# Fluctuation-enhanced conductivity in the Sb-doped Bi-Pb-Sr-Ca-Cu-O superconducting system

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(Received 1 July 1991)

Fluctuations above the transition temperature in the Sb-doped 2:2:2:3 Bi-Pb-Sr-Ca-Cu-O compounds have been studied. The excess conductivity above $T_c$ was determined from both the normal metal and the Anderson-Zou fits to the normal-state resistivity. With use of Aslamazov-Larkin theory, the dimensionality of the materials was determined. The value of the critical exponent ($\lambda=-1$) obtained from the experimental excess conductivity clearly indicates that the superconductivity in the Sb-doped (Bi,Pb)-based system is of a two-dimensional nature. From the fluctuation-enhanced conductivity, a coherence length of $7.9\pm0.8$ Å was obtained for the samples, in good agreement with values obtained from magnetization curves of polycrystalline Bi-Sr-Ca-Cu-O superconductors. The fit of the Anderson-Zou model indicates that, although the crystallites in the polycrystalline samples are randomly oriented, the resistivity in the $a$-$b$ plane dominates in the equivalent parallel resistor network.

## I. INTRODUCTION

The rounding of the resistivity temperature curve near and above the transition temperature of superconductors has been attributed to thermodynamic fluctuations which produce short-lived Cooper pairs that lead to an apparent increase in the conductivity. The excess conductivity ($\Delta\sigma$) is defined as

$$\Delta\sigma=\sigma(T)-\sigma_N(T)\ , \tag{1}$$

where $\sigma_N(T)$ is the background, normal-state conductivity. In the mean-field region, the Aslamazov-Larkin[1] theory predicts that

$$\Delta\sigma/\sigma_{300\ \mathrm{K}}=A\varepsilon^{\lambda}\ , \tag{2}$$

where $A$ is a temperature-independent amplitude, $\lambda$ is a critical exponent, $\varepsilon=(T-T_c)/T_c$, and $\sigma_{300\ \mathrm{K}}$ is the normal-state conductivity at 300 K. Both $A$ and $\lambda$ depend strongly on the superconducting dimensionality, and for three and two dimensions, are given, respectively, by

$$A=(e^2/32\hbar)[\rho_{300\ \mathrm{K}}/\xi(0)]\ ,\quad \lambda=-0.5\ ; \tag{3a}$$

$$A=(e^2/16\hbar)(\rho_{300\ \mathrm{K}}/d)\ ,\quad \lambda=-1.0\ ; \tag{3b}$$

where $\xi(0)$ is the superconducting coherence length at absolute zero, $d$ is the characteristic length of the two-dimensional (2D) system, and $\rho_{300\ \mathrm{K}}$ is the resistivity at 300 K.

From the measurements of the fluctuation-enhanced conductivity, the dimensionality of the superconductor can be established and the coherence length can be obtained.[2,3] Two-dimensional paraconductivity has been reported by Martin *et al.*[4] for single crystals of Bi-Sr-Ca-Cu-O. Vidal *et al.*[5] and Poddar *et al.*[6] studied these effects in polycrystalline samples of the Bi-based high-$T_c$ compounds. Griden *et al.*[7] have reported 2D paraconductivity in the Pb-doped, Bi-based polycrystalline compounds.

Interesting results have been reported for the influence of the incorporation of Sb in the (Bi,Pb)-Sr-Ca-Cu-O compound. The transition temperature is reported to have been raised to 150 K.[8] Also, Chandrahood *et al.*[9] have reported zero resistance at 132 K in lead-free $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_y$. Although other workers have not found evidence of the existence of any superconducting transitions above 110 K,[10] it is observed that the substitution of Sb stabilizes the 110 K phase.[11,12] No single crystal of this material has been reported yet, although a great deal of effort has gone into the preparation and characterization of Sb-doped, Bi-based compounds. In the absence of single crystals, thermodynamic fluctuations in this material can be studied only in ceramic materials.

In this paper we present results of the measurements of the excess conductivity in the 2:2:2:3 phase of the $Bi_{1.7}Pb_{0.3}Sb_xSr_2Ca_2Cu_{3.6}O_y$ superconducting system. We discuss the dimensionality and present the coherence lengths of these samples.

## II. EXPERIMENTAL METHODS

Samples were prepared by the conventional solid state reaction method. High purity powders of $Bi_2O_3$, PbO, $Sb_2O_3$, $SrCO_3$, $CaCO_3$, and CuO were mixed in the nominal ratio of [Bi]:[Pb]:[Sb]:[Sr]:[Ca]:[Cu]= 1.7:0.3:$x$:2:2:3.6 ($x=0.05$ and 0.1) in acetone in an agate mortar. We adopted this nominal composition instead of that of $Bi_2Sr_2Ca_2Cu_3O_y$ because in preliminary work we found it difficult to obtain a single 2:2:2:3 phase with the ideal composition. The mixtures were calcined at a temperature of 820 °C for 5 h and cooled with the furnace turned off. The calcined material was well ground and then pelletized at a pressure of 4 tons/cm$^2$. A pellet with $x=0.05$ was sintered at a temperature of 852 °C for 72 h and cooled at the rate of 0.1 °C/min from 852 °C to 750 °C, 0.2 °C/min from 750 °C to 600 °C, 0.5 °C/min from 600 °C to 400 °C, and furnace cooled to room temperature. This sample is labeled S1A. The second batch

 

of samples with $x$ equal to 0.05 and 0.10 was sintered at 852° C for 30 h and furnace cooled. They were then pressed at the same pressure as for the first pellet and sintered again at 852 °C for 50 h. They were subjected to the cooling conditions described above. These samples are labeled S1B for $x=0.05$ and S2B for $x=0.10$.

Static magnetic susceptibility measurements were performed in a magnetic field of 25 G with a vibrating Foner magnetometer. X-ray diffraction patterns in the $2\theta$ range 20–70° were obtained with a computer controlled Nicolet powder diffractometer. The resistivity was measured by the four-probe method with two current contacts and two potential contacts on rectangularly shaped samples.

## III. RESULTS AND DISCUSSIONS

The magnetization results of S1B and S2B are shown in Fig. 1. They show a single 2:2:2:3 phase with transition temperatures of 107 K and 109 K for S1B and S2B, respectively. The x-ray diffraction patterns of these samples also show a single 2:2:2:3 phase.

Figure 2 shows the temperature dependence of the resistivity of S1A, S1B, and S2B. They all show a quasilinear temperature dependence of the resistivity at $T>2T_c$. The resistivity deviates from linearity around 150 K and finally drops to zero with a characteristic rounding off near $T>T_c$.

The choice of $T_c$ plays a significant role in the evaluation of the excess conductivity. Here $T_c$ is defined as the temperature at which $d\rho/dT$ versus $T$ shows a maximum, or $\rho$ versus $T$ has its inflection point. Figure 3 shows the $d\rho/dt$ versus $T$ curve for S1B. The temperature derivative is numerically determined by a third-order polynomial fit to seven points.

The linear region in each sample was fit to the normal metal formula

$$\rho(T)=a+bT \ . \tag{4}$$

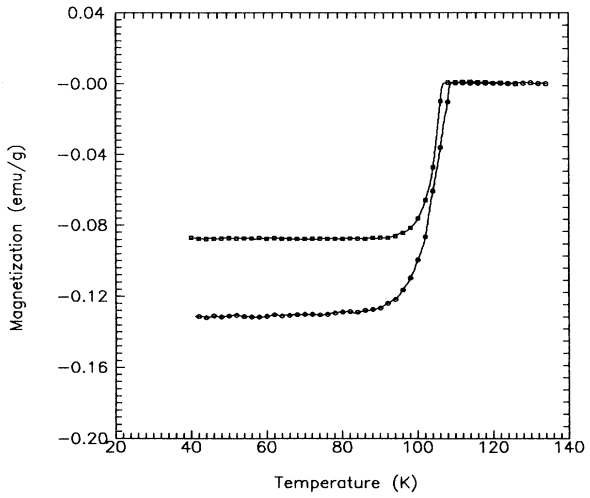


FIG. 1. Temperature dependence on the magnetization at 25 G, (□) S1B and (○) S2B.

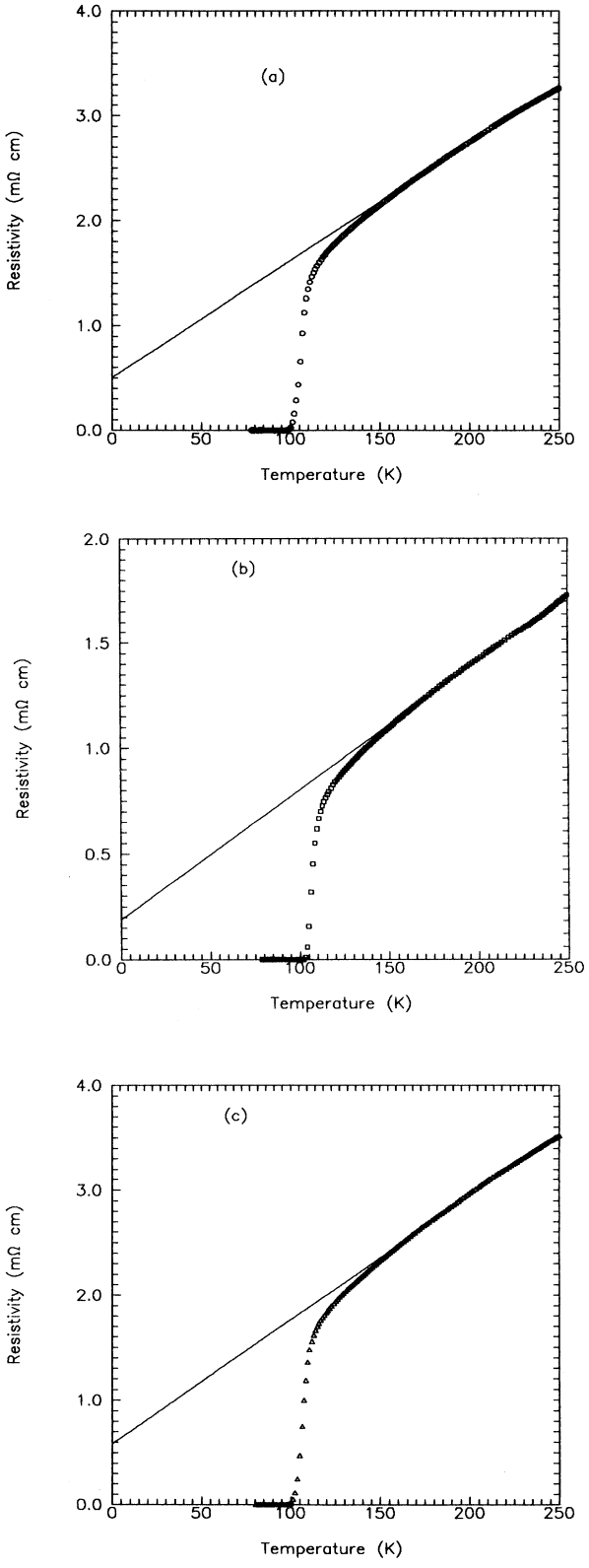


FIG. 2. Temperature dependence of resistivity of (a) S1A, $(Bi_{1.7}Pb_{0.9}Sb_{0.05}Sr_2Ca_2Cu_{3.6}O_y)$, (b) S1B, $(Bi_{1.7}Pb_{0.3}Sb_{0.05}Sr_2Ca_2Cu_{3.6}O_y)$, and (c) S2B, $(Bi_{1.7}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_{3.6}O_y)$.

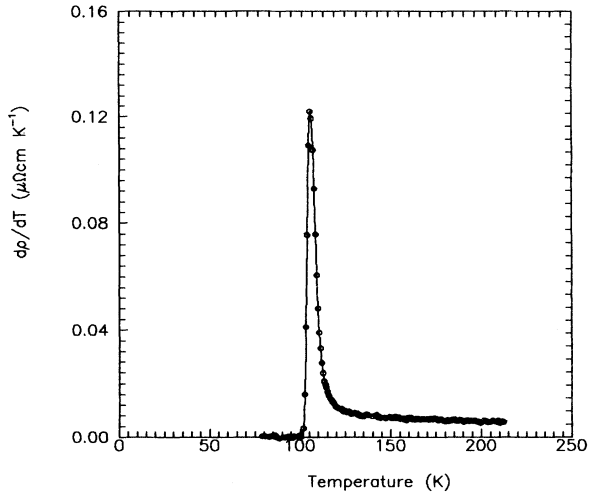


FIG. 3. Plot of $(d\rho/dT)$ vs temperature for S1B.

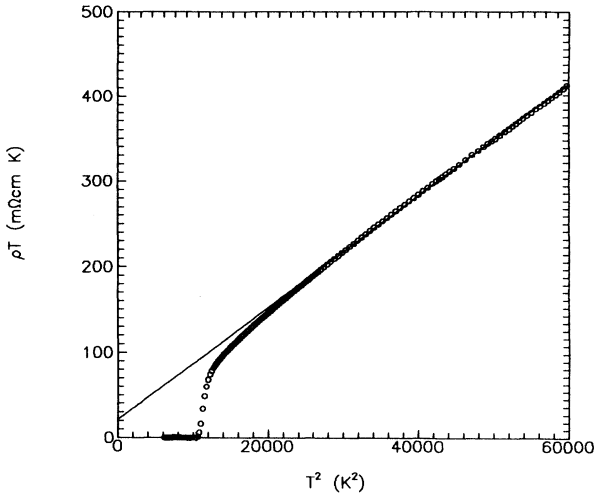


FIG. 4. The Anderson-Zou plot of the resistivity-temperature data of S1B.

This equation was used to calculate the normal resistivity in the fluctuation regions. The fits are represented by the straight lines in Fig. 2. The excess conductivity, $\Delta\sigma$, was calculated from the actual measured resistivity and the extrapolated normal resistivity.

Anderson and Zou[13] have proposed an interesting mechanism for the current transport between adjacent Cu-O planes. In the resonant-valence-bond theory, conduction in the normal state is mediated by holons which are confined to each Cu-O plane. Tunneling between the planes is only possible for real electrons which can be formed by merging the two types of soliton-like excitations of the 2D Cu-O layers, namely, the holon (spin 0, charge 1) with the spinon (spin $\frac{1}{2}$, charge 0). As expected for a scattering of bosons by fermions, the temperature dependence of $\rho_{ab}$ is linear in $T$. The probability of a tunneling process between the planes is proportional to the spinon density which is linear in $T$, leading to a resistivity $\rho_c \sim 1/T$. According to these authors the normal-state resistivity in both the $a$-$b$ planes and the $c$ direction is given by

$$\rho(T)=a'/T+b'T\ , \tag{5}$$

where the hyperbolic term is introduced to model the interplane hopping of carriers. This model has been used to describe the excess conductivity of both single crystal and polycrystalline high-temperature superconducting materials.[3,13,14]

We make use of the Anderson-Zou model by plotting the product $\rho T$ versus $T^2$ in Fig. 4. The samples fulfill the predicted temperature dependence of $\rho$ as indicated by the straight line in Fig. 4. The excess conductivity from the Anderson-Zou model was calculated to provide a second way of determining $\Delta\sigma$.

In order to test the theoretical expressions for two-dimensional and three-dimensional fluctuations and to afford a comparison with the previous results on Bi-Sr-Ca-Cu-O systems, we plotted the normalized excess conductivity, $(\Delta\sigma/\sigma_{300\ \mathrm{K}})$, from both the normal metal fit and the Anderson-Zou fit against the reduced temperature $\varepsilon$. Figure 5 shows the plots for the normal metal fit for S1B. In the normal metal ($N$) case the $\ln(\Delta\sigma/\sigma_{300\ \mathrm{K}})$ versus $\ln\varepsilon$ plot is reasonably linear over a wide range of $\ln\varepsilon$. The critical exponents obtained for these regions are shown in Table I. The average critical exponent for all the samples is $-1.02$.

In the Anderson-Zou (AZ) case, the behavior of the $\ln(\Delta\sigma/\sigma_{300\ \mathrm{K}})$ versus $\ln\varepsilon$ for all the three samples is identical with the normal metal case but with slightly different values of the critical exponent (shown in Table I). However, the average critical exponent for this case is $-1.00$. Thus the Anderson-Zou fit and the normal metal fit are in excellent agreement. The value of the critical

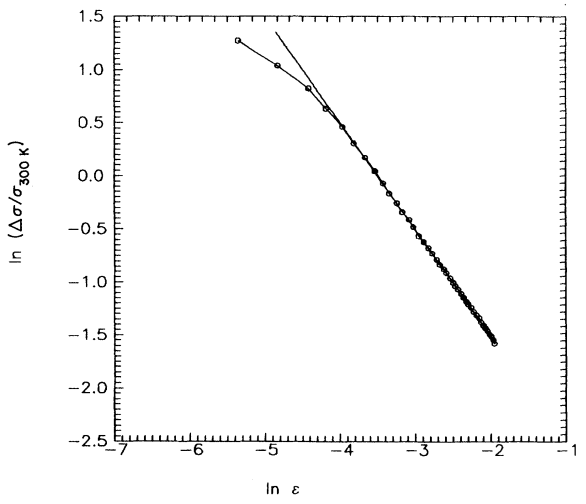


FIG. 5. Log-log plot of the normalized excess conductivity $(\Delta\sigma/\sigma_{300\ \mathrm{K}})$ vs reduced temperature $(\varepsilon)$ for S1B.

TABLE I. Some resistivity parameters and critical exponents of Sb-doped polycrystalline 2:2:2:3 Bi-Pb-Sr-Ca-Cu-O superconducting compounds.

| Sample | $T_c$ (K) | $\rho_0/\rho_{300\ K}$ (%) | $\rho_0/\rho_{150\ K}$ (%) | $\lambda$ ($N$-fit) | $\lambda$ (AZ-fit) | $\xi(0)$ (Å) |
|---|---|---|---|---|---|---|
| S1A | 106.2 | 14.41 | 25.31 | −1.00 | −0.97 | 8.73 |
| S1B | 105.8 | 9.29 | 17.91 | −1.02 | −1.12 | 7.70 |
| S2B | 106.3 | 14.13 | 24.73 | −1.01 | −0.92 | 7.26 |

exponent obtained indicates a 2D superconductivity in our samples.

Results of resistivity measurements of single crystals of both $YBa_2Cu_3O_y$ and Bi-Sr-Ca-Cu-O show that the $a$-$b$-plane resistivity is lower in magnitude than the $c$ direction resistivity.[9,15] The $a$-$b$-plane resistivity, which according to the Anderson-Zou model varies linearly with temperature, therefore, dominates in a parallel circuit network. The fit of the Anderson-Zou model indicates that although the polycrystalline samples consist of randomly oriented crystallites, due to very high anisotropy, the $a$-$b$-plane resistivity dominates in the equivalent parallel resistor network. The resistivity of the polycrystalline samples, then, has the same behavior, and hence yields the same type of information as does $\rho_{ab}$ in a single crystal study.

Two kinds of contributions to the fluctuation-enhanced conductivity $\Delta\sigma$ are usually considered. The Aslamazov-Larkin relation[1] [see Eq. (1)] gives the direct contribution which results from the acceleration of superconducting pairs. An additional indirect contribution due to the interaction of superconducting fluctuations with the normal electrons was calculated by Maki[16] and Thompson.[17]

Neglecting the Maki-Thompson contribution, Lawrence and Doniach[18] calculated the fluctuation-enhanced conductivity parallel to the layers in a superconducting layer compound:

$$\Delta\sigma=(e^2/16\hbar d\varepsilon)\{1+[2\xi_c(0)/d]^2\varepsilon^{-1}\}^{-1/2}\ . \tag{6}$$

For temperatures close to the BCS mean-field transition temperature, $T_c^0$, the ratio $2\xi_c(T)/d \gg 1$ and $\Delta\sigma$ diverges as $\varepsilon^{-1/2}$ which corresponds to the three-dimensional behavior. For temperatures $T > T_c^0$ the ratio $2\xi_c(T)/d \ll 1$ and $\Delta\sigma$ diverges as $\varepsilon^{-1}$ (2D behavior). Due to the very short coherence length $\xi_c(0)$ the dimensional crossover temperature

$$T_0=T_c^0\{1+[2\xi(0)/d]^2\} \tag{7}$$

is expected to be close to $T_c^0$ in a temperature range where $\Delta\sigma$ is still measurable.

To use Eq. (7) to determine the coherence length, we apply a construction suggested by Fiory *et al.*[19] to determine the BCS mean-field transition temperature $T_c^0$, $T_0$, and $d$. Equation (2) is rewritten as

$$(\rho_{300\ K}/\rho-\rho_{300\ K}/\rho_N)^{-1}=d\sigma_{300\ K}(T-T_c^0)/AT_c^0\ . \tag{8}$$

Here we use the fact that our samples show 2D superconductivity. For $\rho_N$ we use the normal metal fit to the resistivity-temperature curves of the samples. Thus by plotting the left-hand side of Eq. (8) versus $T$, we get $T_c^0$ from the point where the extrapolated straight line crosses the temperature axis, and $d$ from the slope of the straight line. We also obtain $T_0$ from the point where the straight line deviates from the curve. Figure 6 shows a representative plot for S1B. Using the values of $T_0$, $T_c^0$, and $d$ that are obtained in this way, the coherence lengths of our samples are calculated. The values for the various samples are shown in Table I. The average coherence length for the samples is 7.9±0.8 Å. Measurements of the critical fields in $Bi_2Sr_2Ca_1Cu_2O_y$ single crystals[20] gave coherence lengths of 30.1 Å in the $a$-$b$ plane and 5.7 Å in the $c$ direction. The difference in the coherence lengths in the two directions is due to the large anisotropy of these materials. The value obtained for our samples is the polycrystalline average. Schnelle *et al.*[21] obtained a coherence length of ≃7–8 Å from magnetization curves of polycrystalline Bi-Sr-Ca-Cu-O superconductors. Gridin *et al.*[7] reported a coherence length of 13 Å for polycrystalline Pb-doped Bi-Sr-Ca-Cu-O material. The value of the coherence length obtained for our samples compares favorably well with the value obtained from the magnetization curves of the polycrystalline samples but is lower than that obtained by Griden *et al.*

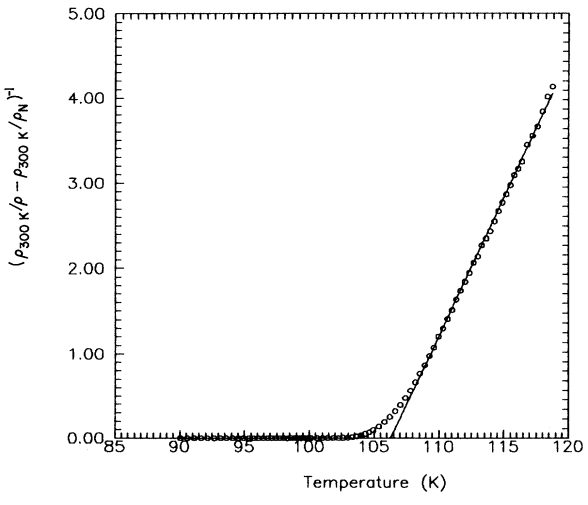


FIG. 6. Construction for the evaluation of $T_c^0$, $T_0$, and $d$ of S1B.

## IV. CONCLUSIONS

The values of the critical exponent, $\lambda$, obtained from the experimental excess conductivity clearly indicate that the superconductivity in the Sb-doped (Bi,Pb)-based system is of a two-dimensional nature. The coherence length of the polycrystalline samples is $7.9\pm0.8$ Å, which agrees quite well with published values of Bi-based polycrystalline superconductors. The Anderson-Zou fit to the data is found to work well in the polycrystalline samples. Although the crystallites in the polycrystalline samples are randomly oriented, the conductivity in the *a-b* plane dominates in the parallel equivalent circuit.

## ACKNOWLEDGMENTS

We thank T. W. Krause and P. K. Ummat for many useful discussions and assistance with the sample preparation. We are also grateful to T. Olech and G. Hewitson for technical assistance. We acknowledge the use of facilities of the Institute of Materials Research at McMaster University. The research was supported by the Natural Sciences and Engineering Research Council of Canada.

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