Carrier concentrations in Bi$_2$Sr$_{2−z}$La$_z$CuO$_{6+δ}$ single crystals and their relation to Hall coefficient and thermopower

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We measured the thermopower $S$ and the Hall coefficients $R_H$ of Bi$_2$Sr$_{2−z}$La$_z$CuO$_{6+δ}$ (BSLCO) single crystals in a wide doping range, in an effort to identify the actual hole concentrations per Cu, $p$, in this system. It is found that the “universal” relation between the room-temperature thermopower and $T_c$ does not hold in the BSLCO system. Instead, comparison of the temperature-dependent $R_H$ data with other cuprate systems is used as a tool to identify the actual $p$ value. To justify this approach, we compare normalized $R_H(T)$ data of BSLCO, La$_2$−$z$Sr$_z$CuO$_4$ (LSCO), YBa$_2$Cu$_3$O$_y$, and Tl$_2$Ba$_2$CuO$_{6+δ}$, and demonstrate that the $R_H(T)$ data of the LSCO system can be used as a template for the estimation of $p$. The resulting phase diagram of $p$ vs $T_c$ suggests that $T_c$ is anomalously suppressed in the underdoped samples, becoming zero at around $p ≃ 0.10$, while the optimum $T_c$ is achieved at $p ≃ 0.16$ as expected.

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Determination of the actual carrier concentration in the high-$T_c$ cuprates is in general a difficult task. The La-214 system [La$_2$−$z$Sr$_z$CuO$_4$ (LSCO) or La$_2$−$z$Ba$_2$CuO$_4$ (LBCO)] is almost the only system where the carrier concentration is nearly unambiguously known; in this system, the hole concentrations per Cu, $p$, is identical to the $x$ value, as long as the oxygen is stoichiometric. In the YBa$_2$Cu$_3$O$_y$ (YBCO) system, the hole concentration in the CuO$_2$ planes is ambiguous because of the existence of the imperfect CuO chains which absorb part of the doped holes. In other systems like Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (Bi-2212), Bi$_2$Sr$_2$CuO$_{6+δ}$ (Bi-2201), or Tl$_2$Ba$_2$CuO$_{6+δ}$ (Tl-2201), the determination of the hole concentration is also ambiguous because Bi and Tl ions have mixed valencies [4].

In ordinary metals or semiconductors, the Hall coefficient $R_H$ is often used for the determination of the carrier concentration. However, $R_H$ of the cuprates has not been considered to be a useful tool to determine $p$, because $R_H$ shows a rather strong temperature dependence. Moreover, it has been reported for LSCO that the magnitude of $R_H$ is several times smaller than that expected from the chemically-determined carrier concentration [5]. On the other hand, it has been proposed [6] that the magnitude of the thermopower at room temperature (290 K), denoted as $S$(290K), can be used for the determination of $p$, based on the observation that the plot of $T_c/T_c^{max}$ vs $S$(290K) is almost “universal” among many cuprates ($T_c^{max}$ is the optimum $T_c$ of each system), although the data of the LSCO system do not follow the “universal” relation [6]. If one assumes another “universal” relation [7] between $p$ and $T_c/T_c^{max}$, so-called the “bell shape”, the measurement of $S$(290K) yields an estimation of $p$ as long as the two “universal” relations hold.

The above mentioned relation between $p$ and $S$(290K) has not been tested in Bi$_2$Sr$_{2−z}$La$_z$CuO$_{6+δ}$ (BSLCO, or La-doped Bi2201), in which the carrier concentration can be changed over a wide range [8]. An increase in the La concentration $z$ in this system leads to a smaller density of holes in the CuO$_2$ planes, and the optimum $T_c$ is achieved with $z ≃ 0.4$. In this paper, we report our systematic measurements of $S$(290K) and $R_H(T)$ for a series of BSLCO single crystals, for which $z$ is varied from 0.2 to 1.0. It is found that the optimally-doped BSLCO crystal show notably smaller $S$(290K) value than that expected from the “universal” relation. This is a strong indication that the “universal” relation does not hold in the BSLCO system and thus one should not use this relation to determine $p$. We therefore tried to use the temperature-dependent $R_H$ for the determination of $p$. We show that, using $R_H(T)$ of the LSCO system as a template, the $R_H(T)$ data can give reasonable estimate of $p$. With the $p$ values thus obtained, we construct the relation between $p$ and $S$(290K), which is actually quite different from the “universal” relation. The final phase diagram of $T_c$ vs $p$ for the BSLCO system suggests that $T_c$ is anomalously suppressed in the underdoped samples, becoming zero at around $p ≃ 0.10$, while the optimum $T_c$ is achieved at $p ≃ 0.16$.

The single crystals of Bi$_2$Sr$_{2−z}$La$_z$CuO$_{6+δ}$ are grown using a floating-zone (FZ) technique [9]. Here we report crystals with $z$ from 0.23 to 1.02. The crystal with $z=0.39$ is optimally-doped; the optimum $T_c$ is 36 K, which is very high for BSLCO [3] and indicates that the crystals reported here are among the best crystals available to date. The actual La concentration in the crystals are determined by employing both the inductively-coupled plasma analysis and the electron-probe microanalysis. For the transport measurements, the crystals are cut into dimensions of typically $2 \times 1 \times 0.05$ mm$^3$. Since the absolute magnitude of the Hall coefficient is important for this work, the thickness of the samples is accurately
determined by measuring their weight with 0.1-μg resolution, and the uncertainty in the absolute magnitude of \( R_H \) is estimated to be less than ±8%. All the crystals are annealed in flowing oxygen at 650°C for 48 hours to guarantee uniform oxygen distribution in the samples.

We define \( T_c \) in this paper by the onset of the Meissner effect measured by dc magnetic susceptibility. We have confirmed that the Meissner-onset \( T_c \) agrees very well with the zero-resistance \( T_c \) for our crystals. The Hall coefficient \( R_H \) is measured together with the in-plane resistivity \( \rho_{ab} \) by using a standard six probe technique. The current contacts are carefully painted to cover two opposing side faces of the platelet-shaped crystals to ensure a uniform current flow. The voltage contacts are painted on the two remaining side faces of the crystals (not on the top or bottom faces), which is important for the accurate Hall effect measurement. The Hall coefficients are measured by sweeping the magnetic field to both plus and minus polarities, while the temperature is stabilized by a combination of the calibrated Cernox sensor and a capacitance sensor. The thermopower is measured with a standard steady-state technique with a reversible temperature gradient of ~1 K, and the thermopower of the gold wires are corrected for.

Figure 1(a) shows the \( \rho_{ab}(T) \) data of the BSLCO crystals for selected \( z \) values from 0.23 - 1.02, which show systematic evolution with changing carrier concentration. One may notice that the residual resistivity \( \rho_0 \) of these samples becomes systematically larger with increasing La doping, although \( \rho_0 \) is very small (~20 μΩcm) at optimum doping; the \( z \) dependence of \( \rho_0 \) is plotted in Fig. 1(b). Figure 1(c) shows the plot of \( T_c/T_{c}^{\text{max}} \) vs \( S(290K) \) of our BSLCO crystals (\( T_{c}^{\text{max}} = 36 \) K), together with the "universal" relation \( z=0.8 \) reproduced as a dashed line. It is clear that the two curves do not agree at all. This is either because the universal relation between \( p \) and \( S(290K) \) does not hold in the BSLCO system or because the \( T_c \) values are somehow reduced from the ideal value (and thus does not correctly reflect the hole concentrations).

To determine which is actually the case, we pay attention to the peaks in Fig. 1(c), which corresponds to the optimum doping; if we can find an evidence from another experiment that the optimum \( T_c \) of BSLCO is indeed realized at \( p \simeq 0.16 \), it is a clear indication that the universal relation of \( T_c/T_{c}^{\text{max}} \) vs \( S(290K) \) is disobeyed in BSLCO. Note that the \( S(290K) \) value of the optimally-doped BSLCO sample (~ −6 μV/K) corresponds to \( p \simeq 0.22 \) in the "universal" relation.

We now demonstrate that the magnitude of the Hall coefficient can be used as a guide to estimate \( p \). It has been pointed out that the fictitious carrier density calculated from the room-temperature value of \( R_H \) does not vary much among different cuprates at the same hole concentration. Therefore, if \( R_H \) is normalized by the unit volume \( V \) and the number of Cu atoms in the unit, \( N \), the resulting \( R_H/NV \) is expected to show similar values for different cuprates at optimum doping (\( p \simeq 0.16 \)).

Note that \( R_H/eNV \) is the electronic charge) gives the inverse of the fictitious hole density per Cu. Figure 2(a) shows the plot of \( R_H/eNV \) vs \( T \) for various cuprates, LSCO, YBCO, Tl-2201, and BSLCO, at optimum doping. The data for Tl-2201 is taken from Ref. 8, and all other data are measured by ourselves paying particular attention to the accuracy in the absolute magnitude. The LSCO sample is a high-purity polycrystal, and the YBCO sample is a high-quality single crystal grown by a flux method using \( Y_2O_3 \) crucible. In the \( R_H \) data of LSCO and YBCO, the uncertainty in the absolute magnitude is less than ±8%. It is clear in Fig. 2(a) that the normalized \( R_H \) of all the optimally-doped cuprates shown here agree reasonably well in the temperature range 150 - 300 K, where the data fall in a rather narrow band of ~20%. This observation is remarkable and has not been emphasized before in the literature.

For the purpose of this paper, Fig. 2(a) strongly suggests that it is reasonable to assert \( p \) to be actually around 0.16 in our optimally-doped BSLCO crystal.

Figure 2(b) shows the comparison of \( R_H/eNV \) vs \( T \) for LSCO and YBCO at three representative dopings: optimum doping, 1/8 doping, and the superconductor-.
Based on this observation, we determine the $p$ values for various $z$ as follows: $p = 0.18, 0.16, 0.15, 0.14, 0.13, 0.12, 0.10, \text{and } 0.03$, for $z = 0.23, 0.39, 0.49, 0.51, 0.66, 0.73, 0.84, \text{and } 1.02$, respectively [1]. Note that these determination are not precise and the expected accuracy would be $\pm 10\%$ at best [13]. This result implies that the superconductivity of our BSLCO is about to disappear at $z = 0.84$ not because the hole concentration is reduced to $p \sim 0.05$. Remember that there is a tendency that $\rho_0$ becomes systematically larger with increasing La doping, as shown in Fig. 1(b). This suggests that one possible reason for the disappearance of superconductivity at $z \approx 0.9$ (which corresponds to $p = 0.09 - 0.10$) is the increased disorder in the heavily-La-doped crystals. In other words, in our BSLCO samples the superconductivity is more significantly suppressed in more underdoped samples because of the larger amount of disorder probed by $\rho_0$. The microscopic origin of this disorder triggered by heavy La doping is yet to be elucidated; it is difficult to imagine that the random potential produced by the replacement of Sr with La itself is responsible to produce $\rho_0$ of as large as 400 $\mu \Omega \text{cm}$.

Figure 4 shows the plot of $S(290\text{K})$ vs $p$ for our BSLCO crystals (where $p$ is determined as above), together with the “universal” relation that is reported to be valid for most of the cuprates except for LSCO [4]. Clearly, the BSLCO system does not follow the “universal” trend. The reason for this deviation is not clear, but it is intriguing to note that both BSLCO and LSCO are peculiar systems in which the optimum $T_c$ is much lower than the “intrinsic” $T_c$ (about 80 K) expected for single-layer cuprates. It has been discussed [4] that these two sys-
tems might share the common trend to stabilize charged stripes, which is known to suppress superconductivity [4].

Using the $p$ values inferred for our BSLCO samples, we can estimate the fictitious $T_c^0$ values for each La concentration by assuming the ordinary "bell shape" for $T_c^0/T_{c\max}$ vs $p$; this $T_c^0$ is the ideal value that would be expected for a given $p$ if there were no cause for the reduction of $T_c$. Since $\rho_0$ of the $z=0.39$ sample is small [Fig. 1(b)], we assume that our optimum $T_c$ is not significantly affected by disorder and thus we take $T_{c\max}^0 = 36$ K for the calculation of $T_c^0$. Figure 5 shows the plot of actual $T_c$ vs $p$ of the BSLCO system, together with the fictitious $T_c^0$ vs $p$. It is clear in Fig. 5 that $T_c(p)$ of the BSLCO system shows a faster drop in both the underdoped and overdoped sides of the phase diagram, which is probably caused by disorder as inferred from the increase in $\rho_0$ when $z$ moves away from the optimum doping [Fig. 1(b)].

In summary, we estimate the hole concentration per Cu, $p$, of a series of BSLCO crystals by using the normalized Hall coefficient $R_{H\nu}/\nu$ and its comparison with other cuprates. It is demonstrated that at optimum doping $R_{H(T)\nu}/\nu$ of various cuprates (LSCO, YBCO, TI-2201, and BSLCO) agree reasonably well in the temperature range 150 - 300 K, where the data fall in a rather narrow band of $\sim 20\%$. This implies that $R_{H\nu}/\nu$ can be used as a guide to estimate $p$. It is found that in the BSLCO system the room-temperature thermopower $S(290K)$ as a function of $p$ does not follow the "universal" trend. The phase diagram of $T_c$ vs $p$ for our BSLCO crystals suggests that $T_c$ is anomalously suppressed in the underdoped samples, where the residual resistivity is found to increase systematically with increasing La doping.

![FIG. 4. $S(290K)$ vs $p$ plot for the BSLCO crystals together with the "universal" relation. The solid line is a guide to the eyes. Inset shows a plot of estimated $p$ vs $z$, together with a straight line fit.](image4)

![FIG. 5. Actual $T_c$ (solid circles) and the fictitious $T_c^0$ (dashed line) plotted vs $p$ for the BSLCO crystals. The $p$ value is calculated from $z$ by using $p = 0.21 - 0.13z$ [3]. The solid line is a guide to the eyes.](image5)

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