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Thermoelectric power of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0-1.0$) system

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The temperature dependence of the thermoelectric power (TEP) of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples are reported for $x=0-0.9$ in the temperature range 77–300 K. TEP is positive and large for large x and decreases with decreasing x (increasing carrier concentration). TEP is negative for the $x=0$ sample. The results are discussed following strong correlation and the Nagaosa and Lee model.

I. INTRODUCTION

The normal state transport properties of oxide superconductors are unusual and systematic studies of them are essential to understand the mechanism of high temperature superconductivity. Thermoelectric power (TEP) is one of the transport properties complementary to the electrical resistivity and Hall effect. Several groups measured the TEP of $La_{2-x}(Sr/Ba)_xCuO_4$,[1] $YBa_2Cu_3O_x$,[2] $Bi_2Sr_2Ca_1Cu_2O_{8+y}$,[3] and Tl system.[4] It is possible to change the carrier concentration in $Bi_2Sr_2Ca_1Cu_2O_{8+y}$ continuously by substituting Ca with Y while maintaining its single-phase character.[5] We have prepared well-characterized $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0-1.0$) samples and measured their TEP in the temperature range 77–300 K. The advantage in studying such a system is that the carrier concentration could be varied from as low as $p=0.003$/Cu ion to 0.44/Cu ion (p is determined from Hall measurements) by changing x from 1.0 to 0.0.[5] For $x>0.55$ the system is an insulator and exhibits a metal-insulator ($M-I$) transition at $x\sim0.55$. Superconductivity appears near $x=0.50$ and maximum T_c (85 K) is observed in sample with $p\sim0.32$ while for $x=0$ sample T_c is 65 K and p is 0.44. In this report we wish to highlight certain interesting general features regarding the temperature and carrier concentration dependence of TEP that emerge from this study.

II. EXPERIMENTAL

We have prepared $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0-1.0$) samples using the solid-state reaction method following the procedure reported earlier.[5] The x-ray diffraction patterns show that all the samples are single phase having orthorhombic structure. The lattice parameters a, b, and c vary systematically with x in the entire range of x.[5] The thermoelectric power of the samples has been measured using a differential technique where a temperature gradient is created across the sample and the voltage developed (ΔE) between the hot and cold ends of the thermocouple formed by the sample and Cu wires is measured. In our apparatus we have used two heaters (one at the top and the other at the bottom of the sample) so that either end of the sample may be heated with respect to the other. The temperature difference ΔT between two ends of the sample was kept in the range $\sim\pm0.5$ K throughout the measured temperature range (77–300 K). The temperature and temperature difference across the sample were measured with Chromel-Alumel thermocouples. The sample temperature was controlled with a Si-diode sensor and a manganin heater. At a particular temperature the values of ΔE and ΔT were recorded with the x-y recorder and TEP (S) of the sample was calculated from the slope of ΔE vs ΔT curve using the following relation:

$$\frac{\Delta E}{\Delta T}=\frac{S_{\mathrm{Cu}}-S}{S_{\mathrm{Chromel}}-S_{\mathrm{Alumel}}} .$$

III. RESULTS AND DISCUSSION

The temperature dependence of TEP (S) of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples for different x is shown in Figs. 1(a)–1(c). For the insulating samples ($x\geq0.55$) (Ref. 5) S is positive and large. For $x=0.6-0.9$ samples S increases with temperature in the measured temperature range, however, the rate dS/dT decreases with increasing temperature and it becomes almost temperature independent at high temperatures. For $x=0.55$ sample S passes through a broad maximum at $T_{\max}\sim225$ K. With decreasing x (increasing carrier concentration) the values of S decrease and $T_{\max}$ shifts to lower temperature. For superconducting samples in the high temperature region S increases with decreasing temperature almost linearly, then passes through a maximum and around T_c it falls sharply. For $x=0.9-0.2$ samples S remains positive in the entire temperature range (77–300 K). On the other hand for $x=0.1$, S changes its sign from positive to negative at $T\sim270$ K, whereas for the undoped sample ($x=0$) S is negative in the measured temperature range. It may be mentioned that for all these samples Hall coefficient is positive for $T\leq300$ K.[5]

Mandrus *et al.*[3] measured the TEP of $Bi_2Sr_2Ca_{0.9-x}Y_xCu_2O_8$ single crystal for $x=0-0.7$. Our results on polycrystalline samples agree qualitatively well with their results. However, Mandrus *et al.* observed positive TEP for their $x=0$ single-crystal sample ($Bi_2Sr_2Ca_{0.9}Cu_2O_8$) whereas we find negative TEP in the polycrystalline $x=0$ sample ($Bi_2Sr_2Ca_1Cu_2O_{8+y}$). It may be mentioned that the nominal composition of $x=0$

single-crystal sample of Mandrus *et al.* is different from our $x=0$ sample. For our $x=0$ sample $T_c=65$ K and $p=0.44$.[5] However, T_c of $x=0$ sample of Mandrus *et al.* is ~80 K. We have observed this T_c(~80 K) in polycrystalline sample with $p=0.33$ (Ref. 5) for which we have found positive TEP. Thus the different signs of TEP in $x=0$ single crystal and polycrystalline samples may be attributed to different carrier concentrations of the samples.

In Fig. 2 we have shown the variation of the room temperature TEP (S_{300}) and resistivity (ρ_{300}) with x. It is seen that the variation of S_{300} and ρ_{300} with x has a striking similarity. Sharp change in ρ_{300} occurs around $x \sim 0.55$ where the resistivity behavior changes from me-

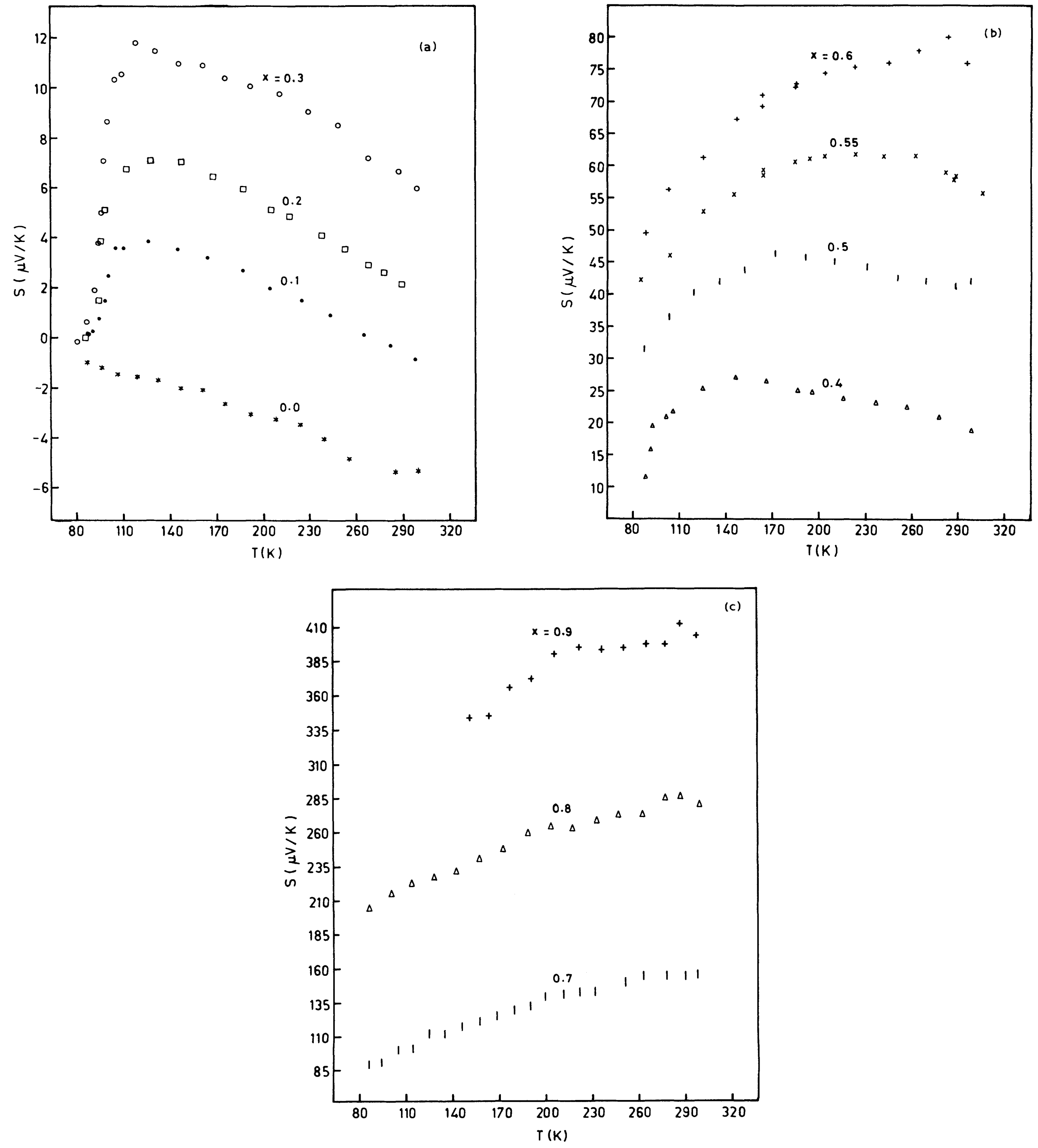

FIG. 1. Temperature dependence of TEP for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.9) samples. The Y contents are (a) $x=0$, 0.1, 0.2, 0.3; (b) 0.4, 0.5, 0.55, 0.6; and (c) 0.7, 0.8, 0.9.

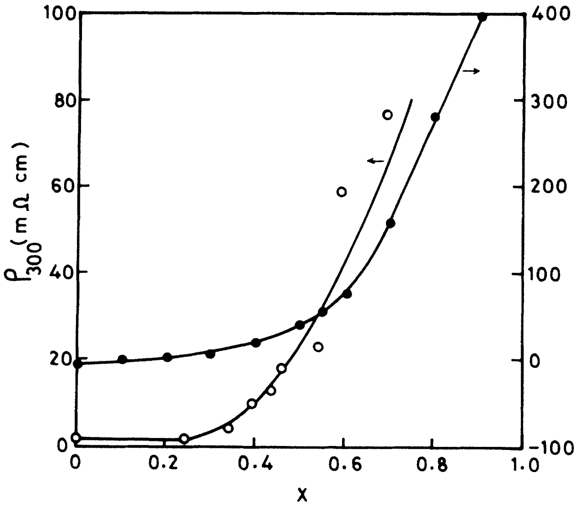

FIG. 2. The variation of room-temperature resistivity and room-temperature thermopower with x for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples.

tallic to insulating.[5] In TEP also we find a large change around the same value of x, suggesting that the same carriers are dominating in resistivity and TEP properties.

The carrier concentration and temperature dependence of S observed in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ are in many ways similar to that reported in polycrystallines $La_{2-x}Sr_xCuO_4$ (Ref. 1), $YBa_2Cu_3O_x$ (Ref. 2), $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ (Ref. 6), $(Y_{1-x}Ca_x)(Ba_{1-y}La_y)_2Cu_4O_8$, (Ref. 6), and in single crystals of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ (Ref. 3) samples. The common characteristics observed in S of high-T_c cuprate systems are the following.

(i) In the low carrier-concentration region (insulating region) S is large and positive and its value decreases with the increase of carrier concentration. In the high temperature region S is weakly dependent on temperature.

(ii) In the intermediate range of carrier concentration (around $M-I$ transition region) S increases with temperature, passes through a broad maximum at $T=T_{\max}$, and then decreases on further increase of temperature. $T_{\max}$ shifts to a lower temperature as the carrier concentration of the sample is increased.

(iii) For superconducting samples S is small and it increases with the lowering of temperature and around T_c it drops rapidly and becomes zero at T_c. It is interesting to note that room temperature TEP $S_{300}\sim 0$ for samples showing highest T_c of different systems. However, in the $La_{2-x}Sr_xCuO_4$ system[1] this behavior is observed in the heavily doped sample with $x=0.25$ which has a $T_c\sim 16$ K $< T_c^{\max}$.

(iv) For samples having high carrier concentration S is negative.

Three different models are generally used to analyze the TEP results of high-T_c systems.

A. Hubbard model

It is more or less established now that high-T_c oxides are strongly correlated systems and Hubbard model describes the basic physics of these materials.[7] For a narrow-band Hubbard model the expression for thermoelectric power at high temperature was derived by different groups[8] and this is given by

$$S=\frac{K_B}{e}\ln\frac{1-p}{2p} , \tag{1}$$

where p is the hole concentration.

Cooper *et al.*[1] measured the thermoelectric power of $La_{2-x}(Sr/Ba)_xCuO_4$ system with Ba and Sr doping and found that for small hole concentrations ($x<0.2$) the thermopower at room temperature is well described by the formula

$$S'=\frac{K_B}{e}\left[\ln\frac{1-p}{2p}-\ln 2\right] , \tag{2}$$

where the extra ln2 term comes from the orbital degrees of freedom (assuming two fold orbital degeneracy). In Fig. 3 we have plotted S' [obtained from Eq. (2)] and S_{300} of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples against hole concentration determined from Hall measurements.[5] The figure shows that the experimental points fit well with the theoretical curve in the low carrier-concentration region ($p<0.06$/Cu) and deviates at higher concentration. For high carrier-concentration ($p>0.18$) the experimental points lie above the theoretical curve. Similar behavior was also found in the TEP of the $La_{2-x}Sr_xCuO_4$ system.[1]

It may be mentioned that in context to high-T_c oxide systems Eq. (2) is an oversimplified expression for TEP. It is derived using a single-band Hubbard model with the assumption that the bandwidth is much less than K_BT. The deviation from Eq. (2) is plausible in that region where the above simple conditions are not valid.

B. Two-band model and a linear T term

The temperature dependence of S in high-T_c systems is strikingly similar to that observed in the mixed valence

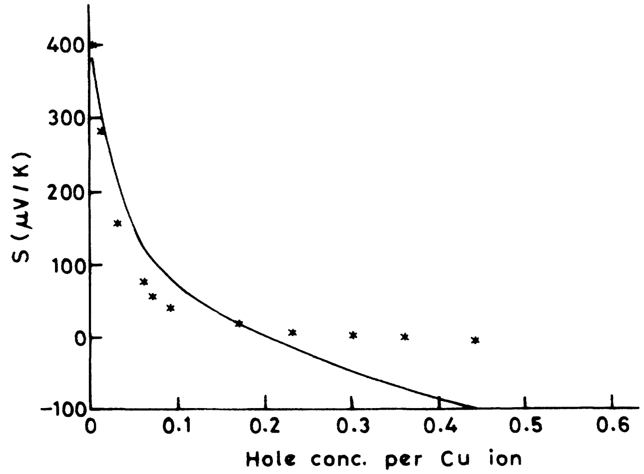

FIG. 3. Room-temperature thermopower vs hole concentration per Cu ion. The solid curve is calculated using Eq. (2).

and heavy fermion systems.[9] Gottwick *et al.*[9] measured TEP of $CeNi_x$ samples and found $S(T)$ is positive, large, and passes through a peak. The magnitude of S decreases and the peak position ($T_{\max}$) increases with the increase of Ni concentration. They analyzed the TEP results using an expression

$$S=\frac{AT}{B^2+T^2}\ . \tag{3}$$

This was derived assuming superposition of two bands: a broad band and a localized band with peak position at ϵ_0 and width Γ. A and B are related to ϵ_0 and Γ through the relation

$$A=\frac{2(\epsilon_0-\epsilon_F)}{|e|},\quad B^2=\frac{(\epsilon_0-\epsilon_F)^2+\Gamma^2}{\pi^2K_B^2}\ ,$$

where ϵ_F is the Fermi energy. Forro *et al.*[3] measured the TEP of $Bi_2Sr_2Ca_1Cu_2O_8$ single crystal. To obtain the best fit they used Eq. (3) in the modified form

$$S=\frac{AT}{B^2+T^2}+\alpha T\ , \tag{4}$$

where αT term is the normal band contribution. We have also fitted the TEP results of our $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples with Eq. (4) and the results are presented in Figs. 4(a) and 4(b). It should be mentioned that for superconducting samples we have not considered the points near T_c for fittings, because the sharp drop in TEP near T_c may originate from thermodynamic superconducting fluctuations.[3] From figures it is seen that the experimental results fit reasonably well with Eq. (4) for all the samples. The best fit parameters A, B, and α obtained for different samples are presented in Table I. ($\epsilon_0-\epsilon_F$) and Γ values are also given in the same table. For $x>0.55$ samples α changes sign and the values are large. However, for $x=0.4$, 0.5, and 0.55, no systematic variation of α is found. Results show that ($\epsilon_0-\epsilon_F$) increases while Γ decreases with the increase of x up to $x=0.50$ and for $x\geq 0.55$ the variation is not systematic.

The electrical resistivity and Hall measurements on

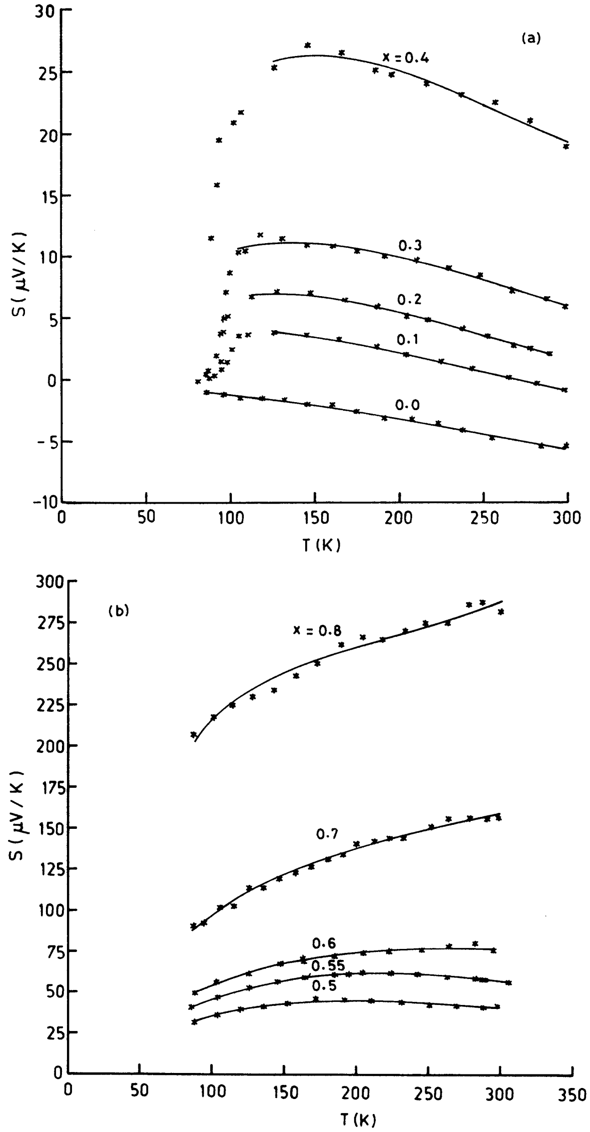

FIG. 4. Best-fit curves (solid lines) for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.8) samples corresponding to Eq. (4): (a) $x=0$, 0.1, 0.2, 0.3, 0.4, and (b) 0.5, 0.55, 0.6, 0.7, 0.8.

TABLE I. The best-fit parameters A, B, and α of Eq. (4) and the corresponding ($\epsilon_0-\epsilon_F$), Γ values for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples.

x	α ($\mu v/K^2$)	A (μv)	B (K)	($\epsilon_0-\epsilon_F$) (K)	Γ (K)
0.0	−0.026	1209.64	283.38	7.01	513.95
0.1	−0.021	2049.96	154.60	11.89	280.16
0.2	−0.021	3021.67	151.00	17.52	273.32
0.3	−0.016	4069.60	148.88	23.60	269.01
0.4	−0.008	8019.46	142.26	46.51	253.80
0.5	0.043	9821.13	117.60	56.96	205.56
0.55	−0.044	35 128.00	244.52	203.74	393.95
0.6	0.084	22 726.09	198.19	131.81	334.44
0.7	0.310	26 788.00	174.57	155.37	275.90
0.8	0.594	38 742.64	121.28	224.70	a

[a] For $x=0.8$ sample Γ becomes imaginary.

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples[5] show (i) resistivity increases with x; (ii) the hole carrier density decreases with increasing x; and (iii) $x=0$ samples is the most metallic sample in this series.

It is expected that with increasing carrier (hole) density the Fermi energy should go down relative to the top of the band. However, Table I shows that $(\epsilon_0-\epsilon_F)$ increases with x (decrease of carrier density). Therefore, if ϵ_0 is fixed in position, the above result suggests that ϵ_F decreases with decreasing carrier density which is not expected for hole carriers. One way to resolve this problem is to assume that ϵ_0 position shifts upward with decreasing carrier density. However, such proposition is too speculative and yet to receive any support from other evidence.

The above model is based on the assumption that there is narrow band superimposed on a broad band and a normal band (which gives contribution αT in TEP). Evidence of such bands in high-T_c oxide system is not obtained. Thus the validity of this model in context to high-T_c oxide systems is questionable.

C. Nagaosa and Lee model

Using a gauge field theory for a uniform RVB state Nagaosa and Lee[10] proposed that for superconducting cuprate there are two contributions in TEP: Fermi part and Bose part:

$$S=S_F+S_B\ ,$$

where

$$S_F=-(K_B/e)\frac{K_BT}{\epsilon_F} \tag{5a}$$

and

$$S_B=(K_B/e)\left[1-\ln\frac{2\pi P_{sh}}{mK_BT}\right]\ , \tag{5b}$$

where P_{sh} is the concentration of holes per (Cu—O) bond and m is the mass of the bosonic carrier.

Ikegawa *et al.*[11] obtained a reasonable fit of S of $(Eu,Ce)_4(Ba,Eu)_4Cu_6O_y$ and $Nd_{1.4}Ce_{0.2}Sr_{0.4}Cu_{1-x}Zn_xO_y$

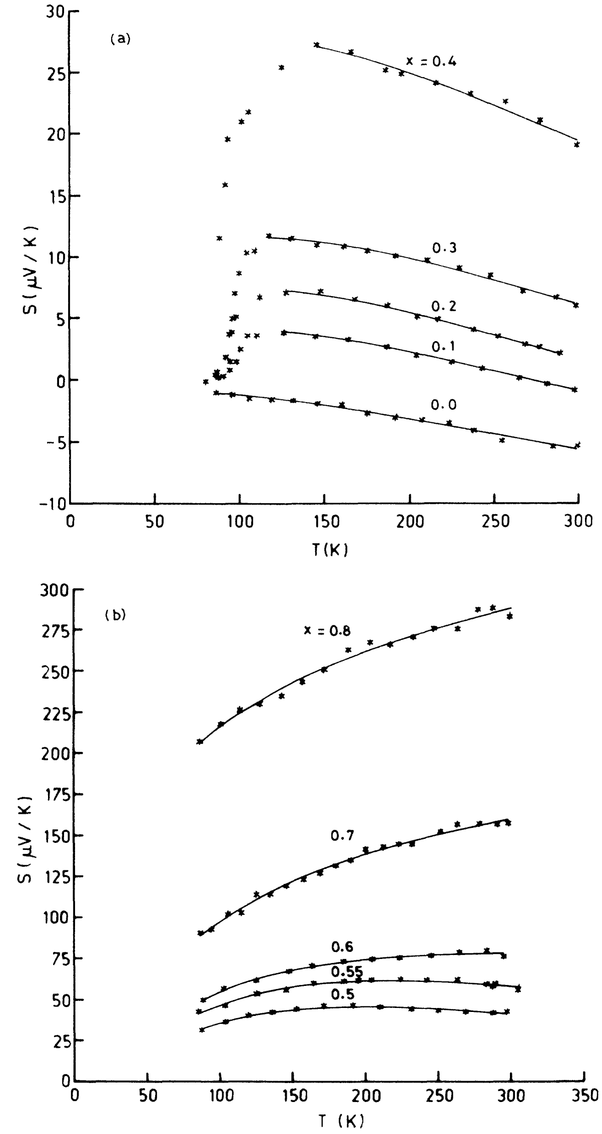

FIG. 5. TEP against temperature for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.8) samples fitted with Nagaosa and Lee model (solid lines): (a) $x=0$, 0.1, 0.2, 0.3, 0.4 and (b) 0.5, 0.55, 0.6, 0.7, 0.8.

TABLE II. Fitted parameters H, F, and G of Eq. (6) for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples.

x	H (K)	F	G (K)
0.0	2651±10	0.0224±0.0002	$(3.1\pm1.2)\times10^{20}$
0.1	1782±8	0.0479±0.0005	$(5.8\pm1.0)\times10^{9}$
0.2	1360±6	0.0733±0.0003	$(5.7\pm0.2)\times10^{6}$
0.3	1267±4	0.0855±0.0005	$(6.2\pm0.3)\times10^{5}$
0.4	935±5	0.1050±0.0012	$(2.1\pm0.1)\times10^{4}$
0.5	326±1	0.6077±0.0016	266±1.1
0.55	298±1	0.7275±0.0020	270±0.5
0.6	456±1	0.6428±0.0008	333±0.3
0.7	1740±10	0.7605±0.0006	414±0.1
0.8	~100 000	~0.763	~318

($x=0$ and 0.015) samples introducing an additional parameter F. The modified expression of S is

$$S=\frac{K_B}{e}\left[1-F\ln\frac{2\pi P_{sh}G}{T}-\frac{T}{H}\right], \tag{6}$$

where F, G, and H are fitting parameters.

We analyze our TEP results on the basis of Eq. (6). In Figs. 5(a) and 5(b) we have presented the best-fit curves for all the samples along with the experimental data points. It is seen that the experimental points fit well with the expression (6). The best-fit parameters are given in Table II. The parameter H, which is proportional to ϵ_F,[11] decreases with x and passes through a minimum at $x=0.55$. On the other hand the multiplication factor F in Bose part increases with x, passes through a peak at the same x value (0.55), and then again increases. The parameter G proportional to m^{-1}, is large for samples having higher carrier concentration.

To show the proportionate contributions of bosons and fermions in TEP, we have plotted in Fig. 6 the variation of S_B and S_F (along with S) with x at $T=300$ K. It is seen for very insulating samples ($x\geq 0.7$) the main contribution to TEP is from the Bose part. S_B is positive and decreases with decreasing x. However, near $x=0.55$ it passes through a peak. On the other hand, S_F is negative. For very large x (0.8) S_F is almost zero and its magnitude increases with decreasing x, shows a maximum at $x\sim 0.55$ and then decreases with further decrease of x. It is interesting to observe that both S_B and $|S_F|$ show peak at $x\sim 0.55$ where the system undergoes the $M-I$ transition. It may be mentioned that we find the same type of behavior of S_B and S_F also at lower temperature ($T=145$ K).

In conclusion, we have found that the thermoelectric power of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system shows a systematic variation with carrier concentration. For insulating samples S is positive and large and it is weakly temperature dependent in the high temperature region and its magnitude decreases with increasing carrier density. The S-T plot shows a broad peak, the peak position shifts to low temperature with increasing carrier density. In the high temperature side S decreases with increase of temperature. S is small for sample having optimum carrier density (for which T_c is highest) and on further increase of carrier concentration S becomes negative.

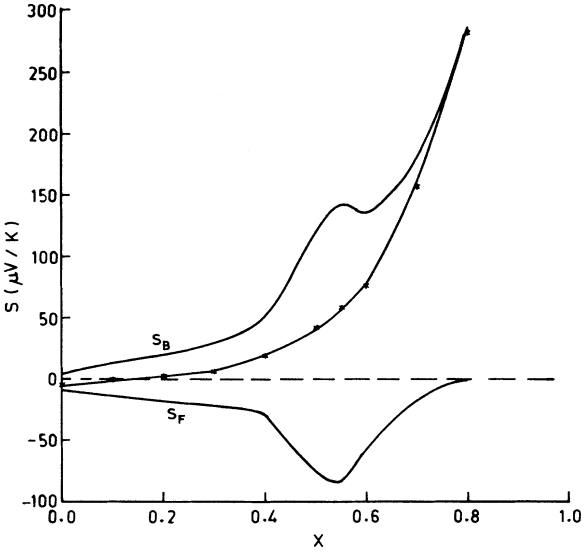

FIG. 6. Plots of S_F, S_B, and S [calculated from Eq. (6)] with x at $T=300$ K. The stars (✱) correspond to experimental points.

For small hole concentration the room-temperature thermoelectric power appears to satisfy a relation obtained from one-band Hubbard model in the strong correlation limit. The temperature variation of S for samples with different doping level is described reasonably well with boson-fermion model of Nagaosa and Lee. However, further works both on experiment and theory are necessary to reveal the actual mechanism.

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