Variation of T_c and transport properties of the Co-doped $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ system

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We report the effect of the substitution of the $3d$ transition metal element Co for Cu on the resistivity, Hall coefficient, and thermopower in the normal state of the $Bi_2Sr_2CaCu_2O_8$ system over a wide range of carrier concentration. The carrier concentration is varied by partial replacement of Ca by Y ions. The superconducting transition temperature (T_c) is found to decrease considerably and a significant enhancement of the thermopower is observed with increasing Co doping. Both T_c and thermopower show linear dependence on Co concentration. The temperature dependence of the thermopower for the underdoped samples shows a weak anomaly above the broad peak. This anomaly may be assigned to the opening of a normal-state gap in the density of states. A scaling behavior for the normal-state thermopower for optimum and underdoped samples has been established from our studies. We have also shown that the thermopower of all underdoped cuprates can be scaled into a single universal functional form. [S0163-1829(99)09325-X]

I. INTRODUCTION

It is well established that the normal-state transport properties of high-temperature superconductors are profoundly different from those of conventional metals and superconductors. The understanding of this unusual normal state is an important step to elucidate the superconducting mechanism in the high-T_c systems. The strongly correlated charge dynamics in the two-dimensional CuO_2 network is the origin of many anomalous transport properties and high superconducting transition temperatures. Several effects due to strong electronic correlation are usually manifested in materials with reduced carrier density, commonly known as underdoped. The universal doping-temperature phase diagram of the cuprates shows the proximity of magnetic ordering, metallic, and superconducting phases, and suggests that they are interrelated. The undoped parent compounds are usually antiferromagnetic (AF) Mott-Hubbard insulators. With increasing carrier doping, magnetic fluctuations suppress long-range ordering and superconductivity evolves in the proximity of the insulator-to-metal (IM) transition. Therefore, the evolution of the metallic phase from the AF insulating phase has received much attention. Recently, a new phenomenon has been discovered in underdoped samples. A gaplike feature in the electronic spectrum of low-energy excitations have been inferred from neutron difraction,[1] NMR,[2] specific heat,[3] electrical[4] and optical[5] conductivity, thermopower,[6] and Raman spectroscopy.[7] In fact all transport properties of high-T_c superconductors exhibit a systematic dependence on hole concentration including, most notably, the thermopower. The thermopower is a simple but highly sensitive tool to detect any changes in the electronic transport mechanism due to small variations of carrier density or disorder in the CuO_2 plane.

In this paper, we report the charge transport characteristics of the Co-doped $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ system with controlled carrier density from highly underdoped to slightly overdoped. In the $YBa_2Cu_3O_7$ system, Zn and Ni occupy Cu sites in the CuO_2 plane whereas Co and Fe go into the CuO chain site and decrease carrier density. However, in the Bi-2212 system Co goes into the CuO_2 plane without affecting the carrier density. In $YBa_2Cu_3O_7$ (Ref. 6), $YBa_2Cu_4O_8$ (Ref. 6), and $La_{2-x}Sr_xCuO_4$ (Ref. 8) systems, thermopower decreases systematically with the doping of Zn and Ni and a clear indication of the normal-state gap opening and its suppression with Zn doping have been reflected in the temperature dependence of the thermopower of the underdoped samples. In the present study, our aim is to investigate whether similar behavior also exists in the Co-doped Bi-2212 system.

II. EXPERIMENTAL TECHNIQUES

Polycrystalline samples of nominal composition $Bi_2Sr_2Ca_{1-x}Y_x(Cu_{1-y}Co_y)_2O_8$ were synthesized by a conventional solid-state reaction method. Stoichiometric amounts of oxides and carbonates were mixed throughly and then reacted in air for several days with intermediate grindings. The heat treatment temperature was increased linearly with x from 860 to 900 °C as Y concentration increases from 0 to 1.0. The x-ray diffraction patterns show that all the samples are single phase having orthorhombic structure. The systematic change of lattice parameters and other physical properties with increasing Co concentration suggest that Co is incorporated in the lattice. The variation of lattice parameters are consistent with the reported results.[9] Energy dispersive x-ray fluorescence analysis was used to estimate the Co concentration in the samples. The photopeak integrals of Cu and Co K lines were obtained with a standard peak fitting program. The concentrations of Cu and Co in the samples were then calculated using the fundamental parameter technique [Eq. (1) of Ref. 10] where the effect of absorption of x rays in the sample as well as in the air gap and the enhancement of the Co K x ray by Cu K x rays were taken into account.[11] The estimated values of y are within 15% of the nominal compositions. The thermopower of the samples has been measured using a differential technique where a small temperature gradient is created across the sample and the voltage developed between the hot and cold junctions of the thermocouple formed by the sample and Cu wires is mea-

sured. The details of the setup and measurement technique have been reported earlier.[12] The electrical resistivity has been measured by dc four probe method. The Hall coefficient measurements have been done at room temperature under the magnetic field of 20 kOe. The magnetic field was reversed to eliminate any magnetoresistance. The average of four to five sets of data were taken to calculate the Hall coefficient for each sample.

III. RESULTS AND DISCUSSIONS

The effect of Co doping on the temperature dependence of the resistivity and superconducting transition temperature of $Bi_2Sr_2Ca_{1-x}Y_x(Cu_{1-y}Co_y)_2O_8$ is shown in Figs. 1(a) and 1(b) for two batches of samples with $x=0$ and 0.3. Both the conductivity and T_c are observed to decrease with increasing Co concentration. The midpoint of the superconducting transition in the ρ vs T plot is defined as T_c here. T_c determined in this way is very close to the temperature at which $d\rho/dT$ is maximum. For $x=0$, all the samples are metallic and superconducting. The ρ vs T of Co-rich samples shows a small upturn or semiconductinglike behavior for higher Y content samples. The x dependence of T_c for the undoped ($y=0$) samples is as reported in the literature.[13,14] The variation of T_c as a function of y is shown in Fig. 1(c) for samples with different x. From the figure, it is clear that T_c decreases linearly with Co doping. From the figure we can see that the slope of T_c vs y curves, i.e., the rate of T_c suppression with Co doping, is a function of the Y concentration. The slope increases with increasing Y content. This suggests that the T_c suppression is stronger in the underdoped regime.

There are various ways to explain the T_c suppression by magnetic and nonmagnetic impurities. In the framework of conventional Abrikosov-Gorkov (AG) theory, it can be interpreted as the incorporation of magnetic impurities into a superconductor. However, in CaBa-123 (Ref. 15) magnetic (Ni) and nonmagnetic impurity (Zn) depress T_c with equal effectiveness. Sun and Maki[16] studied the impurity effect in d-wave superconductors and found that the T_c reduction for elastic scattering in weak-coupling d-wave superconductors follows the AG equation. Tallon,[17] using the AG equation, analyzed the experimental results of different high-T_c systems and found that the initial slope of the depression in T_c with impurity concentration (dT_c/dy) is constant for overdoped samples where the pseudogap is absent and rises rapidly in the underdoped region with the appearence of the pseudogap. Our present findings that show dT_c/dy is stronger in the underdoped region and weaker in the overdoped region are in conformity with their observations and analysis.

The thermopower S for samples with different x and y are plotted against temperature in Fig. 2. For the $Bi_2Sr_2CaCu_2O_{8+\delta}$ ($x=0$ and $y=0$) sample, S is negative from 310 K down to T_c, and decreases linearly with increasing T. S increases systematically with increasing impurity (y) concentration but remains mostly negative and maintains its linear dependence on T up to the highest doping level of Co. The following clear characteristics are observed in the S vs T curve with increasing Y doping (x): (1) S changes from negative to positive and becomes nonlinear in T, (2) a broad peak appears and this peak shifts towards higher temperatures, (3) a small anomaly appears slightly above the peak in the S vs T curve for $x \geq 0.3$ samples (clearly depicted in Fig. 3). The small, negative and linear T dependence of S in the overdoped regime is consistent with the metallic nature of the resistivity. It has been pointed out[6] that the appearance of the broad peak in the S-T curve with increasing x (decreasing carrier density) is due to the opening of a gap in the normal state termed the ''pseudogap'' or ''spin gap.'' The rapid

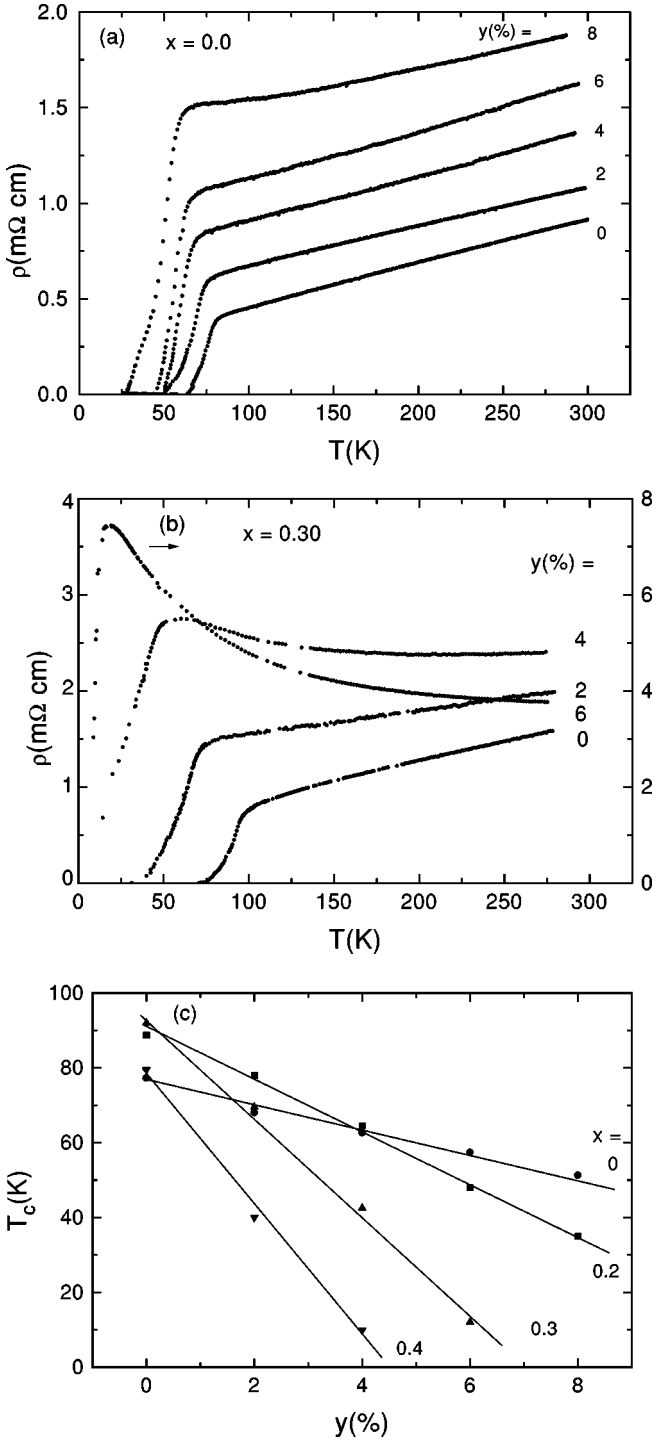

FIG. 1. Temperature dependence of the electrical resistivities ρ of $Bi_2Sr_2Ca_{1-x}Y_x(Cu_{1-y}Co_y)_2O_8$ for various Co doping. (a) $x=0.0$, (b) $x=0.30$. (c) The suppression of T_c for $Bi_2Sr_2Ca_{1-x}Y_x(Cu_{1-y}Co_y)_2O_8$ as a function of Co concentration for various Y contents (x). T_c is determined from the resistive transition.

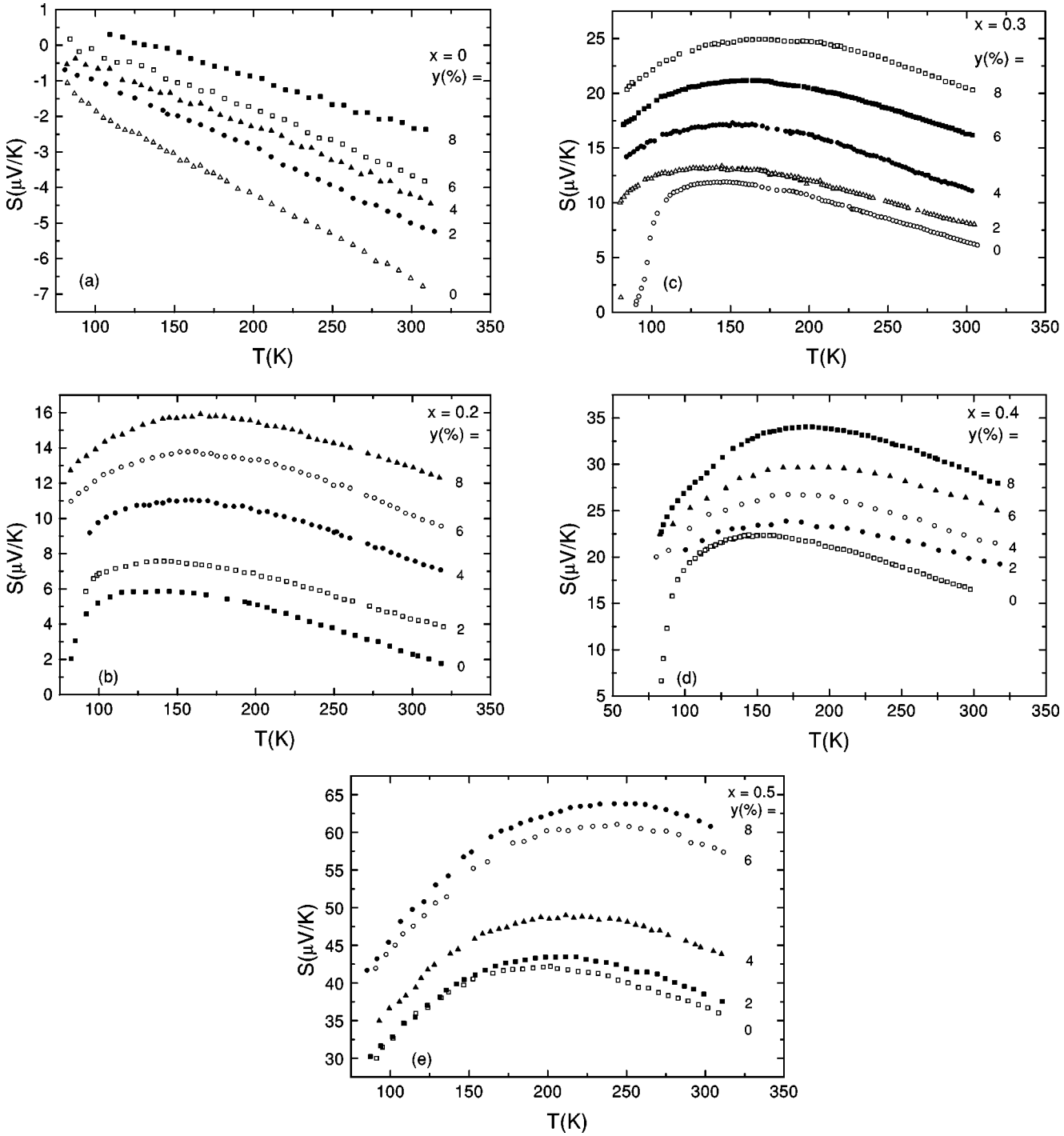

FIG. 2. Temperature dependence of the thermopower S of $Bi_2Sr_2Ca_{1-x}Y_x(Cu_{1-y}Co_y)_2O_8$ samples for various impurity concentrations (y). (a) $x=0.0$. (b) $x=0.20$. (c) $x=0.30$. (d) $x=0.40$. (e) $x=0.50$.

decrease of S below this peak is also due to the opening of this gap. In the Zn-substituted $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ samples, this broad peak is suppressed considerably and the thermopower is enhanced at low temperatures well below the peak.[6] The disorder introduced in the CuO_2 plane by the random distribution of Zn ions suppresses the gap. The temperature at which S of Zn-doped samples deviates from the undoped one has been assigned as the gap-opening temperature. In the $La_{2-x}Sr_xCuO_4$ system too, thermopower decreases considerably with Zn and Ni doping.[8] This behavior is seen in the underdoped as well as in the highly overdoped samples. Sera *et al.*[8] proposed that S consists of two parts: a T-linear part and an anomalous part. The linear term is usual and ascribed to electron diffusion in metals while the anomalous term is due to the spin fluctuations or spin correlation. They suggested that the decrease of S by Zn substitution is due to the decrease of the anomalous spin fluctuation term. However, the thermopower of Bi-2212 system shows a different kind of behavior with Co doping. S is observed to increase monotonically with Co concentration up to the highest value of y and shows a broad peak for optimum and underdoped samples. Also, we have not seen any enhance-

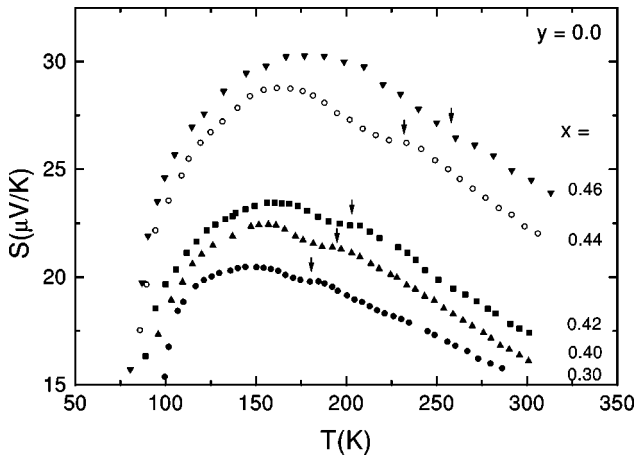

FIG. 3. Temperature dependence of the thermopower for the underdoped $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ samples with $x=0.30$, 0.40, 0.42, 0.44, and 0.46. For $x=0.30$ sample, S has been shifted upward by 8.5 μV/K. The arrows indicate the appearance of a weak anomaly due to the opening of the normal-state gap.

ment of S below the peak in the Co-substituted samples as observed in Zn-doped $YBa_2Cu_3O_7$ (Ref. 6). Except for a small shift in the peak towards the higher temperature, the nature of the T dependence of S for the Co-doped samples is similar to that of undoped samples. The above unusual behavior of S with Co doping cannot be ascribed to a decrease in the carrier density. Maeda *et al.*[18] measured the Hall coefficient of Zn-, Ni-, Co-, and Fe-doped Bi-2212 and did not observe any decrease in the carrier density. In fact, their results show a small decrease in the Hall coefficient for Fe-doped samples as compared to the undoped one. We have also measured the Hall coefficient at room temperature for an $x=0.4$ sample for different Co concentrations and observed that R_H does not depend on the impurity concentration. Thus the increase of S with Co doping must have a different origin.

In Fig. 3, we show the temperature dependence of S for the underdoped samples ($x \geqslant 0.3$) with $y=0$. Above the peak, thermopower shows a small anomaly below a characteristic temperature (T_S^*). This feature was reproduced in several measurements. It may be noted that Co-doped samples with different x also show a similar anomaly above the peak. As has already been discussed, the broad peak in S arises due to the opening of the normal-state gap. The temperature T_S^* below which S shows anomaly is assigned to the gap opening temperature. A deviation from the linear resistivity[19,20] behavior below a certain temperature and a small anomaly in the thermopower[20] close to this temperature has been observed for oxygen deficient Bi-2212 samples. It has been suggested that the normal state gap opens below this temperature.[19,20] The gap opening temperatures T_S^* are 179, 196, 203, 230, and 258 K, respectively, for our samples with $x=0.3$, 0.4, 0.42, 0.44, and 0.46. These temperatures (T_S^*) are comparable with those reported by others for samples with similar T_c and doping level.[5,7,19,20]

Due to the complicated temperature dependence of thermopower in high-T_c superconductors, it is difficult to determine the carrier density or other normal-state parameters related to electron transport in these systems. Several theoretical models have been proposed to explain the temperature dependence of S but at this moment it is hard to judge which one is best to describe the thermopower of high-T_c materials. Nevertheless, efforts have been made to find whether any correlation between the thermopower and other physical parameters such as carrier density, T_c, etc., exists.[21–23] With the variation of carrier level, a strong dependence of T_c on room-temperature thermopower ($S_{300\ K}$) similar to that of T_c vs carrier density has been observed in different systems. To observe whether the Co-doped Bi-2212 system shows a similar behavior we have plotted $S_{300\ K}$ as a function of T_c and Co concentration in Fig. 4. Figure 4(a) shows that for a given Y concentration, T_c decreases linearly with $S_{300\ K}$. This behavior is quite different from that of parabolic dependence of T_c on $S_{300\ K}$ in oxygen deficient systems[21] where T_c is suppressed due to the decrease of carrier density. Thus the effects of T_c suppression on normal-state thermopower due to the disorder in the CuO_2 plane and due to changes in carrier density are different in nature. It is clear from the Fig. 4(b) that $S_{300\ K}$ increases linearly with Co concentration for samples with $x<0.50$. For $x=0.5$ sample, a strong deviation from linear behavior is observed. It may be mentioned that the $x=0.5$ doping is close to the metal-to-insulator transition in this system. This suggests that the in-

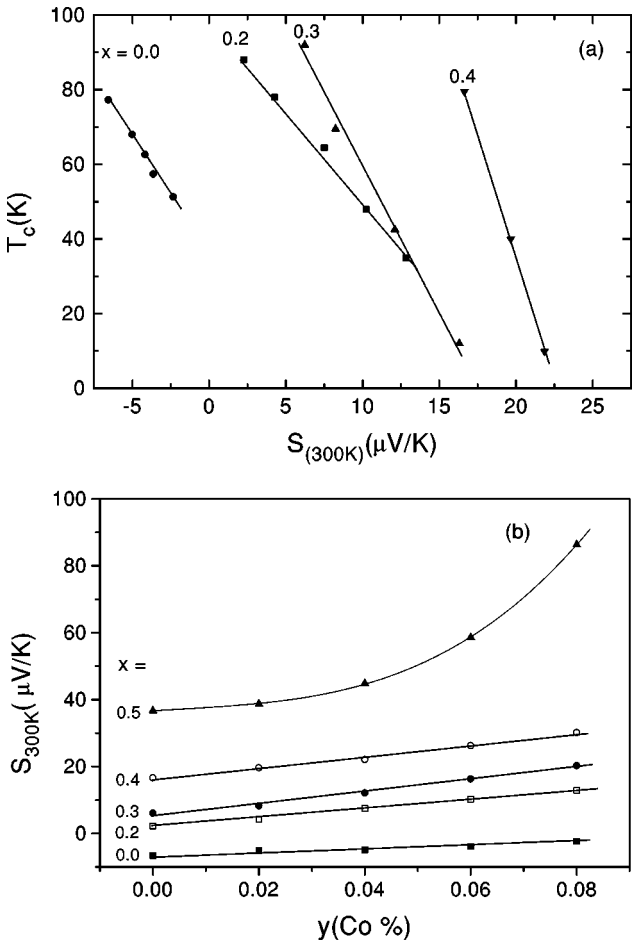

FIG. 4. (a) The variation of T_c with room-temperature thermopower ($S_{300\ K}$) for various values of x in $Bi_2Sr_2Ca_{1-x}Y_x(Cu_{1-y}Co_y)_2O_8$ samples. (b) The dependence of room temperature thermopower ($S_{300\ K}$) on Co concentration for various Y content $Bi_2Sr_2Ca_{1-x}Y_x(Cu_{1-y}Co_y)_2O_8$ samples.

fluence of Co substitution on S is different in the metallic and in the insulating regimes.

The various normal-state transport parameters of high-T_c superconductors can be scaled to universal master curves. Uchida[4] showed that the in-plane resistivity of $YBa_2Cu_3O_{7-\delta}$ deviates from linear behavior below a characteristic temperature T_ρ^* well above the T_c and observed that all the ρ_{ab} vs T plots for underdoped samples including $HgBa_2Ca_2Cu_3O_{8+y}$ fall into a single curve by scaling T/T_ρ^* and $\rho_{ab}(T)/\rho_{ab}(T_\rho^*)$. Hwang *et al.*[24] found that the Hall coefficient $R_H(T)$ of $La_{2-x}Sr_xCuO_4$ can be scaled to a universal functional form $R_H(T)=R_H^0+R_H^* f(T/T_H^*)$. $R_H(T)$ is temperature dependent below a characteristic temperature T_H^* and becomes T independent (R_H^0) above T_H^*. The temperature T_H^* is found close to the characteristic temperatures where the susceptibility and the Knight shift show peaks. As in the other cases, T_H^* is also found to increase with the depletion of carrier density. For the Y-123 system, similar type of scaling behavior for the Hall coefficient is confirmed by Chen *et al.*[25] They observed that the characteristic temperatures T_ρ^* and T_H^* are close to each other. So far the scaling has been done on materials with finite T_c and the physical properties considered mainly resistivity and Hall coefficient. Mandal *et al.*[22] established a scaling of thermopower for the nonsuperconducting Bi-2212 and Tl-2212 samples. They observed that the S vs T plots for the nonsuperconducting samples fall into a single curve by scaling $S(T)/S^*$ and T/T^* as in the case of resistivity. Here, T^* is the temperature where S shows its maximum value S^*. Similar scaling behavior for S has also been reported recently by Cooper and Loram[23] for $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ systems. They observed that the temperature (T_χ^*) where χ shows maximum is approximately two times higher than that of T^*. To investigate whether a similar type of scaling is also applicable for Co-doped samples we have plotted S/S^* vs T/T^* in Fig. 5. It is clear that all the S vs T plots for superconducting as well as nonsuperconducting samples of Fig. 2 which show broad peaks can be scaled to a single curve. For some superconducting samples, the low-temperature data deviate and are not plotted in this figure. This is due to the high superconducting onset temperature which is closer to the peak as compared to other samples.

It has been observed[4] that the opening of the pseudogap strongly modifies the temperature dependence of in-plane resistivity below T_ρ^*. ρ_{ab} remains linear above T_ρ^* but follows $T^{2.5}$ dependence below T_ρ^*. This behavior is universal for all underdoped cuprates. This suggests that the resistivity for all the underdoped cuprates can be scaled into a single universal curve after subtracting the residual resistivity.[4] Now the question arises of whether a similar type of universal scaling also exists for other transport coefficients. For this we have plotted the thermopower data for $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) (Ref. 26), $La_{2-x}Sr_xCuO_4$ (LSCO) (Ref. 23), and $YBa_2Cu_3O_{7-\delta}$ (YBCO) (Ref. 23) systems in Fig. 5. One can see that all the curves for different systems fall onto a single curve. For the $La_{2-x}Sr_xCuO_4$ system, the small deviation may be due to the scattering of experimental data.[23] Thus as

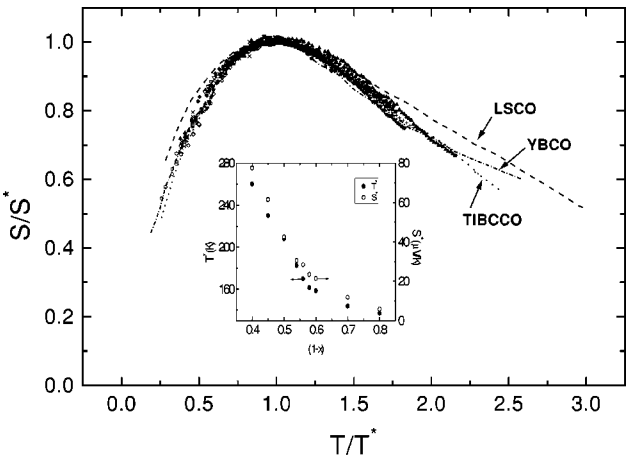

FIG. 5. The thermopower for $Bi_2Sr_2Ca_{1-x}Y_x(Cu_{1-y}Co_y)_2O_8$ samples of Fig. 2 with $0.20 \leqslant x \leqslant 0.60$, plotted rescaled as S/S^* vs T/T^*. The symbols are for present work. All samples are not plotted in this figure to avoid overlapping. The scaling behavior for $La_{2-x}Sr_xCu_2O_4$ (Ref. 23), $YBa_2Cu_3O_7$ (Ref. 23), and Y-doped $Tl_2Ba_2CaCu_2O_8$ (Ref. 26) systems are also shown in this figure. Inset: The variation of T^* and S^* with $(1-x)$.

in the case of resistivity and Hall coefficient, one can scale thermopower also into a single universal curve of the form $S/S^*=f(T/T^*)$. As S is zero at $T=0$, the function $f(T/T^*)$ should also vanish at $T=0$. The inset of Fig. 5 shows the variation of T^* and S^* with Y concentration (carrier density). The nature of variation of these two parameters with carrier density are qualitatively similar to that for the $La_{2-x}Sr_xCuO_4$ (Refs. 23,24) and $YBa_2Cu_3O_{7-\delta}$ (Ref. 23) systems.

In summary, we have investigated the normal-state transport properties of Co-doped Bi-2212 system over a wide range of carrier concentration by means of resistivity, thermopower, and Hall coefficient. Our studies reveal the following. (1) T_c decreases linearly with increasing Co impurity. (2) In the optimum and underdoped regimes, S vs T shows a weak anomaly above the broad peak associated with the normal-state gap opening phenomenon. The gap opening temperatures obtained from the thermopower measurements are close to those reported from other measurements. (3) Thermopower increases monotonically with Co doping and the room-temperature thermopower for $x<0.5$ samples shows a linear dependence on Co concentration. For the $x=0.5$ sample, S increases with Co at a rate much faster than linear. (4) All the S vs T plots showing broad peaks fall into a single curve by scaling T/T_S^* and $S(T)/S^*$. (5) As with the resistivity the thermopower of underdoped cuprates can be scaled into a single functional form.

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