Thermoelectric power of $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($0 \leq x \leq 0.6$) samples

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We report the thermoelectric power (TEP) of $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples as a function of temperature in the temperature range 77–300 K. For the $x=0$ sample ($T_c=85$ K), the room-temperature value of the TEP is negative. For $x>0$, the TEP is positive and its magnitude increases with increasing x (decreasing carrier concentration). A comparative study of our results with that of other high-T_c systems shows that the room-temperature value of the TEP is almost zero for samples with $T_c \sim T_c^{\max}$. The results are analyzed with three different models.

I. INTRODUCTION

The thermoelectric power (TEP) is highly sensitive to the changes in the electrical transport mechanism, and so the measurement of this appears to be a fruitful way of understanding the nature of the carriers and the mechanism of transport in high-temperature superconductors. Studies of the TEP as a function of carrier concentration and temperature have already been made on $La_{2-x}Sr_xCuO_4$,[1] $YBa_2Cu_3O_{7-\delta}$,[2] Bi,[3,4] and Tl (Refs. 4–8) systems. It has been found that TEP (S) of all (hole-doped) high-T_c oxide systems shows the following general features.

(i) In semiconducting or, insulating samples with low carrier concentration, S is large and positive and its value decreases with the increase of carrier concentration.

(ii) In metallic samples S is small and shows almost linear temperature dependence at high temperatures with negative slope.

(iii) For overdoped samples with higher carrier densities S is negative.

It is interesting to note that for electron-doped oxide superconductors[9] the TEP is large but negative for semiconducting samples and the magnitude of S decreases with increasing electron carrier density and S changes sign (from negative to positive) at a higher carrier concentration. One important characteristic of both hole- and electron-doped oxide superconductors is that the Hall coefficient does not change sign at the doping concentration where S shows a sign change.

In an earlier paper[10] we have reported the temperature dependence of the TEP of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–1.0) and analyzed the data following some of the existing theories. In this paper we report a similar systematic study of the TEP on $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples. The carrier concentration of the samples is changed by varying the amount of Y in the system. Our earlier measurements[11] showed that the carrier density per copper atom (p) in $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ changes from 0.16 to <0.03 as x is changed from 0 to 0.6. Here we present the temperature variation of the TEP of the Tl 2:2:1:2 system for different carrier densities $0.03<p\leq 0.16$ and the results are analyzed on the basis of the existing models.

II. EXPERIMENT

The method followed to prepare $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples was reported earlier.[11] X-ray results indicate that the samples are single phase having orthorhombic structure. The lattice parameters vary systematically with x. The apparatus used for measuring the TEP of the samples was reported in an earlier paper.[10]

III. RESULTS AND DISCUSSIONS

The thermoelectric power (S) for $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) is plotted against temperature in Fig. 1. For superconducting metallic samples (small x), S is small and shows an almost linear

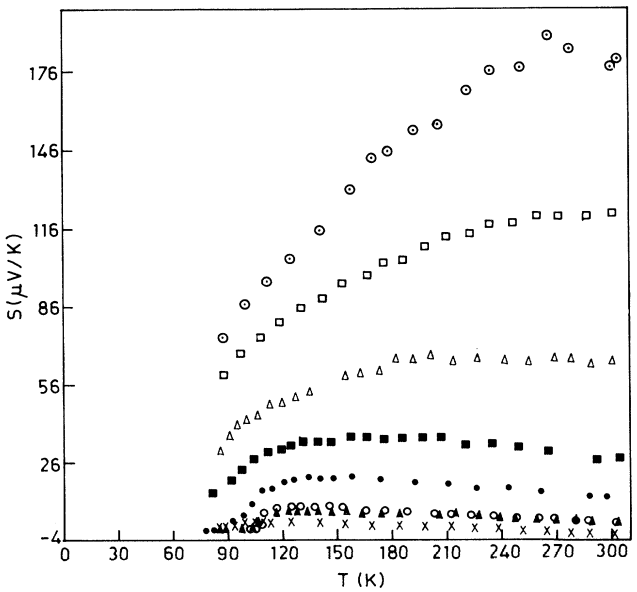

FIG. 1. The TEP against temperature for $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples. The yttrium contents are $x=0.0$ (with $T_c=85$ K) (×); 0.1 (▲); 0.0 (with $T_c=105$ K)(○); 0.2 (●); 0.25 (■); 0.35 (△); 0.5 (□); 0.6 (⊙).

variation with T with a negative slope ($\sim -0.02\ \mu V/K^2$) at high temperature. As T decreases S increases, passes through a maximum, and around T_c it falls sharply. In Fig. 1 we have presented the TEP data of two $x=0$ samples (prepared under different conditions and having different carrier concentrations) with $T_c \sim 85$ and ~ 105 K. For the first sample S is positive up to 212 K, above which S is negative. For the second sample S is positive throughout the measured temperature range. For the substituted samples ($x \neq 0$) the TEP is positive and its magnitude increases with the increase of Y content (decreasing carrier density). For the semiconducting or insulating samples S increases with increasing temperature, however, the rate dS/dT decreases with increasing temperature and it becomes more or less flat at high temperatures.

The variation of room-temperature TEP (S_{300}) against the hole (carrier) concentration determined from Hall measurements for Tl 2:2:1:2 and Bi 2:2:1:2 systems is shown in Fig. 2(a). For comparison we have plotted the results of other high-T_c systems reported by Obertelli *et al.*[5] and Smits *et al.*[12] Figure 2 shows that S_{300} for the superconducting samples varies almost linearly with p. However, S_{300}-p is not universal for all high-T_c systems. The S_{300}-p slope is higher for samples whose T_c^{max} occurs at low p_c (the carrier concentration at which T_c is T_c^{max}) and it is lower for Bi 2:2:0:1, Bi 2:2:1:2, and $(Tl_{0.5}Pb_{0.5})Sr_2Ca_{1-x}Y_xCu_2O_7$ samples whose p_c is comparatively higher. In Fig. 2(b) the plot of T_c/T_c^{max} against S_{300} is shown for Tl 2:2:1:2 and Bi 2:2:1:2 systems along with other high-T_c oxide systems. Figure 2 shows that data points of all the high-T_c systems (including electron superconductor) fall more or less on the same curve and $S_{300} \sim 0$ for samples with $T_c \sim T_c^{max}$. These experimental results suggest that some compensation in the TEP occurs for superconducting samples with a maximum T_c. However, the origin of such compensation in all high-T_c systems is yet to be discovered. In this paper we analyze the TEP results of $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples following three different models, as used in Ref. 10.

A. Hubbard model

Different groups[13] derived an expression for the thermoelectric power of the narrow-band Hubbard system at high temperatures which is given by

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

where p is hole concentration per Cu ion. Taking into account of the twofold orbital degeneracy, Eq. (1) can be modified as

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

which was used by Cooper *et al.*[1] to explain their TEP results for $La_{2-x}Sr/Ba_xCuO_4$ samples.

We have plotted S' and S_{300} of the Tl 2:2:1:2 sample against p in Fig. 3. It is seen that the experimental points are far away from the theoretical points [calculated from Eq. (2)]. It may be mentioned that, for La 2:1:4 (Ref. 1) and Bi 2:2:1:2 (Ref. 10) systems, S_{300} agrees with S' for low carrier concentration and deviates from the theoreti-

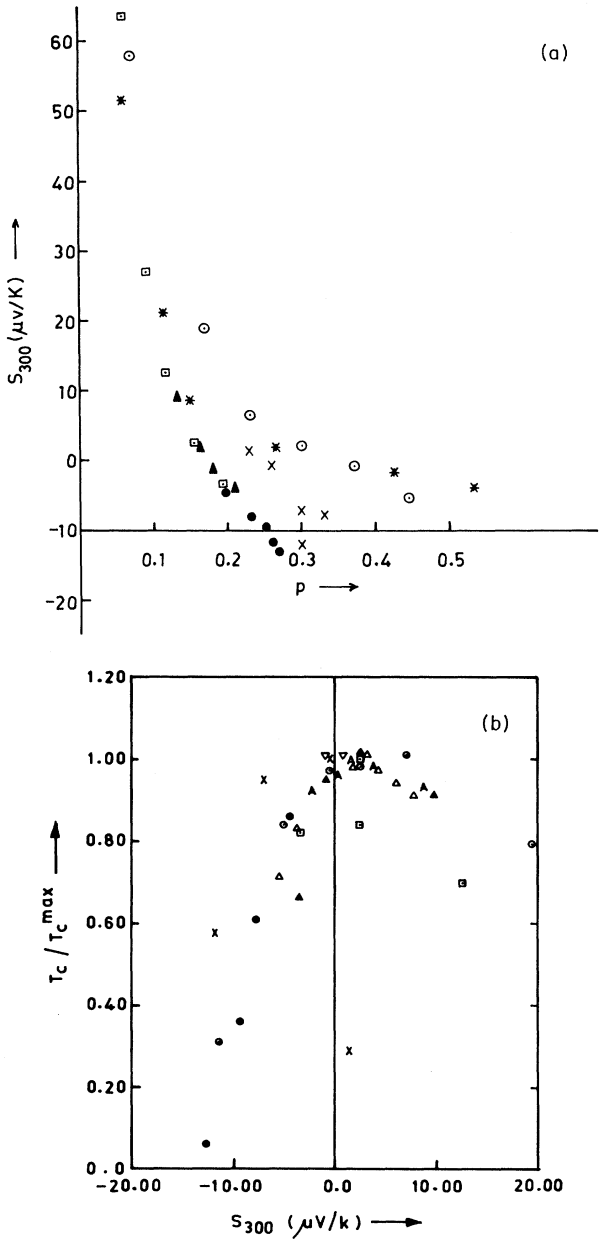

FIG. 2. (a) The variation of room-temperature thermopower with carrier concentration for samples Bi 2:2:1:2 (⊙) from our previous work (Ref. 10); $(Tl_{0.5}Pb_{0.5})Sr_2Ca_{1-x}Y_xCu_2O_7$ (*) from Ref. 16; Bi 2:2:0:1 (×) from Smits *et al.* (Ref. 12); Tl 1:2:1:2: (▲) and Tl 2:2:0:1 (●) from Obertelli *et al.* (Ref. 5); Tl 2:2:1:2 (⊡), this work. (b) The ratio T_c/T_c^{max} vs room-temperature thermopower for samples Bi 2:2:1:2 (△); Tl 2:2:0:1 (●), Tl 1:2:1:2 (▲), and Y 1:2:3 (A) from Obertelli *et al.* (Ref. 5); $Nd_{2-x}Ce_xCuO_4$ (▽) from Xu *et al.* (Ref. 9); Bi 2:2:0:1 (×) from Smits *et al.* (Ref. 12); Bi 2:2:1:2 (⊙) from our previous work (Ref. 10); Tl 2:2:1:2 (⊡), our present work.

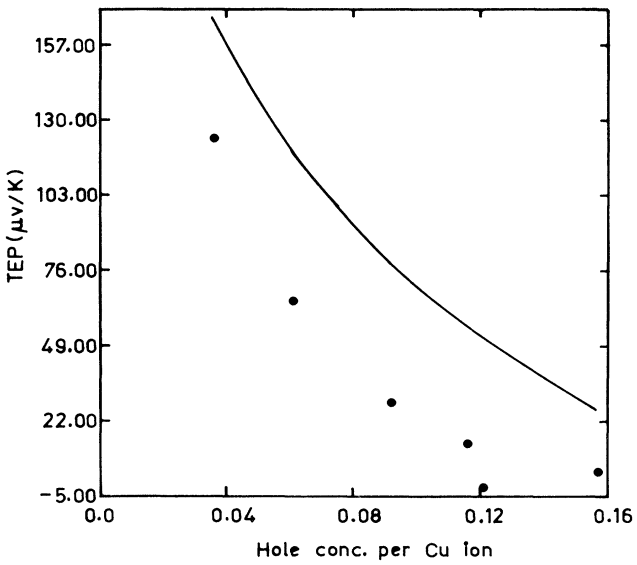

FIG. 3. The variation of room-temperature thermopower with hole concentration per Cu ion for the Tl 2:2:1:2 sample. The solid curve has been calculated from Eq. (2).

cal curve at higher concentrations. However, for the Tl 2:2:1:2 system deviation occurs even at low carrier concentration.

Formula (1) is valid for a single-band Hubbard model only in the high-temperature limit, when $k_B T$ is greater than the bandwidth W but much less than the on-site Coulomb repulsion U. Thus, Eqs. (1) and (2) should have limited applicability.

B. Two-band model with an extra linear T term

In our previous work[10] we had fitted the results of the TEP in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples using the following expression:

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

as used by Forro *et al.*[3] Here the second term is the normal band contribution. The first term, as proposed by Gottwick *et al.*[14] for the analysis of the TEP data of $CeNi_x$ samples, is obtained by assuming superposition of a broadband and a localized band with a peak position at ε_0 and width Γ. A and B are given by

$$A=\frac{2(\varepsilon_0-\varepsilon_F)}{|e|}\ ,\quad B^2=\frac{(\varepsilon_0-\varepsilon_F)^2+\Gamma^2}{\pi^2 k_B^2}\ ,$$

where ε_F is the Fermi energy. The TEP results of $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples have been fitted with Eq. (3) and are shown in Figs. 4(a)–4(c). For superconducting samples, the points near T_c are not considered for fit because the sharp drop in the TEP near T_c may originate from superconducting fluctuations.[3] The best-fit parameters A, B, and α are given in Table I along with the values of $(\varepsilon_0-\varepsilon_F)$ and Γ. For all the samples α is negative. It takes the values ranging from -0.01 to $-0.04\ \mu V/K^2$ for the $x=0$–0.5 samples whereas for the $x=0.6$ sample it is quite large ($\sim -10\mu V/K^2$). With the increase of x, i.e., with the decrease of carrier concentrations, $(\varepsilon_0-\varepsilon_F)$ increases as obtained for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ samples.[10] But no systematic variation of Γ with x is observed.

C. Nagaosa-Lee model

A quite good fit of the TEP results for Bi 2:2:1:2 samples has been obtained by using the Nagaosa-Lee model[15] with a slight modification as introduced by Ikegawa *et al.*[15] Nagaosa and Lee proposed that, for a superconducting cuprate, there are two contributions in the TEP, one coming from bosons and another from fermions:

$$S=S_B+S_F$$

with

$$S_B=\frac{k_B}{e}\left[1-\ln\frac{2\pi p}{mk_BT}\right] \tag{4a}$$

and

$$S_F=-\left[\frac{k_B}{e}\right]\frac{k_BT}{\varepsilon_F}\ , \tag{4b}$$

where p is the concentration of holes per (Cu-O) bond and m is the mass of the Bosonic carrier.

To fit the TEP results of some superconducting as well as nonsuperconducting compounds, Ikegawa *et al.*[15] modified the above equation in the following form:

$$S=\frac{k_B}{e}\left[1-F\ln\frac{2\pi pG}{T}-\frac{T}{H}\right]\ , \tag{5}$$

TABLE I. The best-fit parameters A, B, α of Eq. (3) and $(\varepsilon_0-\varepsilon_F)$, Γ values determined from A and B for $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples.

x	T_c (K)	α ($\mu V/K^2$)	A (μV)	B (K)	$(\varepsilon_0-\varepsilon_F)$ (K)	Γ (K)
0.0	85	−0.028	2 129.19	183.30	12.349	332.24
0.0	105	−0.016	2 546.61	113.46	14.770	205.26
0.1	88	−0.021	3 404.69	169.09	19.747	306.07
0.2	74	−0.023	7 244.71	153.17	42.019	274.63
0.25	58	−0.040	1 6580.00	193.67	96.164	337.86
0.35	30	−0.035	3 8886.20	263.64	225.539	421.67
0.5		−0.011	8 3023.70	324.74	481.537	354.74
0.6		−9.997	3.7789×10^7	1 862.50	219 176.2	Imaginary

where F, G, and H are the fitting parameters.

We have fitted the TEP results of the Tl 2:2:1:2 sample with Eq. (5). The best-fit curves along with the experimental points are presented in Figs. 5(a)–5(c). It is seen that the experimental points fit well with Eq. (5). The parameters F, H, and G show similar variation with x, as observed in the Bi 2:2:1:2 system.[10] From Table II it is seen that F increases with increasing x, whereas H and G decrease with increasing x for metallic samples. H shows a minimum value for $x=0.35$, around which the M-I transition occurs in the Tl 2:2:1:2 system.[11] The parameter G which is proportional to m^{-1} is larger for more metallic samples.

In Fig. 6, we have shown the variation of the proportionate contributions of bosons and fermions (S_B and S_F) to the TEP at room temperature with a dopant concentration (x). The total value of the TEP ($S=S_B+S_F$) and the experimental data points are presented in the same figure. The Bose part (S_B) is positive and increases with increasing x showing a peak at $x=0.35$. S_F is negative

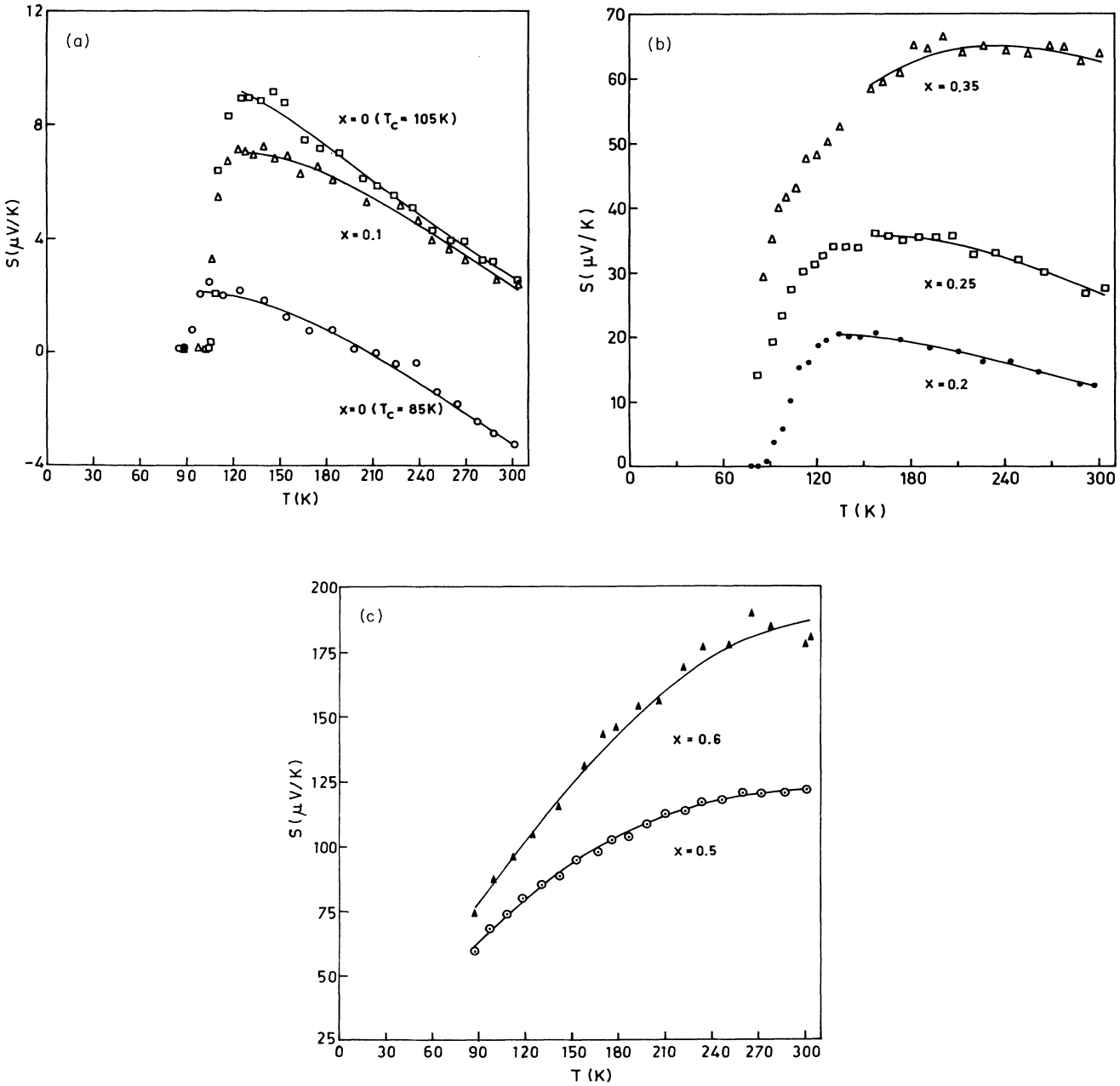

FIG. 4. Best-fit curves (solid lines) for $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples corresponding to Eq. (3): (a) $x=0.0$ ($T_c=85$ K); 0.1, 0.0 ($T_c=105$ K); (b) 0.2, 0.25, 0.35; and (c) 0.5, 0.6.

TABLE II. Fitted parameters F, H, and G of Eq. (5) for $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples.

x	T_c (K)	F	H (K)	G (K)
0.0	85	0.060 0±0.000 1	1 563.73±1	(5.256 01±0.075)×10^8
0.0	105	0.001 4±0.000 2	2 190.99±5	(2.088 88±0.042)×10^6
0.1	88	0.085 0±0.000 2	1 343.27±2	(9.385 79±0.324)×10^3
0.2	74	0.149 5±0.000 6	762.96±1.6	(439.10±20.16)
0.25	58	0.401 6 ±0.002 1	395.24±1.7	(293.66±9.92)
0.35	30	0.981 3±0.003 8	239.11±1	(436.42±45.91)
0.5		1.017 2±0.001 0	411.616±1	
0.6		1.679 5±0.006 1	299.84±3	

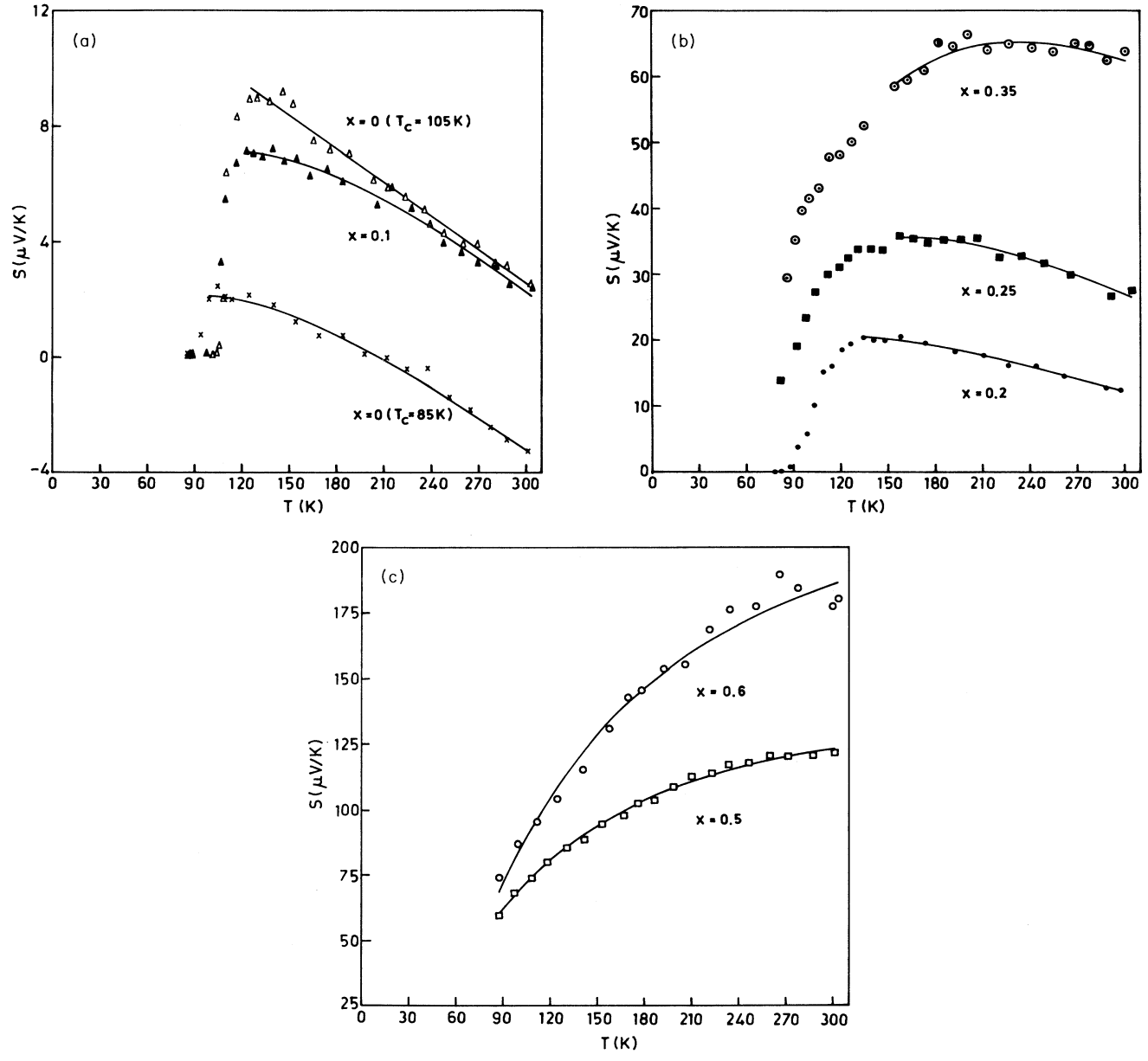

FIG. 5. Best-fit curves (solid lines) for $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ ($x=0$–0.6) samples using Eq. (5): (a) $x=0.0$ ($T_c=85$ K), 0.1, 0.0 ($T_c=105$ K); (b) 0.2, 0.25; 0.35; and (c) 0.5, 0.6.

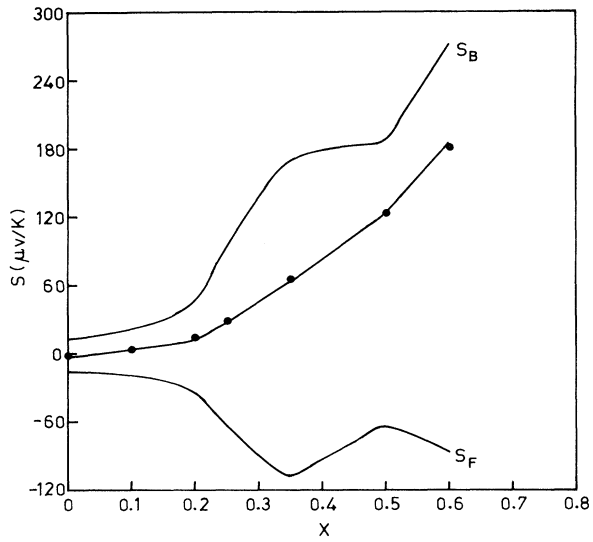

FIG. 6. Plots of S_F, S_B, and S [calculated from Eq. (5)] with x at $T=300$ K. The solid circles (●) correspond to experimental points.

and its magnitude increases with increasing x for metallic samples. S_F also shows a peak around $x=0.35$. It is of particular interest to note that both S_B and S_F show a peak at $x=0.35$, around which the M-I transition in the Tl 2:2:1:2 system occurs. Similar behavior was also found in the Bi 2:2:1:2 system. But for Bi 2:2:1:2 samples S_F is small for insulating samples whereas in Tl 2:2:1:2 it has a significant contribution.

In conclusion, we have found that the thermoelectric power of $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_{8+y}$ varies systematically with the carrier concentration as the carrier concentration is changed by substituting Y at the Ca site. The general behavior of the TEP of the Tl system is in agreement with that of Bi 2:2:1:2 and other high-T_c oxide systems. For insulating samples the TEP is large and positive and it increases with temperature in the measured temperature range but dS/dT decreases with increasing temperature. For metallic samples (higher carrier concentration) dS/dT is negative in the high-temperature region. For samples with optimum carrier concentration (p_c), for which T_c is maximum, the room-temperature TEP is ~ 0. S is negative at high temperatures for samples with higher carrier concentrations ($p > p_c$).

The S_{300}-p results of the Tl 2:2:1:2 system do not satisfy the relation obtained from the single-band Hubbard model (in the narrow-band limit) even for small carrier concentration. The temperature dependence of S fits reasonably well with the boson-fermion model of Nagaosa and Lee.

ACKNOWLEDGMENTS

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