PHYSICAL REVIEW B VOLUME 46, NUMBER 18 1 NOVEMBER 1992-II

# Thermoelectric power for the overdoped superconductors (Yb,Ca)(Ba,Sr)$_2$Cu$_3$O$_z$

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(Received 20 May 1992)

We have made a measurement of Seebeck coefficients for overdoped superconductors, $(\mathrm{Yb}_{1-x}\mathrm{Ca}_x)(\mathrm{Ba}_{0.8}\mathrm{Sr}_{0.2})_2\mathrm{Cu}_3\mathrm{O}_z$. The hole concentration was controlled by cation substitution and/or oxygen nonstoichiometry. For the sample where $x=0.3$, as the oxygen content ($z$) increased, the magnitude of the Seebeck coefficient at room temperature ($S_{300\,\mathrm{K}}$) decreased from positive several tens of $\mu$V/K for $z=6.10$ down to minus tens of $\mu$V/K for $z=6.78$, passing through the zero value. For the sample where $S_{300\,\mathrm{K}} \sim 0\ \mu$V/K, the $T_c$ was the highest. For the samples with a high oxygen content of $z=6.83\pm0.06$ and various Ca contents, $S_{300\,\mathrm{K}}$'s were negative, and, as $x$ increased, both $T_c$ and $S_{300\,\mathrm{K}}$ decreased. This indicated that these samples were in the region of overdoped holes. Combining these results with those for the samples with various values of $z$, we could conclude then that $S_{300\,\mathrm{K}}$ decreased monotonically with increasing hole concentration in the CuO$_2$ plane, from positive values in the region of underdoped holes to negative values in the region of overdoped holes. This composition dependence of Seebeck coefficients may reflect the change in the electronic picture from the strongly correlated system to the weakly correlated Fermi-liquid metal.

## I. INTRODUCTION

Since the discovery of high-$T_c$ superconductors, there have been a large number of experimental and theoretical studies on the mechanism of high-$T_c$ superconductivity, but the mechanism has not yet been completely understood. The thermoelectric-power measurement allows us to probe electronic properties of conductors for its high sensitivity to the electron-energy-band structure. Such studies would contribute to the theoretical understanding of high-$T_c$ superconductivity. It has been observed[1] that the thermoelectric-power coefficients of high-$T_c$ superconductors show an unusual temperature dependence and are highly sensitive to variation in the oxygen content or in the amount of doped cations.

A number of studies on thermoelectric power for $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ (1:2:3) superconductors and related compounds have been reported.[1-3] It has been commonly observed that thermoelectric power increases as oxygen deficiency ($\delta$) increases. The thermoelectric power is small for a sample with a small value of $\delta$ and negative only for the samples with very small values of $\delta$.[2] It is well known that the $T_c$ of the 1:2:3 superconductor increases as $\delta$ decreases.[4] On the other hand, several experiments have shown that $T_c$ decreases as $\delta$ approaches zero,[5,6] which suggests that a sample where $\delta=0$ may be in a state of overdoped holes. This indicates that the negative values of thermoelectric power for the samples with very small oxygen deficiency correspond to the states of overdoped holes. However, no thermoelectric-power data have been reported for 1:2:3-type superconductors with definitely overdoped holes.

Recently, we were successful in preparing 1:2:3 samples $(\mathrm{Yb}_{1-x}\mathrm{Ca}_x)(\mathrm{Ba}_{0.8}\mathrm{Sr}_{0.2})_2\mathrm{Cu}_3\mathrm{O}_z$ $(0\le x\le 0.3)$ with a wide range of hole concentrations and confirmed that the $T_c$ decreased in the region of overdoped holes.[7] This was also observed in other high-$T_c$ systems such as $(\mathrm{La}_{1-x}\mathrm{Sr}_x)_2\mathrm{CuO}_4$ (Ref. 8) and $\mathrm{Tl}(\mathrm{Ba}_{1+x}\mathrm{La}_{1-x})\mathrm{CuO}_5$.[9] The $(\mathrm{Yb}_{1-x}\mathrm{Ca}_x)(\mathrm{Ba}_{0.8}\mathrm{Sr}_{0.2})_2\mathrm{Cu}_3\mathrm{O}_z$ compounds exhibited a tetragonal-orthorhombic structural phase transition as the oxygen content $z$ varied. Note that both the tetragonal (for $6.10\le z\le 6.56$) and the orthorhombic phases (for $6.56<z\le 6.78$) of $(\mathrm{Yb}_{0.7}\mathrm{Ca}_{0.3})(\mathrm{Ba}_{0.8}\mathrm{Sr}_{0.2})_2\mathrm{Cu}_3\mathrm{O}_z$ showed superconductivity, and the maximum $T_c$ was observed at around $z=6.6$.

In this work we measured the thermoelectric power for cation-substituted samples $(\mathrm{Yb}_{1-x}\mathrm{Ca}_x)(\mathrm{Ba}_{0.8}\mathrm{Sr}_{0.2})_2\mathrm{Cu}_3\mathrm{O}_z$ $(0\le x\le 0.3)$ with a wide range of $z$ and studied the effect of cation substitution and oxygen nonstoichiometry on thermoelectric power for the 1:2:3-type superconductors. We also discussed the hole-doping effect on the thermoelectric power of the high-$T_c$ superconductors.

## II. EXPERIMENTAL DETAILS

Two series of $(\mathrm{Yb}_{1-x}\mathrm{Ca}_x)(\mathrm{Ba}_{0.8}\mathrm{Sr}_{0.2})_2\mathrm{Cu}_3\mathrm{O}_z$ samples were prepared. In one of the series (series I), the Ca content was fixed at a high value ($x=0.3$) and the oxygen content varied through a wide range of $z=6.10-6.78$. In the other series (series II), the oxygen content was maintained at a high value of $z=6.83\pm0.06$ and $x$ was varied from 0 to 0.3.

The samples used in this study were prepared by a conventional solid-state reaction method. High-purity powders of Yb$_2$O$_3$, CaCO$_3$, BaCO$_3$, SrCO$_3$, and CuO were used as starting materials. Appropriate amounts of the powders were mixed to the nominal compositions of $(\mathrm{Yb}_{1-x}\mathrm{Ca}_x)(\mathrm{Ba}_{0.8}\mathrm{Sr}_{0.2})_2\mathrm{Cu}_3\mathrm{O}_z$ and then calcined. The calcined powders were compacted into parallelepiped bars of 3 mm × 3 mm × 20 mm. The bars were sintered at

850 °C for 20 h in flowing (99% $N_2$ + 1% $O_2$) gas and then held in flowing $O_2$ gas successively at 400 °C for 20 h and at 300 °C for 20 h. In order to control the oxygen content, the sample where $x = 0.3$ was heat treated again at 300 or 500 °C for 3 h in air and then quenched in liquid nitrogen. Some of the samples quenched from 500 °C were then reduced at around 500 °C using appropriate amounts of $Ti_2O_3$ powder sealed in evacuated silica tubes together with the samples. The sample preparation and characterization procedures are described in detail elsewhere.[7]

The lattice constants were determined by x-ray diffraction using Cu $K\alpha$ radiation. The average valence of copper was analyzed by a coulometric titration technique.[10,11] The oxygen content was calculated from the average Cu valence. The superconducting transition temperature $T_c$ was defined at the onset of the diamagnetic signal. The dc magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). Electrical resistivity was measured employing a standard four-probe technique.

The thermoelectric power was studied by measuring the Seebeck coefficients. The Seebeck coefficient was obtained using a dc method employing a 10-nV-resolution digital voltmeter at temperatures between 30 and 310 K. The sample temperature was measured by means of a calibrated Si diode sensor. The temperature difference between the two ends of the sample bar was measured by using two pairs of Cu-Constantan thermocouples. The two pairs of thermocouples were contacted onto the hot and cold ends of the sample. The collection of the Seebeck-coefficient data was fully computer controlled.

## III. RESULTS

### A. $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ samples with various oxygen contents (series I)

Figure 1 shows the temperature dependence of the Seebeck coefficient for $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$, in which the oxygen content ranges from $z = 6.10$ to 6.78. As $z$ increases, the Seebeck coefficient monotonically decreases at a fixed temperature. For the low oxygen contents, i.e., where $z = 6.10$, 6.43, and 6.56, the Seebeck coefficient is positive and it changes its sign for the high oxygen contents, i.e., where $z = 6.73$ and 6.78. In the superconducting state below $T_c$, the Seebeck coefficients were, needless to say, zero for all the samples. For the samples with positive Seebeck coefficients, the temperature dependence of the Seebeck coefficient exhibited a broad peak, and the peak shifted toward the high-temperature side as $z$ decreased. For the samples with negative Seebeck coefficients, the Seebeck coefficient decreased up to about 100 K, while, above 100 K, the Seebeck-coefficient curve changed its gradient from weakly positive to negative as $x$ increased.

### B. $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ samples with high oxygen contents (series II)

Figure 2 shows the temperature dependences of the Seebeck coefficient for the $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ samples with various values of $x$, in which the oxygen content is high ($z = 6.83 \pm 0.06$). The Seebeck coefficients for all the samples were negative, and the absolute value of the Seebeck coefficient increased with increasing $x$ over the whole temperature range. As the temperature increased, the Seebeck coefficient was exactly zero up to the superconducting temperature $T_c$ and decreased rapidly to about 100 K for all the samples. As the Ca content ($x$) increased, the Seebeck-coefficient curve changed its tangent from positive to negative at temperatures above 100 K. The general features of the curve given in Fig. 2 are quite similar to those of typical $n$-type superconductors.[12] The monotonical decrease of negative thermoelectric power with increasing temperature was first observed at $x = 0.3$. This is supposed to correspond to the data at higher hole concentration than that found in Ouseph and O'Bryan.[2] If we could increase the value of $x$ beyond the solubility limit of 0.3, the temperature dependence of the Seebeck coefficient might become normal metallic.

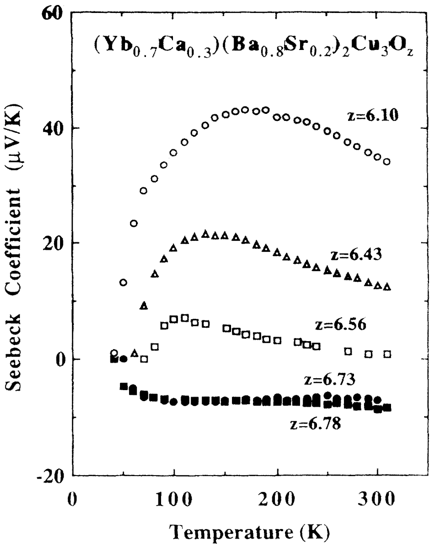

FIG. 1. Temperature dependence of the Seebeck coefficient for $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$.

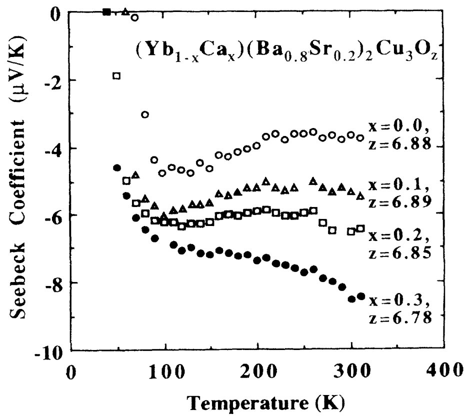

FIG. 2. Temperature dependence of the Seebeck coefficient for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ ($x = 0.0$, 0.1, 0.2, and 0.3).

## IV. DISCUSSION

Figure 3 shows the $z$ dependences of the following physical parameters for $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ (series I): the lattice parameters ($a$, $b$, and $c$), average copper valence [$V$(Cu)], resistivity at 200 K ($R_{200\,K}$), superconducting transition temperature ($T_c$), and Seebeck coefficient at 300 K ($S_{300\,K}$). The $c$ axis linearly decreased with increasing $z$, and a tetragonal-orthorhombic structural transition occurred around $z = 6.6$. Crossing over the phase-transition point, the $V$(Cu) continuously increased with increasing $z$. $R_{200\,K}$ linearly increased with increasing $z$ in both the tetragonal and orthorhombic phases, but the slope of the $R_{200\,K}$-vs-$z$ curve changed around the phase-transition point. With increasing $z$, $T_c$ linearly increased for the tetragonal phase, while it sharply decreased in the orthorhombic phase. The sample where $z = 6.56$ was tetragonal and had the highest $T_c$ value, 82 K, within series I. $S_{300\,K}$ monotonically decreased with increasing $z$, passing through the tetragonal-to-orthorhombic phase boundary. The slope of the $S_{300\,K}$-vs-$z$ curve, however, changed around the phase-transition point, as was observed for the $R_{200\,K}$-vs-$z$ curve. The sign of $S_{300\,K}$ also changed around the $T_{c\,\max}$ composition.

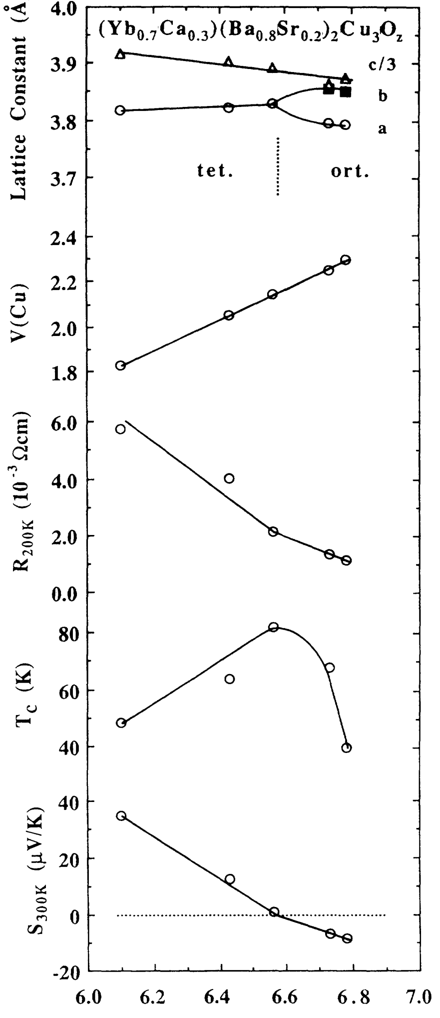

FIG. 3. Dependence on the oxygen content $z$ of parameters for the $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ samples, where $z = 6.10$–$6.78$, i.e., the lattice parameters ($a$, $b$, and $c$), the average copper valence [$V$(Cu)], the resistivity at 200 K ($R_{200\,K}$), and the Seebeck coefficient at 300 K ($S_{300\,K}$).

Recently, Miyatake *et al.*[13] reported that the pressure derivative of $T_c$ ($dT_c/dp$) was positive for the tetragonal phase and was negative for the orthorhombic phase in series I. For the orthorhombic phase, the depression of $T_c$ and the negative value of $dT_c/dp$ would indicate that the samples were in the overdoped region of the electronic phase diagram. However, the tetragonal-to-orthorhombic phase transition may not be directly related to the transition from the underdoped to the overdoped region. This is because, for the nondoped 1:2:3 compound, this structural phase transition occurs in the underdoped region. It is rather related to the Cu(1)-O chain formation for the oxygen content where $z > 6.5$. Namely, it is coincidental that the tetragonal-to-orthorhombic phase transition occurred at the maximum $T_c$ composition. Note that, as $z$ increased, $V$(Cu) linearly increased, but the transport parameters $R_{200\,K}$ and $S_{300\,K}$ decreased, yielding kinks around the tetragonal-orthorhombic transition point. Therefore it is likely that this structural phase transition would not affect the electronic properties drastically, but it caused only small changes in the relations of $R_{200\,K}$ vs $z$ and $S_{300\,K}$ vs $z$, through change in the band structure in the vicinity of the Fermi surface induced by changes in the crystallographic symmetry.

$S_{300\,K}$ continuously decreased as the hole concentration increased from an underdoped to an overdoped state. The change in its sign does not lead to the simple interpretation that the decrease in $S_{300\,K}$ leads to an increase in hole concentration. It rather suggests a gradual change in the electronic picture from a doped charge-transfer (CT) insulator to a Fermi-liquid metal without a CT gap, as was previously discussed for the Hall coefficient.[14,15] For the overdoped region, the calculation of the band structure could explain the transport coefficients, including the Hall coefficient,[16] which suggested that the carriers are electrons.

The critical concentration at which the transition point of $S_{300\,K}$ changes from a positive to a negative value seems to depend on the material. For example, it was at the $T_{c\,\max}$ composition for the Y 1:2:3 system[2] and Bi 2:2:1:2 system[17] and at an overdoped composition for the La 2:1:4 system.[18] If a two-carrier model is assumed, the sign of the thermoelectric power may be determined by a delicate balance between electron and hole concentrations.

Figure 4 shows the Ca-content dependences of the same parameters as those in Fig. 3 for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$. All the samples had orthorhombic 1:2:3-type structures. As $x$ increased, both $a$ and $c$ axes increased, while the $b$ axis decreased. Since $z$ monotonically decreased with increasing $x$, $V$(Cu) was nearly constant at about +2.3. $R_{200\ \mathrm{K}}$ is nearly independent of $x$. Judging from the values of $V$(Cu) and $R_{200\ \mathrm{K}}$, all the samples might be overdoped in terms of the hole concentration. $T_c$ linearly decreased with $x$, suggesting that the hole concentration in the $CuO_2$ plane increased, while the hole concentration in the CuO chain decreased.

$S_{300\ \mathrm{K}}$ monotonically decreased with increasing the hole concentration in the $CuO_2$ plane (with decreasing $T_c$), which was consistent with the result in Fig. 3. This implies that the thermoelectric power was dominated by the hole concentration within the plane, but not by that in the CuO chain, which seems to be strange. It may result from a drastic change of the electric state within the plane from a strongly correlated state to a weakly correlated one, which may overwhelm the contribution from the CuO chain. On the other hand, the electrical resistivity was affected by the conductions from both the $CuO_2$ plane and CuO chain.

Finally, we evaluated the hole concentration in the $CuO_2$ plane ($P_{\mathrm{pl}}$) for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ using the model of Tokura *et al.*[4] and discussed the relationship between $P_{\mathrm{pl}}$ and $S_{300\ \mathrm{K}}$. Tokura *et al.* proposed a model for the 1:2:3 system in which the hole concentration in the $CuO_2$ plane mainly determined the $T_c$ and the CuO chain merely provided an insulating reservoir of holes. The hole concentration in the $CuO_2$ plane ($P_{\mathrm{pl}}$) was calculated by the equation

$$P_{\mathrm{pl}}=3(P-P_c)/2\ ,$$

where $P$ [$=V(\mathrm{Cu})-2$] is the average hole concentration and $P_c$ is defined by $P_c=-2.21+0.34z$. Figure 5 shows the dependences of $T_c$ and $S_{300\ \mathrm{K}}$ on $P_{\mathrm{pl}}$ for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$. Note that for the $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6.10}$ sample, although it showed superconductivity, $P_{\mathrm{pl}}$ was a negative value and the corresponding data plots are not in agreement with the general trend. This indicates that the above empirical model cannot be applied for such a low oxygen content,

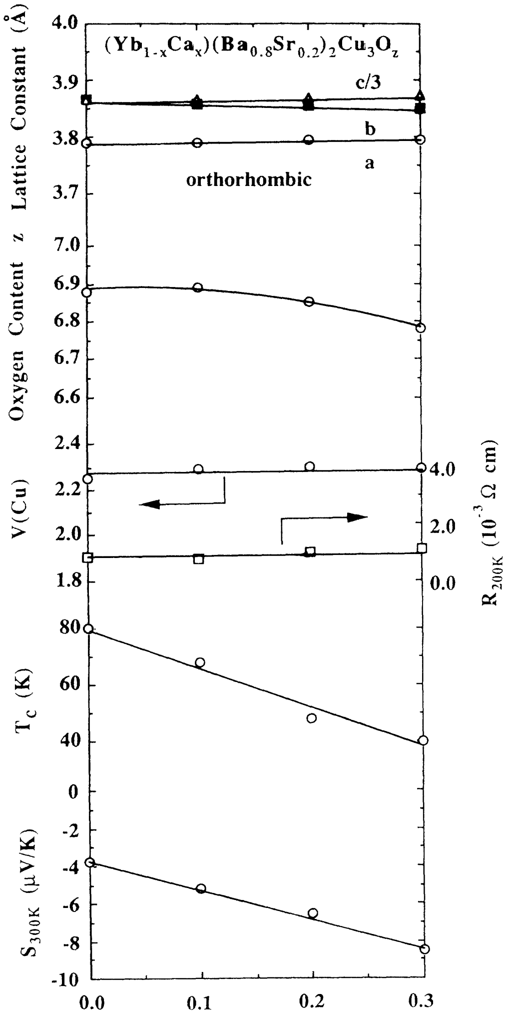

FIG. 4. Dependence on the Ca content $x$ of a variety of parameters for the $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ samples, i.e., the lattice parameters ($a$, $b$, and $c$), the oxygen content ($z$), the average copper valence [$V$(Cu)], the resistivity at 200 K ($R_{200\ \mathrm{K}}$), the superconducting transition temperature ($T_c$), and the Seebeck coefficient at 300 K ($S_{300\ \mathrm{K}}$).

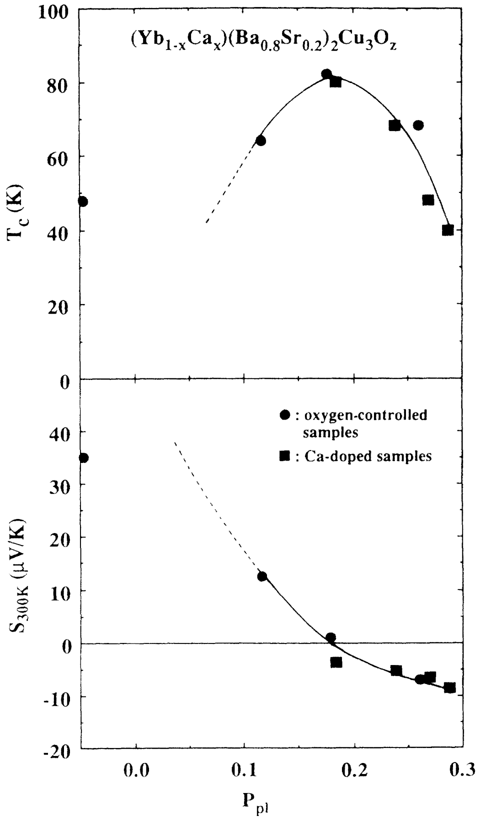

FIG. 5. Dependence on the hole concentration ($P_{\mathrm{pl}}$) of the superconducting transition temperature ($T_c$) and the Seebeck coefficient at 300 K ($S_{300\ \mathrm{K}}$) for the $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ system [sample with a fixed value for $x$, i.e., $x=0.3$, and various values for $z$ (●) and samples with various values of $x$ and nearly constant values of $z$ ($z=6.83\pm0.06$) (■)].

which may be due to an ordering of oxygen in the CuO chain site, as has been pointed out in previous works.[19,20] Thus the actual $P_{\mathrm{pl}}$ may be larger than the value in Fig. 5. Roughly speaking, both the series-I (oxygen-controlled) samples and the series-II (Ca-doped) samples have a common relationship between $P_{\mathrm{pl}}$ and $S_{300\ \mathrm{K}}$. This would mean that both cation substitution and oxygen nonstoichiometry give rise to a common change in the electronic state or doping level within the $\mathrm{CuO_2}$ plane. Furthermore, it may indicate that most of the thermoelectric power is contributed by holes (or electrons) in the $\mathrm{CuO_2}$-plane bands, but not by those in the CuO-chain band. A small deviation in $S_{300\ \mathrm{K}}$ for the low-$x$ samples from the guide curve may be attributed to the fact that the scattering due to the substituted Ca is depressed. $S_{300\ \mathrm{K}}$ continuously varies with the change in the doping level, from positive to negative value, reflecting the change in the electric picture from the doped CT insulator (strong-coupling limit) to the weakly correlated Fermi-liquid metal. Therefore the Seebeck coefficient at 300 K ($S_{300\ \mathrm{K}}$) may be a good parameter for probing the electronic state or doping level in the $\mathrm{CuO_2}$ plane.

## V. CONCLUSION

The Seebeck coefficients were measured for the 1:2:3-type superconductors $(\mathrm{Yb}_{1-x}\mathrm{Ca}_x)(\mathrm{Ba}_{0.8}\mathrm{Sr}_{0.2})_2\mathrm{Cu}_3\mathrm{O}_z$ with a wide range of hole concentrations. The hole concentrations were controlled by cation substitution and/or oxygen nonstoichiometry such that samples with overdoped hole concentrations, as well as those with underdoped hole concentrations, might be obtained.

The sign of the Seebeck coefficient at 300 K ($S_{300\ \mathrm{K}}$) changed around the $T_{c\ \max}$ composition, and the positive and negative $S_{300\ \mathrm{K}}$ regions corresponded to the underdoped and overdoped regions of holes, respectively.

Both the oxygen-controlled samples (series I) and the Ca-doped samples (series II) exhibited a common relationship between the hole concentration in the $\mathrm{CuO_2}$ plane ($P_{\mathrm{pl}}$) and $S_{300\ \mathrm{K}}$. This would mean that both cation substitution and oxygen nonstoichiometry gave rise to a common change in the electronic state or doping level in the $\mathrm{CuO_2}$ plane. $S_{300\ \mathrm{K}}$ continuously varied as the doping level changed. $S_{300\ \mathrm{K}}$ was considered to be a good parameter for probing the electronic state or doping level in the $\mathrm{CuO_2}$ plane.

## ACKNOWLEDGMENTS

We would like to thank Dr. A. Ichinose, T. Kawano, T. Miyatake, and K. Kubo of SRL-ISTEC for their helpful discussions. This work was partially supported by the New Energy and Industrial Technology Development Organization for the Programme of R&D of Basic Technology for Future Industries.

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