Thermodynamic fluctuations and the thermoelectric coefficient in $(Bi_{1.6}Pb_{0.4})Sr_2Ca_3(Cu_{1-x}Ag_x)_4O_{12+\delta}$ superconductors

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We present a study of the thermoelectric coefficient $L(T)$ of polycrystalline silver doped $(Bi_{1.6}Pb_{0.4})Sr_2Ca_3(Cu_{1-x}Ag_x)_4O_{12+\delta}$ samples. $L(T)$ relates the thermopower $S(T)$ with electrical conductivity, $\sigma(T)$, and gives an indication of the influence of the order parameter fluctuations (OPF) on $S(T)$ in the mean field region (MFR). The results of $L(T)$ indicate that the critical behavior of $S(T)$ above the superconducting transition is driven essentially by $\sigma(T)$. These results suggest that, in the MFR, $L(T)$ is not affected by thermodynamic fluctuations of the superconducting order parameter (OPF). The OPF effects show a bi-dimensional character in the entire MFR, which is not affected by Ag doping. For low Ag concentrations, the experimental data $\Delta\sigma/\sigma_B$ fit well to the Lawrence-Doniach model for layered superconductors in the MFR. Furthermore, the behavior of ΔL is nearly temperature independent. [S0163-1829(99)13533-1]

INTRODUCTION

Since in the copper-oxide superconductors $\xi(0)$ is typically two orders of magnitude smaller than in low temperature superconductors and the superconducting transition temperature (T_C) is one order of magnitude higher, order parameter fluctuations (OPF) can be observed at accessible temperatures close to T_C. Measurements of electrical resistivity $\rho(T)$ and magnetic susceptibility $\chi(T)$ show OPF effects even 10 K above the critical temperature.[1,2]

An important and still controversial aspect of the OPF effects in high temperature superconductors (HTSC) is related with their influence on the in-plane thermoelectric coefficient $L(T)$, which relates the in-plane thermopower $S(T)$ and the in plane $\rho(T)$. Different experimental groups have reported an anomalous peak, sometimes very sharp, in $S(T)$ of polycrystalline and single crystal HTSC samples near T_C. This anomaly however has not been observed in $\rho(T)$ and therefore a strong critical divergence of $L(T)$ near T_C attributed to intrinsic OPF effects would be observed.

On the other hand, some authors have suggested the existence of a relationship between the anomalous $S(T)$ peak and sample inhomogeneities, temperature gradient inhomogeneities, or even experimental artifacts.[3–5] In the YBCO systems, in the case of fully oxygenated samples, some results indicate that the thermoelectric coefficient does not present any sharp critical divergence close and above T_C.[6,7] In order to give some insight on the above fundamental questions, we discuss in this paper detailed measurements of the thermoelectric power $S(T)$ and the electrical resistivity $\rho(T)$ rounding above T_C of silver doped $(BiPb)_2Sr_2Ca_3Cu_4O_{12-\delta}$ (BSCCO) polycrystalline samples. We analyze the OPF effects on both magnitudes in terms of the existing theories.

EXPERIMENT

Polycrystalline samples of nominal composition $(Bi_{1.6}Pb_{0.4})Sr_2Ca_3(Cu_{1-x}Ag_x)_4O_{12+\delta}$, BSCCO-2234, with $0 \leqslant x \leqslant 0.1$, were prepared by the solid-state reaction method using high purity powders of BiO_2, PbO, SrO_3, $CaCO_3$, CuO, and $AgNO_3$. The materials were ground thoroughly, preheated at 800 °C for 20 h and then grounded and pressed (9 ton/cm^2) in the form of small pellets. Thereafter the pellets were sintered at 850 °C for 140 h in air and cooled with the furnace turned off.

The Ag doping affects the superconducting properties of the BSCCO-2234 system but does not affect the structure of high-T_C phase (110 K) as observed with x-ray diffraction. An increasing of the critical current density $(\mathbf{J}_C)$ was observed for $x<0.01$ and could be associated to microstructural changes. Part of Ag segregates on the BSCCO grain boundaries. This effect can either increase the contact surface between grains by decreasing the grain size or change the weak link type. Larger doping levels $(x>0.01)$ inhibit the formation of the high-T_C phase (110 K) and decrease J_C. For $x>0.01$ the x-ray diffraction patterns display both multiphase samples (110 K, 80 K, and nonsuperconducting) and Ag diffractive peaks, which increase by increasing x.[8]

The electrical resistivity measurements were carried out by the four probe dc method, while the thermoelectric data were obtained using the differential technique with a temperature gradient, $\Delta T \approx 0.1$ K across the sample. The temperature was monitored with calibrated copper-constantan thermocuples. Pt-100 sensors were used to know and control the bare temperature for each measured point. All voltages were measured using a Keithly nanovoltmeter model 182 with a resolution of 0.05 μV. The estimated absolute accuracy of the TEP is ~3%.[9,10]

RESULTS AND DISCUSSION

For small thermal gradients the thermoelectric power and the electrical conductivity are related by the thermoelectric coefficient $L(T)$, which is defined by[11,12]

$$L(T) \equiv S(T)\sigma(T). \tag{1}$$

Therefore in the presence of order parameter fluctuations the measurements of $S(T)$ can be directly affected by $\sigma(T)$ or

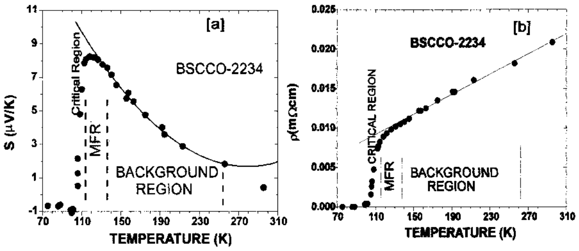

FIG. 1. Typical behavior of $S(T)$ and $\rho(T)$ of Ag-doped BSCCO-2234 samples. The MFR near the transition temperature and the background region are displayed.

$L(T)$. In order to analyze the rounding effects on $S(T)$ and $\rho(T)$ close above the transition temperature and the influence of OPF on $S(\varepsilon)$, $\sigma(\varepsilon)$, and $L(\varepsilon)$, it is necessary to determine and quantify the corresponding excess $\Delta\sigma$, $\Delta\rho$, and ΔL, which are defined as[13]

$$\Delta S(\varepsilon)=S(\varepsilon)-S_B(\varepsilon), \tag{2a}$$

$$\Delta \sigma(\varepsilon)=\sigma(\varepsilon)-\sigma_B(\varepsilon), \tag{2b}$$

$$\Delta L(\varepsilon)=L(\varepsilon)-L_B(\varepsilon), \tag{2c}$$

where ε is the reduced temperature defined as $\varepsilon \equiv \ln(T/T_{CS}) \approx (T-T_{CS})/T_{CS}$, in the case of the thermopower and $\varepsilon \approx (T-T_{C\rho})/T_{C\rho}$ in the case of resistivity. T_{CS} and $T_{C\rho}$ are the temperatures where $\rho(T)$ and $S(T)$ near the superconducting transition have the inflection point. For each sample the difference between T_{CS} and $T_{C\rho}$ is less than 0.3 K, which can be attributed to experimental errors (hereafter referred to as T_C).

The excess thermopower, $\Delta S(\varepsilon)$, close and above T_C is calculated from the difference between measured thermopower, $S(\varepsilon)$, and the extrapolated one, $S_B(\varepsilon)$, to low temperatures from the region where the OPF effects are not present. In our case we use a possible $S(T)$ functional form in the normal region far away from the transition temperature in order to diminish one of the largest uncertainty causes. This uncertainty is related to the thermopower background choice and due to the absence of an unambiguous functional form for $S(T)$ in the normal region of HTSC. After several polynomial fittings to our experimental results we have concluded that in the range $150\,\mathrm{K} \leqslant T \leqslant 250\,\mathrm{K}$, $S(T)$ discomposes mainly in two terms $s(T)=\alpha T+\beta/T$, i.e., higher order terms are negligible [see Fig. 1(a)]. The first term αT is attributed to the carrier diffusion and the second one, proportional to $1/T$, has been associated with the phonon drag but it should obviously include more than one contribution.[9,10] The main characteristic of the $S(T)$ curves for each sample are displayed in Table I. In a similar form the measured resistivity $\rho(T)$ above T_C (in the normal state) in zero applied magnetic field can be well described for all samples, Fig. 1(b), as $\rho_B(T)=c+dT$. This expression represents the resistivity of each sample in the normal state above 150 K, only the slopes and the constant terms varied from sample to sample (Table I).

TABLE I. Characteristic values of resistivity $\rho(T)$ and thermopower $S(T)$ of Ag-doped BSCCO-2234 superconducting samples.

	ρ(300 K) mΩ cm	T_C (K)	$d\rho/dT$ (mΩ cm/K)	S (300 K) (μV/K)
PURE	0.053	108.0	0.00015	1.060
Ag(0.001)	0.027	108.4	0.00008	0.815
Ag(0.004)	0.021	108.4	0.00006	0.840
Ag(0.005)	0.017	107.5	0.00005	0.820
Ag(0.01)	0.011	107.5	0.00004	0.804
Ag(0.02)	0.018	108.2	0.00005	0.811
Ag(0.1)	0.050	107.3	0.00012	0.851

Figure 1 shows additionally the behavior of $S(T)$ [Fig. 1(a)] and $\rho(T)$ [Fig. 1(b)] in the background and the mean field region respectively. In our case the mean field region (MFR) lay between $\varepsilon \sim 0.03$ and $\varepsilon \sim 0.18$, i.e., in the reduced temperature range where the time-dependent Ginzburg-Landau like approaches and the Gaussian approximations for OPF in zero magnetic field are expected to be valid.[13,14]

The enhancement in the electrical conductivity $\Delta\sigma(\varepsilon)$ is defined as the difference between measured conductivity $\sigma(\varepsilon)$ and $\sigma_B(\varepsilon)$. The later one is the extrapolation to zero temperature from the straight line trend of the normal region $(150 \leqslant T \leqslant 250\,\mathrm{K})$, with $\sigma_B(T) \equiv 1/\sigma_B(T)$.

Then $\Delta L(\varepsilon)$ can be related with the corresponding excess $\Delta S(\varepsilon)$ and $\Delta\sigma(\varepsilon)$ by

$$\Delta L(\varepsilon) \equiv S_B(\varepsilon)\Delta\sigma(\varepsilon)+\sigma(\varepsilon)\Delta S(\varepsilon), \tag{3}$$

which can be rewritten as

$$\frac{\Delta L(\varepsilon)}{L_B(\varepsilon)}=\frac{\Delta\sigma(\varepsilon)}{\sigma_B(\varepsilon)}-\frac{\sigma(\varepsilon)}{\sigma_B(\varepsilon)}\frac{\Delta S(\varepsilon)}{S_B(\varepsilon)}. \tag{4}$$

From the experimental results we observe that the dependence of $\Delta S(\varepsilon)$ and $\Delta\sigma(\varepsilon)$ with the reduced temperature is similar for all samples in all the MFR, Fig. 2. However the

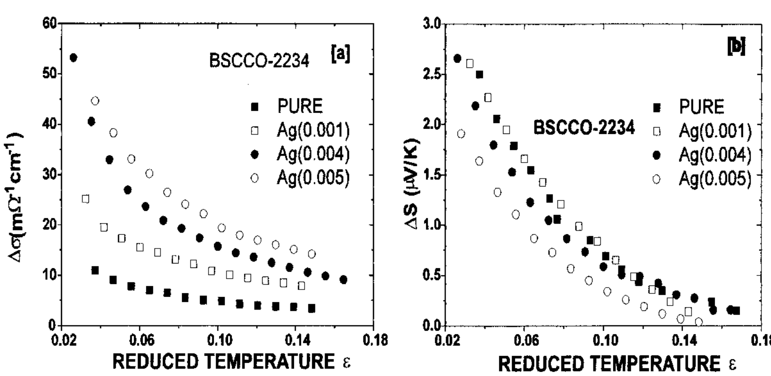

FIG. 2. ΔS and $\Delta\sigma$ as a function of reduced temperature in MFR for low Ag-doped level $(0 \leqslant x \leqslant 0.005)$ BSCCO-2234 samples.

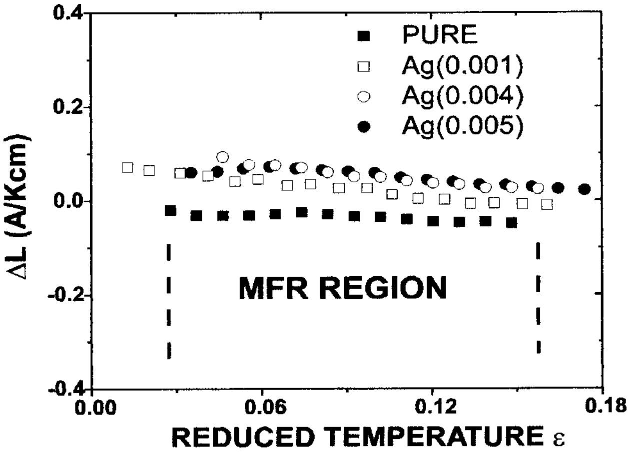

FIG. 3. Experimental behavior of $\Delta L(\varepsilon)$ for low Ag-doped level ($0 \leqslant x \leqslant 0.005$) BSCCO-2234 superconducting samples.

relative amplitude changes from sample to sample and these changes are more important in $\Delta\sigma(\varepsilon)$ that in $\Delta S(\varepsilon)$. These results confirm that $S(T)$ is less sensitive than $\rho(T)$ to the structural changes produced by Ag doping. On the other hand, in contrast with the changes in amplitude, the experimental data show that the changes in the $S(T)$ behavior are more evident from sample to sample than those in $\rho(T)$. This result can be associated to a higher sensitivity of $S(T)$ to short length, compositional or structural, inhomogeneities at interatomic scales.[3,13,16,17]

Figure 3 shows the behavior of the thermoelectric coefficient $\Delta L(\varepsilon)$ for different silver concentrations. $\Delta L(\varepsilon)$ is approximately temperature independent, within the experimental uncertainty, which suggests that $L(T)$ is not affected by thermodynamic fluctuations of the superconducting order parameter, i.e., all the critical effects observed in $S(T)$ above the superconducting transition are mainly due to $\sigma(\varepsilon)$. Assuming that our samples have different structural inhomogeneities generated by the silver addition, they do not affect significantly the behavior of $\Delta L(\varepsilon)$. Similar results have been obtained for other authors in well-oxygenated YBCO superconducting samples characterized by structural inhomogeneities at large length scales.[6,19]

It is worthwhile to note that in addition to the fact that $L(\varepsilon)$ is not affected within the experimental resolution by the presence of superconducting order parameter fluctuations in the MFR, a slight increase of the amplitude ΔL as increasing x is observed (see Fig. 3). This behavior would be confirmed also by the fact that $\rho(T)$ is more sensitive to the structural inhomogeneities produced in this case by the silver addition.[3,15–18]

COMPARISON WITH THE EXISTING THEORIES

The effect of the OPF on electrical conductivity $\sigma(T)$ on layered superconductors in the clean limit is determined by the theoretical approximation of Lawrence-Doniach:[1,20]

$$\Delta\sigma(\varepsilon)=\frac{A_\sigma}{\varepsilon}\left[1+\frac{B_{\mathrm{LD}}}{\varepsilon}\right]^{-1/2}, \tag{5}$$

where B_{LD} is the so-called Lawrence-Doniach coefficient which is defined by

$$B_{\mathrm{LD}}=\left(\frac{2\xi_C(0)}{s}\right)^2, \tag{6}$$

where ξ_C (0) is the c-axis direction coherence length (at $T=0$ K), and s is the distance between superconducting planes. The system dimensionality is controlled by B_{LD} parameter. A_σ is an important amplitude which depends on the pairing state, the number n of the real components of the order parameter, and the number N of superconducting layers per unit cell of length s. This can be expressed as $A_\sigma = gNA_{\mathrm{AL}}$, where g is the number of complex components of

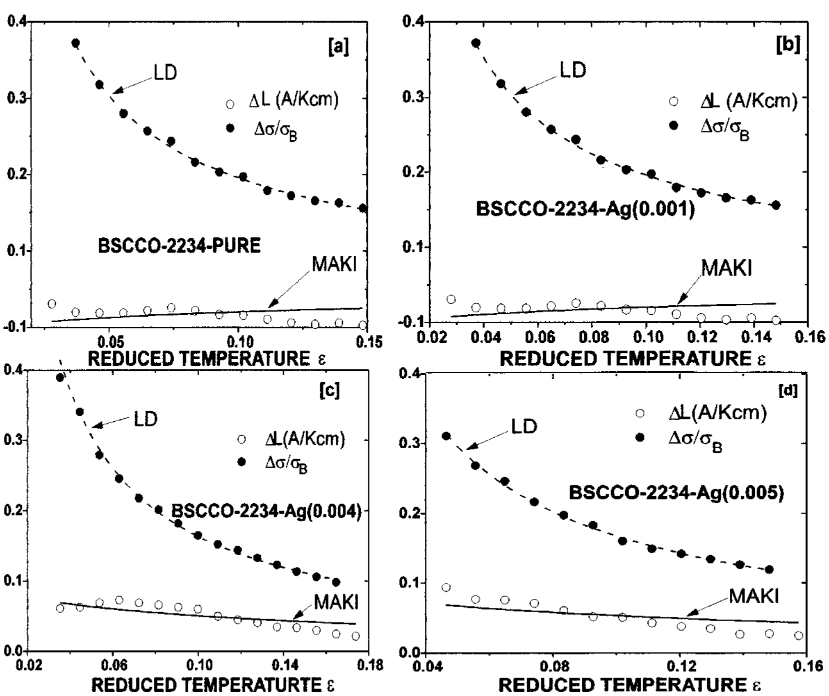

FIG. 4. (a)–(d) $\Delta\sigma/\sigma_B$ and ΔL as a function of reduced temperature in MFR for different Ag concentrations. The dotted line is the best fit of experimental data ($\Delta\sigma/\sigma_B$) to the LD model and the solid line is the best fit to the Maki model [$\Delta L(\varepsilon)$] in MFR.

TABLE II. Coefficients B_{LD} and A_σ obtained from the best fit to the Lawrence-Doniach model of the experimental data for the low Ag-doped level $(0 \leqslant x \leqslant 0.005)$ of BSCCO-2234 samples.

	B_{LD}	A_σ $(\Omega\,\mathrm{cm})^{-1}$
PURE	0.03656	569
Ag(0.001)	0.06568	1371
Ag(0.004)	0.04671	1915
Ag(0.005)	0.03926	2404

the superconducting order parameter and $A_{AL}=e^2/16\hbar s$ is the universal Aslamazov-Larkin and Lawrence-Doniach conductivity.

The dotted lines in Figs. 4(a)–4(d) are the best fits of Eq. (5) to $\Delta\sigma(\varepsilon)/\sigma_B(\varepsilon)$ in the MFR for each sample with A_σ and B_{LD} as free parameters (see Table II). Additionally to the good qualitative agreement with the experimental data, the values of $B_{LD}(B_{LD}<\varepsilon)$ lead to a two-dimensional character (2D) for the fluctuations of the order parameter. These results are in agreement with that obtained in BSCCO samples from paraconductivity measurements.[21] Furthermore the values obtained for B_{LD} show that low Ag doping levels $(0<x<0.005)$ do not affect significantly the dimensionality of the system. However, the general behavior observed for samples with $x>0.005$ shows that there is not agreement between experimental data and Eq. (5), showing both a change in the dependence of $\Delta\sigma(\varepsilon)$ with ε and an increasing of the amplitude of $\Delta\sigma$ (see Fig. 5). The behavior of $\Delta\sigma(\varepsilon)$ with reduced temperature seem to be due to a possible increase of the critical region and the consequence decrease of MFR. Other effects like that produced by the presence of Maki-Thomson processes could be present, and contribute to the decreasing of MFR.[22–24]

The effect of OPF on the thermoelectric coefficient as given by the theoretical approximation proposed by Maki for s-wave layered superconductors in the clean limit is[6,13]

$$\Delta L=A_L \ln\left[\frac{2}{\varepsilon(1+\alpha+\sqrt{1+2\alpha})}\right], \tag{7}$$

where $\alpha=B_{LD}/2\varepsilon$.

The full line in Fig. 4(a) is the best fit of Eq. (7) to the experimental data, $\Delta L(\varepsilon)$, in MFR using the B_{LD} values obtained from LD fit to $\Delta\sigma/\sigma_B(\varepsilon)$ data (Table II). The results indicate that the model proposed by Maki accounts reasonably well with our experimental data for low Ag-doped levels of BSCCO-2234 samples. The temperature dependence of $\Delta L(\varepsilon)$ is soft and their amplitude is small. In other words as this result is found for low Ag-doped samples $(0 \leqslant x \leqslant 0.005)$ with different structural changes, we could conclude that this behavior is intrinsic to BSCCO-2234 samples.

Let us stress here however, that the reasonable agreement between experimental data and the Maki model does not allow us to conclude about the pairing state of the order parameter. Within the experimental resolution and since amplitude of $L(\varepsilon)$ is very small compared with $\sigma\Delta S(\varepsilon)$ in the MFR any soft functional form of the order parameter could fit reasonably well the experimental data.

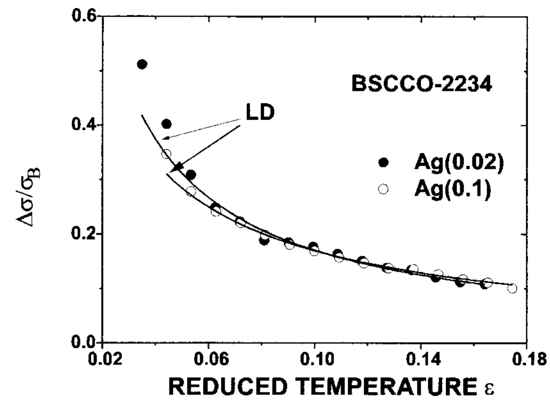

FIG. 5. ΔS and $\Delta\sigma$ as a function of reduced temperature in MFR for high Ag-doped level $(x>0.005)$ BSCCO-2234 samples.

Studies of the magnetic field dependence of the thermoelectric coefficient below T_C might provide a deeper insight into the symmetry of the gap parameter.[25] Results on this subject will be analyzed in a forthcoming paper.

CONCLUSIONS

For low-Ag doped $(0 \leqslant x \leqslant 0.005)$ BSCCO-2234 samples the behavior with reduced temperature of $S(\varepsilon)$ and $\sigma(\varepsilon)$ is similar for all samples and independent of Ag addition. However, the changes in the amplitude of $\Delta\sigma(\varepsilon)$ are larger than in $\Delta S(\varepsilon)$. Which confirm that $S(T)$ is less sensitive than $\rho(T)$ to the inhomogeneities produced by Ag doping.

The OPF effects on the $S(T)$ are driven mainly by $\sigma(T)$ because L is nearly temperature independent, i.e., the inhomogeneities generated by the silver addition do not affect substantially the behavior of $L(\varepsilon)$ in all MFR.

There exist an excellent agreement between the experimental results obtained for $\Delta\sigma(\varepsilon)/\sigma_B(\varepsilon)$ and the model proposed by LD. The fluctuations of the order parameter (OPF) in MFR are substantially of two-dimensional character for low doping levels. The changes in $\Delta L(\varepsilon)$ in MFR are soft and their amplitude is small in agreement with the model proposed by Maki for layered s-wave type superconductors. The experimental resolution and the very small amplitude of $L(\varepsilon)$ in the MFR do not allow a definite conclusion about the pairing state of the order parameter.

For high Ag-doping level $x>0.005$, the experimental values of $\Delta\sigma/\sigma_B$ are not in agreement with the LD model. This behavior could be associated with the presence of other effects like Maki-Thomson process.

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