the flakes and mounted by Dupont 4929 silver paste. After the measurement of the temperature dependence of the resistivity, the crystal was annealed in 1 bar of oxygen at 600 °C, and an optimally doped sample was recovered.

## 3. Results and analysis

Resistivity $\rho(T)$ data normalized to the 300 K value of the sample annealed in 1 bar of oxygen are shown for one crystal in Fig. 1. The numbers on the curves refer to the oxygen partial pressure in bars at the annealing temperature [14]. In order to obtain the corresponding fluctuation plots in Fig. 2, the normal state resistance was fitted to a straight line as shown in Fig. 1. The deviations below this

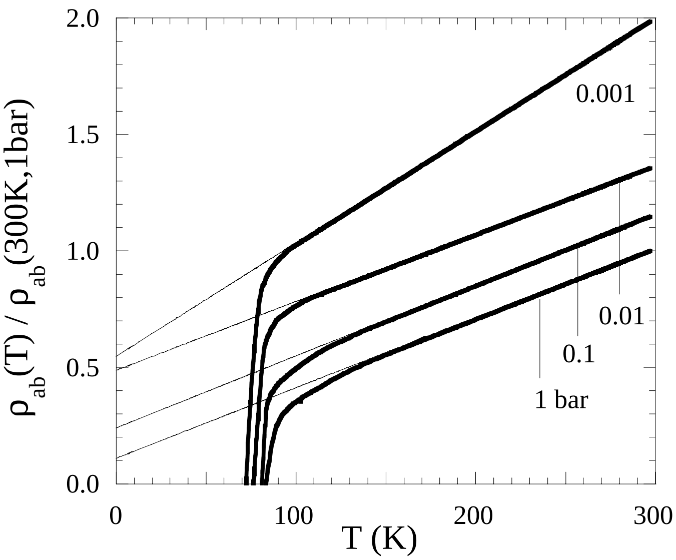


*Fig. 1. Normalized resistivity measured in the ab plane for the same single crystal of* $Bi_2Sr_2CaCu_2O_{8-y}$ *at various oxygen contents y. The numbers on the curve refer to the oxygen partial pressure (in bars) at the annealing temperature [14].*

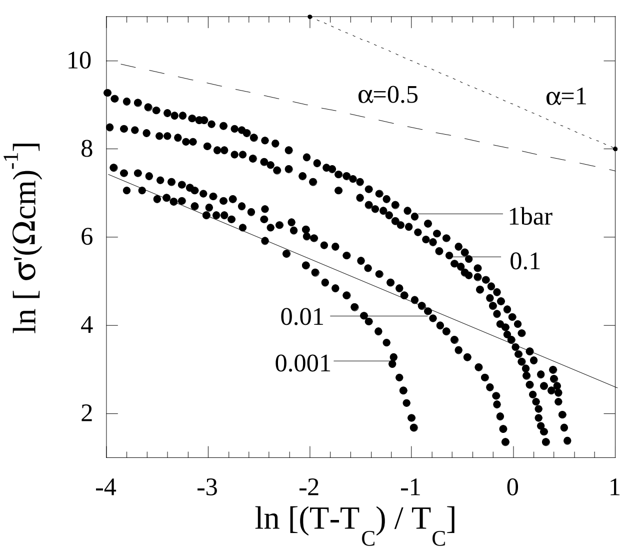


*Fig. 2. Fluctuation analysis of data in Fig. 1, $\sigma'$ is the excess conductivity . The dashed lines show the slopes expected ($-0.5$ and $-1$) in the 3D and 2D limits of Eq. (1). The straight solid line shows the 2D limit of Eq. (1) using $S = 1.5$ nm and a room temperature resistivity of 150 $\mu\Omega$cm.*

line were attributed to an extra conductivity $\sigma'$ arising from fluctuations. A strong suppression of the fluctuation conductivity as $T_c$ is reduced from 85 K to 76 K can already be seen from the raw data in Fig. 1, the resistivity remains linear closer to $T_c$. Usually the opposite tendency is observed in reduced $T_c$ samples, the transition becomes more and more rounded, wider in temperature as one goes away from the optimally doped sample. This is probably due to structural fluctuations, that is to a distribution of $T_c$'s due to the structural inhomogeneities. Other phenomena, which can further "pollute" the evaluation of the excess conductivity due to superconducting fluctuations, are pseudogap and localization effects in reduced $T_c$ samples. The former gives faster decrease of the resistivity than linear below a $T^*$ temperature due to the opening of a pseudogap in the spin excitation spectrum [17].

Furthermore, in inhomogeneous samples an increase of the resistivity is observed at lower temperatures, which is short circuited on further cooling by the superconducting fraction of the sample. This can compensate the decrease of the resistivity due to fluctuations. Usually these effects are present in strongly reduced $T_c$ samples where the pseudogap shows up or where it is difficult to control the sample homogeneity. We believe that none of these spurious effects influence our analysis since we stay close to the optimal $T_c$ (76 and 58 K are the lowest $T_c$ in oxygen depleted samples). For the log-log plots in Fig. 2, $T_c$ was taken as the temperature at which $\rho(T)$ was equal to 50% of its linearly extrapolated normal state value (the straight lines in Fig. 1). It corresponds to the temperature of the maximum slope of $\rho(T)$ to within approximately 1 K. A strong suppression of the fluctuation conductivity as $T_c$ is reduced from 85 K to 76 K can already be seen from the raw data in Fig. 1. It is more apparent in Fig. 2 where $\ln\sigma'$ is plotted versus $\ln((T-T_c)/T_c)$. In the middle of the region where Ginsburg – Landau theory is usually valid ($(T-T_c)/T_c = 1.05$ or $\ln(T-T_c)/T_c = -3$), this relatively small change in $T_c$ has lead to a reduction in $\sigma$' by a factor of 7.4. Standard Aslamazov – Larkin (AL) theory, for small, non-critical fluctuations of the order parameter gives the following Lawrence-Doniach expression [18] for the fluctuation conductivity:

$$\sigma' = \left(\frac{e^2}{16\hbar S}\right)\tau^{-1/2}(\tau+4K)^{-1/2}\,, \tag{1}$$

where $S$ in the interlayer spacing, $\tau = (T-T_c)/T_c$, $K = (\xi_c/S)^2$ and $\xi_c$ is the zero temperature coherence length perpendicular to the $CuO_2$ planes. If the two adjacent planes in BISCO are strongly coupled and fluctuate together, as is almost certainly the case, then $S \approx 1.5$ nm and at high temperatures $\sigma' = e^2/16\hbar S\tau^{-1}$, with no adjustable parameters. This line is drawn in Fig. 2 (taking an average room temperature resistivity for many crystals of $150\mu\Omega$ cm). As $S$ is not changed by oxygen depletion, according to Eq. (1), all curves should tend towards this line at high temperatures. This is clearly not the case. However, the line which has no free parameters does roughly correspond to the observed magnitude of $\sigma'$. For example, at $\ln\tau = -2$ ($\tau = 0.135$), the highest value of $T_c$ corresponds to the experimental values of $\sigma'$ 3.3 times larger than the AL theory and the lowest value to $\sigma'$ 2.7 times smaller than AL theory. There is also evidence for a crossover to a slope of 0.5, the 3D limit of Eq. (1), below $\tau = 0.08 - 0.05$ in all cases.

Data for a second oxygen depleted crystal (not plotted here), where a $T_c$ value (mid-point) is as low as 58 K, give qualitatively the same results as shown in Fig. 2.

We have studied the excess conductivity in the overdoped region of BISCO as well. Figure 3 shows the temperature dependence of two samples overdoped in high oxygen pressures of 4.4 and 2.1 kbar, respectively. The sample treated at 4.4 kbar was annealed at ambient pressure and this is shown in Fig. 3 with the 1 bar label. Here, the analysis of the superconducting fluctuations has no well established "routine", as in the optimally doped case, because the resistivity has a superlinear, $T^m$ $(m > 1)$, temperature dependence. For example, in our samples heat treated in 4.4 kbar of oxygen, $m = 1.65$, while for the 2.1 kbar of oxygen pressure $m = 1.16$. The extrapolation of this behaviour to the transition region is probably as questionable as the linear extrapolation in the optimally doped case. But since we want to show the robust effects on the excess conductivity and not to study the details of the temperature dependence of $\sigma'$, we think it is instructive to plot $\ln \sigma'$ versus $\tau$ (Fig. 4), just to stress the effect already apparent in Fig. 3., the decrease of $\sigma'$ with decreasing $T_c$.

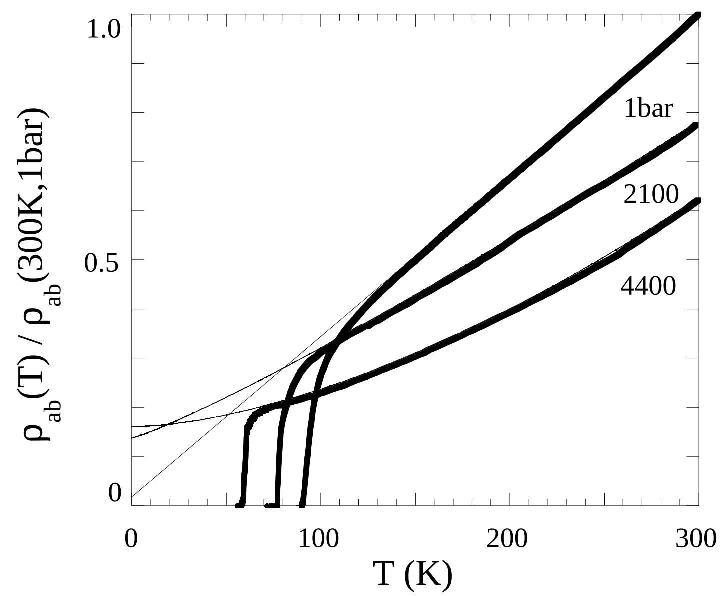


*Fig. 3. Normalized resistivity measured in the ab plane of* $Bi_2Sr_2CaCu_2O_{8-y}$ *overdoped at high oxygen pressure (marked in bars at the annealing temperature of 450 °C). The 4400 and 1 bar curves correspond to the same crystal.*

Therefore, within the AL approach the problem is how to understand the large and $T$-dependent values of $\sigma'$ for the optimum doping levels and its decrease in reduced $T_c$ samples. It seems quite probable that at optimal doping levels there is a large Maki – Thompson [19] contribution to $\sigma'$ as well. This contribution arises from the increase in single particle (hole) conductivity by the presence of fluctuations, because of correlations which persist in the normal state after the superconducting "droplets" have decayed away. Unlike the standard AL term, it is very sensitive to pair breaking [19]. However, if the pair breaking parameter ($\delta$) is small, for example $\delta = 0.02$ [20], then at $\tau = 0.1$ in the 2D limits the anomalous contribution [19] to $\sigma'$ will be 4 times larger than the regular one (Eq. (1)). This factor rises to 5.1 at $\tau = 0.2$. In other words, for $\tau \gg \delta$, it will enhance the value of $\sigma'$ without drastically altering its temperature dependence. For $\tau \approx \delta$, the slow flattening off of the Maki – Thompson term may be difficult to distinguish from the 2D-3D cross-over. This anomalous term will fall off strongly as $\delta$ is increased.

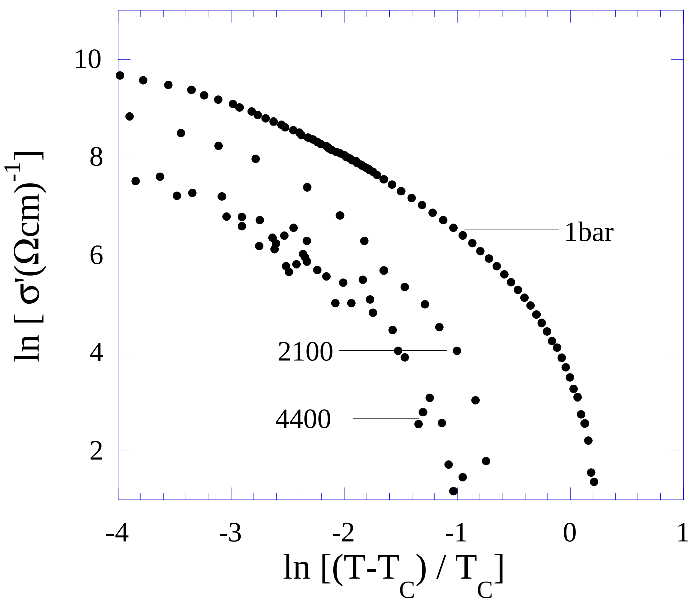


*Fig. 4. Fluctuation analysis of data in Fig. 3. The excess conductivity was extracted by the extrapolation of the $T_m$ superlinear behaviour of the temperature dependence of the resistivity of the overdoped samples ($m = 1.16$ and 1.65 for the 2100 and 4400 samples, respectively).*

## 4. *Conclusion*

We have presented experimental data showing how the *ab* plane conductivity of single crystals of $Bi_2Sr_2CaCu_2O_8$ is influenced by the superconducting fluctuations and that for the same crystal, the fluctuation conductivity is suppressed both by oxygen depletion and oxygen insertion (or equivalently by the removal or adding of holes from/to the $CuO_2$ planes). The magnitude of $\sigma'$ suggests the presence of a Maki – Thompson term. The present interpretation implies that there is a strong pair breaking mechanism (possibly associated with magnetic fluctuations) which sets in as the hole concentration is reduced below the optimal value. In the overdoped region, defects, evidenced by the increasing residual resistivity in the overdoped samples, might act as pair breakers. It would be of interest to extend the present work to lower hole concentrations by working with yttrium doped crystals [21].

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It is a great pleasure for me to participate in the special edition of Fizika A in honour of Professor Boran Leontić. We had a fruitful collaboration in the "gold rush" era of high-$T_c$ superconductivity. His attitude of working methodologically, step by step from sample preparation, through the measurements, until the in-depth understanding of the underlying physics served me as an example in my later activity. I dedicate this work to him.

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References

1) See articles by D. M. Ginsberg and M. B. Salamon in *Physical Properties of High Temperature Superconductors*, Vol. I, World Scientific, Singapore (1989);

2) L. N. Bulaevskii, V. L. Ginsburg and A. A. Sobyanin, Sov. Phys. JETP **68** (1988) 1499;

3) P. P. Freitas, C. C. Tsuei and T. S. Plaskett, Phys. Rev. B **30** (1987) 833;

4) Minuru Suzuki and Makoto Mikita, Phys. Rev. B **44** (1991) 249;

5) R. Hopfengrtner, B. Hensel and G. Saemann, Ischenko, Phys. Rev. B **44** (1991) 741;

6) J. R. Cooper, S. D. Obertelli, A. Carrington and J. W. Loram, Phys. Rev. B **44** (1991) 12089;

7) K. Semba, T. Ishii and A. Matsuda, Phys. Rev. Lett. **67** (1991) 769;

8) J. Sugarava, H. Iwasaki, N. Kobayashi, H. Yamane and T. Hirai, Phys. Rev. B **46** (1992) 14818;

9) G. Balestrino, M. Marinelli, E. Milani, L. Reggiani, R. Veglio and A. A. Varlamov, Phys. Rev. B **46** (1992) 14919;

10) C. Baraduc, V. Pagnon, A. Buzdin, J. Y. Henry and C. Ayache, Phys. Lett. A **166** (1992) 267;

11) A. Gauzzi and D. Pavuna, Phys. Rev. B **51** (1995) 15420;

12) For example, M. R. Presland, J. L. Tallon, R. G. Buckley, R. S. Liu and N. E. Flower, Physica C **176** (1991) 95;

13) J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang and S. S. P. Parkin, Phys. Rev. Lett. **61** (1988) 1127;

14) L. Forró and J.R. Cooper, Europhys. Lett. **11** (1990) 55;

15) J. R. Cooper, L. Forró and B. Keszei, Nature **343** (1990) 444; L. Forró, J. R. Cooper, B. Leontić and Keszei, Europhys Lett. **10** (1989) 37;

16) L. Mihaly, C. Kendziora, J. Hartge, D. Mandrus and L. Forró, Rev. Sci. Instrum. **64** (1993) 2397;

17) H. Y. Hwang, B. Batlogg, H. Takagi, H. L. Kao, J. Kwo, R. J. Cava, J.-J. Krajewski and W. F. Peck, Jr, Phys. Rev. Lett. **72** (1994) 2636;

18) W. E. Lawrence and S. Doniach, *Proc. 12th Int. Conf. on Low Temperature Physics*, Kyoto (1970), ed. Eijo Kanda, Tokyo (1971) p. 361;

19) K. Maki and R. S. Thompson, Phys. Rev. B **39** (1989) 2767;

20) Experimental evidence for the importance of a Maki-Thompson term in $YBa_2Cu_3O_{7-y}$ is given by studies involving Zn doping (E. Fung and J.R. Cooper, unpublished);

21) D. Mandrus, L. Forró, C. Kendziora and L. Mihaly, Phys. Rev. B **44** (1991) 2418.

## SMANJENJE SUPRAVODLJIVIH FLUKTUACIJA ELEKTRIČNE VODLJIVOSTI U MONOKRISTALIMA $Bi_2Sr_2CaCu_2O_8$ SA SMANJENIM I POVEĆANIM SADRŽAJEM KISIKA

Mjerili smo vodljivost u *ab* ravnini jednog monokristala $Bi_2Sr_2CaCu_2O_8$ za razne stehiometrijske sadržaje kisika. Smanjenjem sadržaja kisika, kristal postaje pod-dopiran i prijelazna temperatura se smanji od 85 na 58 K. Povećanjem sadržaja kisika kristal postaje pre-dopiran i $T_c$ se opet smanjuje. Doprinos električnoj vodljivosti od supravodljivih fluktuacija iznad $T_c$ jako se smanjuje ako koncentracija kisika odstupa od optimalne. Moguć sklad dobivenih podataka obrazlažemo relativno velikim Maki-Thompsonovim doprinosom koji snažno opada i u pod- i nad-dopiranom području, vjerojatno zbog kidanja parova.