Doping dependence of normal-state transport properties in La- and Pb-doped $Bi_2Sr_2CuO_y$

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We report measurements of the electrical resistivity, thermoelectric power, and Hall coefficient on La- and Pb-doped $Bi_2Sr_2CuO_y$ compounds as a function of temperature. Both insulating and overdoped nonsuperconducting-metal samples have been obtained. Analysis of the electrical resistivity in the insulating region suggests that the conduction is governed by a variable-range-hopping mechanism in the low-temperature region. As the system changes from a superconductor to an overdoped nonsuperconducting-metal, the resistivity undergoes a change from a linear temperature dependence to a power-law temperature dependence with exponent $n \sim 1.5$. This $n \sim 1.5$ behavior occurs over a wide temperature range. Remarkable changes associated with the insulator–superconductor–nonsuperconducting-metal transition are also observed both in the thermoelectric power and the Hall coefficient. A significant difference is that the thermoelectric power becomes negative at the higher doping level, while the Hall coefficient remains positive. We explain the experimental results from a two-carrier model by assuming that the Cu $3d_{x^2-y^2}$ electrons undergo a change from a localized state to a partially delocalized state with an increase in the number of dopant O $2p$ holes.

I. INTRODUCTION

It is generally realized that the physical properties of the CuO_2-based superconducting systems are strongly related to the carrier concentration. The undoped parent compound is a charge-transfer insulator with long-range three-dimensional (3D) antiferromagnetic (AF) ordering. This is the case due to the strong on-site electron interactions, which are well understood in the framework of the Hubbard model in the large-U limit. Upon doping, the long-range 3D antiferromagnetic ordering collapses dramatically, and gives way to superconductivity. Neutron-scattering measurements indicate that 2D dynamic AF fluctuations persist in the superconducting state, but the AF correlation length is much shorter. In the heavily doped region the system becomes a nonsuperconducting metal. Results of various spectroscopic measurements suggest that the introduced extra holes reside near O sites since the holes are found to have mainly O $2p$ character. These changes in the physical properties with a varying carrier density has been of central concern for the experiments and theories aiming to elucidate the high-T_c superconducting mechanism. A question of fundamental importance is how doping affects the electronic structure of the CuO_2 layers. Does the Cu^{2+} $3d_{x^2-y^2}$ antibonding state remain localized or become delocalized as the number of dopant holes increases? The heavily doped region in the phase diagram is often labeled as that of a normal metal. Is the metal in this region really normal? In other words, can Landau Fermi-liquid theory provide a reasonable explanation for the properties in the overdoped region? These questions can be answered by performing various experiments. Among these, transport-property measurements can provide useful information on the electronic states of these materials, and serve as a test of the theories.

Until now, most studies have focused on the properties of the high-T_c materials in the lower- and intermediate-carrier-concentration regions where the materials are insulating or superconducting. The reason is that samples with such carrier concentrations are readily available for most systems. Comparatively less amount of work has been done in the heavily doped regions. The nonsuperconducting metallic samples have been achieved only for a few systems, for example, in the $La_{2-x}Sr_xCuO_4$,[1–3] Tl 2:2:0:1 systems.[4] In order to probe the nature of the property change as a function of doping, additional experiments especially in the higher doped region, will be required. Recently we have achieved both insulating and overdoped nonsuperconducting-metal samples in the Bi 2:2:0:1 system by doping La and Pb into the system, respectively. Therefore, the La- and Pb-doped Bi 2:2:0:1 system provides another system with which to study the change of physical properties spanning the whole insulator–superconductor–nonsuperconducting-metal transition regions. In the present work we have studied the electrical resistivity, thermoelectric power, and Hall coefficient of $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ and $Bi_{2-x}Pb_xSr_2CuO_y$ samples. Special attention is paid for the properties of the samples in the higher doped region.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Ceramics of $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ ($x=0-1.0$) and $Bi_{2-x}Pb_xSr_2CuO_y$ ($x=0.05-0.6$) were prepared by a solid-state reaction from a mixture of stoichiometric amounts of the constituent oxides. The phase-forming temperature decreases with increasing Pb content, but increases with increasing La content. Therefore the sintering temperatures for different samples in the La- and Pb-doped Bi-based 2:2:0:1 system change greatly. Typical sintering temperatures are in the range 880–910 °C for the La-doped 2:2:0:1 system, and 880–856 °C for the Pb-doped 2:2:0:1 system. The sintering processes were repeated several times so as to make high-quality single-phase samples. All samples were finally annealed at 400 °C for 12 h.

Powder x-ray diffraction (XRD) and transmission electron microscope (TEM) were used to characterize these samples. All samples but the undoped as well as the higher Pb-doped one (the Pb content $x=0.6$) were confirmed to be single phase. The variation of the lattice parameters a, b, and c of the La- and Pb-doped 2:2:0:1 compounds vs x is shown in Figs. 1(a) and 1(b), respectively. The c parameter in both La- and Pb-doped 2:2:0:1 compounds decreases systematically as x increases but the a and b parameters show an opposite trend. With increasing number of dopant, the a and b parameters increase in the La-doped system but show a decrease in the Pb-doped compounds. We suggest that the decrease of the c parameter in the two substituted systems is of different origins. The shortening in the La-doped system is due to the smaller size of La^{3+} ion compared with the Sr^{2+} ion, while that in the Pb-doped system is due to the removal of the oxygen atoms residing within the double Bi_2O_2 layers. This is consistent with results of the TEM measurement to be presented below. Usually, the lengths in the a and b axes are considered to be controlled by the in-plane Cu—O bond distance, which is closely related to the carrier concentration.[5] The increase in the a and b parameters in the La-doped system is due to the decrease of hole concentration that weakens the Cu—O bonding. On the other hand it has been demonstrated[6] that lead doped in these 2:2:0:1 materials is as Pb^{2+} but not Pb^{4+}, thus the substitution of a 2+ cation for a 3+ cation results in the increase of carrier concentration, which causes a decrease in the a- and b-axis lattice parameters. TEM was used to study the microstructure of these samples. The results demonstrate that the modulation structure along the b axis in these samples changes appreciably. The modulation period (q_b/b) along the b axis decreases from 4.9 to 3.73 as the La content (x) increases from 0 to 1.0, but increases in the Pb-doped system. The sample with Pb content $x=0.6$ is completely modulation-free. Details of the change in the modulation period of these samples are listed in Table I, which is similar to those of previous reports.[6,7] Because the modulation structure along the b axis is associated with oxygen atoms within the double Bi_2O_2 layers,[8] an increase in the modulation period implies a gradual removal of these oxygen atoms. So, in the La-doped compounds, the number of the oxygen atoms residing within the double Bi_2O_2 layers increases slightly. Roughly speaking, it increases from one atom per 4.9 unit cells to one atom per 3.73 unit cells with the La content going form 0 to 1.0. But the number of oxygen atoms decreases in the Pb-doped system. These results are consistent with the fact that the substitution by a higher-valence-state ion results in an increase in the oxygen content, while the substitution by a lower-valence-state ion results in a decrease in the oxygen content.

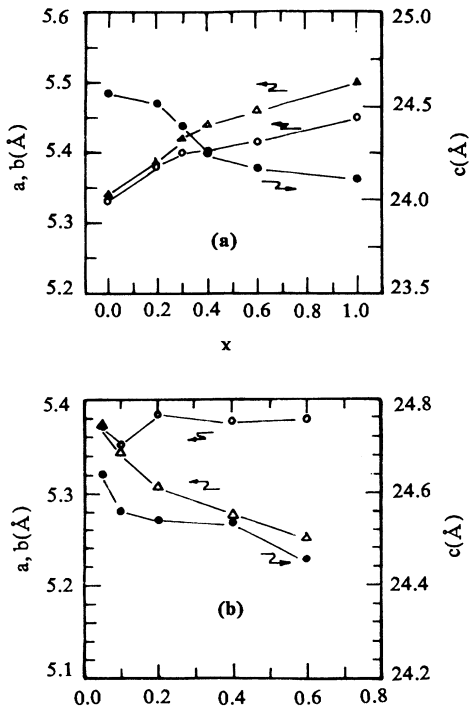

FIG. 1. (a) Variation of lattice parameters a, b, and c with La content x in $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ samples: (b) variation of lattice parameters a, b, and c with Pb content x in $Bi_{2-x}Pb_xSr_2CuO_y$ samples.

The temperature-dependence dc resistivity and Hall coefficient were measured by use of a standard four-probe technique using silver-paint contacts. A current from a constant-current source was passed through the sample and the voltage was measured with a Keithley 181 nanovolmeter. The Hall coefficient was measured under a magnetic field of 2 T. A current of 30 mA was generally passed through the sample. At a fixed temperature, four measurements of the transverse voltage, with reversals of current and field, were performed to obtain the Hall voltage. The thermoelectric power was measured by use of a differential method.

III. RESULTS AND DISCUSSIONS

A. Electrical resistivity

The variation of resistivity with temperature for the $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ ($x=0-1.0$) and $Bi_{2-x}Pb_xSr_2CuO_y$

TABLE I. The modulation period (q_b/b) along the b axis in La- and Pb-doped Bi 2:2:0:1 systems.

$Bi_{2.1}Sr_{1.9-x}La_xCuO_y$	$x=0$	0.2	0.4	0.6	1.0
	4.90	4.33	4.15	4.09	3.73
$Bi_{2-x}Pb_xSr_2CuO_y$	$x=0.05$	0.2	0.3	0.6	
	5.4	7.6	Difficult to measure	Modulation free	

($x=0.05$–0.6) samples is shown in Figs. 2(a) and 2(b). For the La-doped 2:2:0:1 system, the superconducting transition temperature T_c increases with increasing dopant concentration, reaches a maximum of about 20 K (inset) at $x=0.2$, and then decreases sharply. Samples with $x<0.3$ are superconducting and show metallic behavior in the normal state with the nearly linear temperature dependence of resistivity. With increasing x, the resistance shows a change from metallic behavior to a semiconductorlike behavior, especially in the low-temperature region. The $x=0.3$ sample shows a metallic behavior at high temperature ($T>50$ K) and a semiconductorlike behavior in the low temperature ($T<50$ K). (The sharp drop in resistivity at a temperature of 10 K is due to superconducting transition.) These two regions are separated by a shallow minimum (ρ_{min}). With x increasing, the minimum in resistivity shifts towards higher temperature. For example, the ρ_{min} for the $x=0.4$ sample appears at a temperature of 150 K. For the $x=0.6$ and 1.0 samples, ρ_{min} was not observed in the measured temperature range <300 K, which suggests that ρ_{min} in these samples occurs at relatively higher temperature (>300 K). From Fig. 2(a), we can see that the metal-insulator (M-I) transition appears near the composition of $x=0.4$.

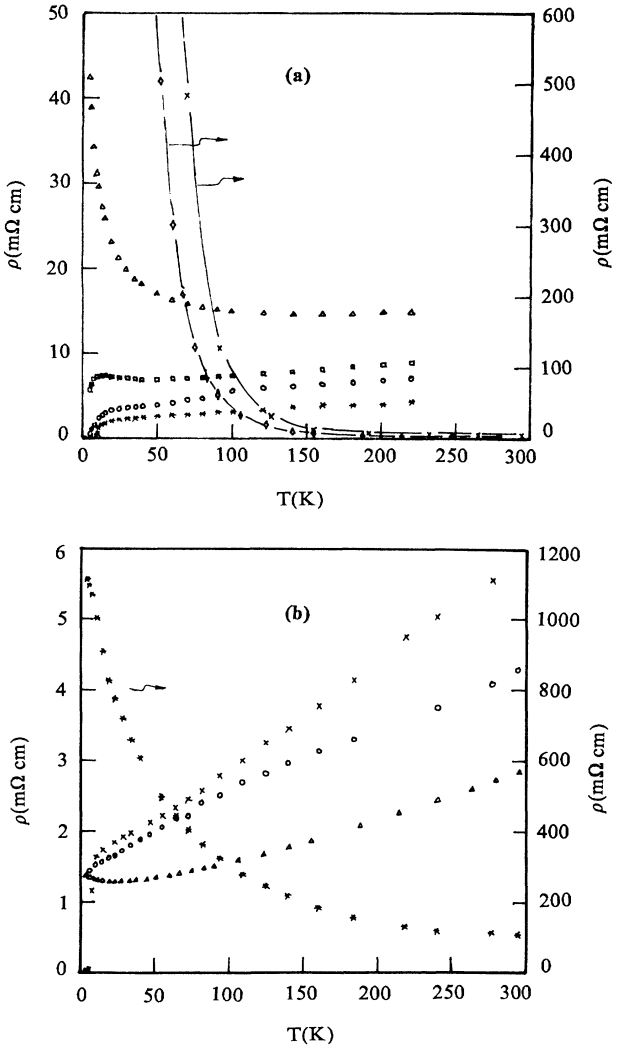

FIG. 2. (a) Temperature dependence of resistivity for $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ (*, $x=0.1$; ○, $x=0.2$; □, $x=0.3$; △, $x=0.4$; ◇, $x=0.6$; ×, $x=1.0$) samples. (b) Temperature dependence of resistivity for $Bi_{2-x}Pb_xSr_2CuO_y$ (×, $x=0.05$; ○, $x=0.1$; △, $x=0.3$; *, $x=0.6$) samples.

If conduction in the semiconducting region occurs by a d-dimensional Mott variable-range-hopping (VRH) mechanism, a linear dependence in the plot of $\ln\rho$ vs T^{-n} is expected with $n=1/(d+1)$.[9] The resistivity of the $x=0.4$ sample does follow the VRH dependence in the temperature range 4.8–60 K with $n=1/4$, which implies a 3-dimensional VRH conduction mechanism, as shown in Fig. 3. However, for samples with high concentration x (e.g., $x=1.0$), we could measure the resistivity below a temperature of 50 K because the very large resistance of the sample makes it difficult to keep our current source at constant current. Though the limited range in T does not permit accurate determination of n, a preliminary fit with the VRH relation over the measured temperature range 50–150 K for the $x=1.0$ sample suggests that n is near $\frac{1}{3}$. In general, a crossover from $n=\frac{1}{2}$ to $\frac{1}{4}$ behavior with increasing carrier densities is believed to take place.[10] The observed experimental data are likely to be con-

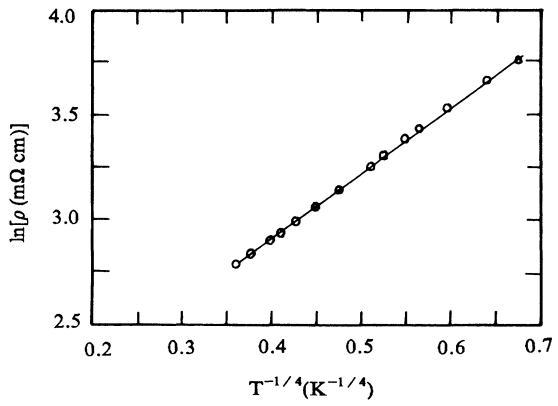

FIG. 3. Logarithm of low-temperasture resistivity as a function of $T^{-1/4}$ for the $x=0.4$ sample in the La-doped system.

sistent with this trend. It may imply that in the insulating phase conduction is governed by a two-dimensional VRH mechanism and a crossover from 2D to 3D VRH behavior occurs as the metal-to-insulator transition is approached. A similar behavior (2D to 3D crossover) has also been observed in Y-doped Bi 2:2:1:2 (Ref. 5) and $La_{2-x}Sr_xCuO_4$ systems.[11] Yamazaki *et al.*[12] have confirmed an antiferromagnetic ordering in the insulating phase of $Bi_2(Sr,La)_2CuO_y$. So this is just the case due to strong electron correlations which are well understood on the basis of the Hubbard model in the large-U limit.

We now turn to the Pb-doped 2:2:0:1 system. As mentioned above, the lead dopant in these 2:2:0:1 materials has the valence state Pb^{2+}. Thus, the substitution of a 2+ cation for a 3+ cation results in an increase in the carrier concentration, which may correspond to the overdoped region in the phase diagram. This increase in the carrier density has been confirmed from the results of Hall-effect measurements, which will be presented later. From Fig. 2(b), we see that the superconducting transition temperature T_c is reduced as more Pb is introduced into the system. However, the resistivity did not increase, which is contrary to the case of a La-doped system. The $x=0.3$ compound becomes nonsuperconducting down to liquid-helium temperatures. It is found that at low temperatures ($T<15$ K) the resistivity shows slight increase with decreasing temperasture, suggesting that the carriers tend to be localized at low temperatures, while at high temperatures ($T>15$ K) the metallic behavior deviates appreciably from the linear temperature dependence. To analyze the temperature dependence at high temperatures we fit the data with a power-law expression,

$$\rho=\rho_0+AT^n$$

and get an exponent $n\sim1.5$ in the temperature range 30–290 K (Fig. 4). It should be mentioned that a similar behavior is found in other overdoped systems. For the $Tl_2Ba_2CuO_{6+y}$ system,[4] the exponent n changes gradually from ~1 to 2 with the samples changing from a superconductor to an overdoped normal metal. In $La_{2-x}Sr_xCuO_4$,[3] an exponent $n\sim2$ is obtained for the overdoped sample with $x=0.3$.

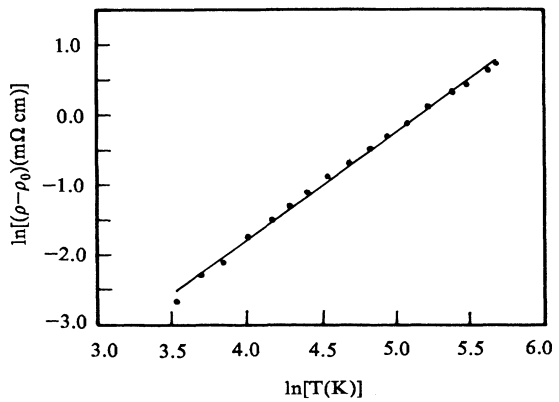

FIG. 4. Fit of the resistivity of the $x=0.3$ sample in the Pb-doped system to the power-law temperature dependence AT^n shown on a log-log scale ($n\sim1.5$).

Commonly the linearly temperature-dependent resistivity is an anomaly specific to the unconventional normal-state properties of high-T_c materials and is believed to be due to the strong electron-correlation effect, while a quadratic temperature-dependent resistivity is taken to be a signature of the ordinary Fermi-liquid state due to electron-electron scattering. Therefore, the metal in the overdoped region in the phase diagram is usually claimed to be a normal metal which obeys Landau Fermi-liquid theory. We argue that even in this overdoped region the temperature-dependent resistivity remains elusive. In the case of the Landau Fermi-liquid scenario, the T^2 behavior should be seen only at very low temperatures and serve as a small correction to the temperature-independent impurity-scattering term. At high temperatures, e.g., room temperature, the electron-phonon interaction dominates the resistivity, which is of the usual linear T dependence. However, for the high-T_c system in the overdoped region, the resistivity almost always rises faster than a linear T dependence, which is seen more clearly at the relatively higher temperature. Our experiments suggest that the exponent n in the Bi 2:2:0:1 system is close to 1.5. We do not get samples with exponent near 2. This $n\sim1.5$ behavior persists going from low temperature to room temperature. It should be mentioned that Kubo's work on the Tl 2:2:0:1 system[4] indicated that the exponent n, which had experienced the gradual change form 1 to 2 as a function of doping, also remained unchanged over a wide temperature range. These behaviors are difficult to interpret in ordinary-Fermi-liquid theory. We suggest that this more rapid than linear increase in resistivity should also be taken as an unusual property of the high-T_c materials in such overdoped regions. Of course, the electronic states of these materials can also be detected from other transport coefficient measurements, which will be presented below. The electronic states of Cu $3d_{x^2-y^2}$ electrons and O $2p$ holes will be discussed.

Upon further introducing Pb into the system, for instance, $x=0.6$ a metal-to-semiconductor transition appears once again [Fig. 2(b)]. We believe that this M-I transition is different from the La-doped system in nature. It is not caused by the reduction of hole concentration (hole filling) in CuO_2 layers. Because powder x-ray-diffraction results indicate that the sample with higher Pb content is not single phase, the resistivity should increase substantially if the impurity phase is not metallic. Besides, cation substitutions may cause random disorders in the system, which can make the conducting carriers localized. So this M-I transition may be of Anderson type.

B. Thermoelectric power

The thermoelectric power (TEP) is another transport coefficient of interest that can provide information on the sign of the conduction carriers, the electronic band structure, and the transport mechanism in these oxides. However, despite considerable experimental efforts, the thermoelectric power remains poorly understood in the cuprates [see review article (Ref. 13)]. The experimental re-

sults varied in both magnitude and sign from one laboratory to another. Some authors reported positive TEP from 300 K down to transition temperature,[14,15] while others presented negative TEP in the same temperature range.[16,17]

In Fig. 5, we have shown the temperature dependence of TEP of several samples in the doped Bi 2:2:0:1 system which can represent the change from insulator to overdoped nonsuperconducting metal. The measured temperature range is within 80–270 K. The TEP of the insulating sample $Bi_{2.1}Sr_{1.3}La_{0.6}CuO_y$ is positive with a large value. A broad peak at the temperature of about 200 K can be observed. The value of TEP decreases with increasing hole concentration, consistent with results of electrical-resistivity measurements exhibiting a gradual change from semiconducting to metallic type. The TEP value for the superconducting samples $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ ($x=0.1$ and 0.2) are several μV/K, which is similar to those of ordinary metals. In the measured temperature range, the TEP decreases with increasing temperature. It should be noted that the TEP of $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ ($x=0.1$) changes sign from positive to negative at about 150 K. Furthermore, the TEP for the overdoped nonsuperconducting metal $Bi_{1.7}Pb_{0.3}Sr_2CuO_y$ shows a more negative value. A similar sign change from positive to negative was also observed in the $YBa_2Cu_3O_{7-y}$ system with increasing oxygen content.[18]

Though a sign change in S is possible in a single-band picture, many authors have postulated a two-conduction-band model to explain the experimental results.[19–21] Nearly all of them have adopted the picture that holes are in CuO_2 layers and electrons in the Cu-O chains in the $YBa_2Cu_3O_{7-y}$ system or in Bi-O or Tl-O layers in Bi- and Tl-based system, respectively. Such a two-band model may be consistent with results of band-structure calculations or measurements, but it is still unsatisfactory because many experiments have demonstrated that the Bi-O or Tl-O layers or Cu-O chains are insulating. We believe that the anomalous transport properties in the normal state of high-T_c cuprates are essentially associated with strong electron correlations in the CuO_2 layers. In analogy to the two-band model, here we propose another two-carrier model concerning the O $2p$ holes and Cu $3d_{x^2-y^2}$ electrons in the CuO_2 layers to explain the above results. The total carrier diffusion TEP is contributed from both the O $2p$ holes and Cu $3d_{x^2-y^2}$ electrons. It is well known that, for the p-type cuprates, in the low-carrier-concentration region in the phase diagram, the Cu $3d_{x^2-y^2}$ electrons are highly localized with a antiferromagnetic spin correlation due to the large on-site Coulomb repulsion energy U. The conduction is dominated by the O $2p$ holes which may also be localized at very small concentrations. Thus, the TEP may be mainly contributed to by the holes with O $2p$ character and has a large positive value in this localized insulating region. With increasing number of dopant O $2p$ holes, the effective Coulomb repulsion energy is somewhat decreased due to the increasing screening effect, the Cu $3d_{x^2-y^2}$ electrons may become gradually delocalized so that they may contribute to conduction. In the overdoped region, the itinerant Cu $3d_{x^2-y^2}$ electrons may play an important role in the transport mechanism and thus result in a negative TEP. One must be careful that the sign of TEP is not determined only by the sign of the carriers. The complex transport mechanism and the shape of the Fermi surface always complicates the problem. The superconducting region is just between the two extreme cases, and shows a more complicated situation. In this way, we have explained qualitatively the trend from positive towards negative S observed in the experiments.

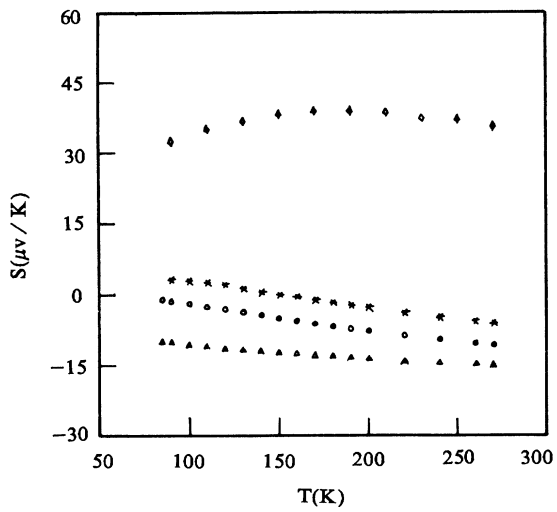

FIG. 5. Temperature dependence of TEP for $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ (◇, $x=0.6$; *, $x=0.2$; ○, $x=0.1$) and $Bi_{1.7}Pb_{0.3}Sr_2CuO_y$ (△) samples.

Generally speaking the carrier diffusion TEP has the form

$$S=\frac{\pi^2k_B^2T}{3e}\frac{\partial \ln\sigma(E)}{\partial E}\bigg|_{E=\mu_F},$$

where $\sigma(E)$ is the energy-dependent conductivity. For the free-electron gas, this reduced to $S\sim(\pi^2k_B^2/3\mu_E e)T$, yielding the familiar linear temperature dependence. However, such a linear temperature dependence cannot fit well with the experimental results in the measured temperature range. The phonon-drag component $S=1/T$ may also be present, but it should be less important in such a relatively higher temperature. We speculate that the strong coupling of O $2p$ holes and the Cu $3d_{x^2-y^2}$ spin system in the superconducting region as well as the complicated shape of the Fermi surface make it very difficult to wholly understand the temperature-dependent TEP of this superconducting system.

C. Hall coefficient

The Hall coefficients of three samples corresponding to different doping levels are shown in Fig. 6. A sample with the composition $Bi_{2.1}Sr_{1.6}La_{0.3}CuO_y$, sample A,

shows metallic behavior at temperatures higher than 50 K, but a semiconductorlike behavior at $T < 50$ K in its resistivity vs T curve with a sharp drop near 10 K due to superconducting transition. So sample A is in the region near the M-I transition. $Bi_{2.1}Sr_{1.3}La_{0.1}CuO_y$, sample B, is a superconductor with a linear temperature-dependent resistivity in its normal state. Whereas $Bi_{1.7}Ph_{0.3}Sr_2CuO_y$, sample C, is a nonsuperconducting metallic sample which is in the overdoped region. From Fig. 6, we see that the Hall coefficient decreases with increasing doping level. The R_H's for sample A and B are similar to those reported,[22] but the R_H for the overdoped sample C is of order 10^{-4} cm^3/C, which is almost smaller by an order of magnitude compared with other superconducting materials. This undoubtedly demonstrates that the number of mobile carriers increases with increasing doping level. In addition, the 2:2:0:1 compounds exhibit a weaker temperature dependence in R_H. Only the superconducting sample with an optimum composition shows a trend of R_H decreasing with increasing temperature. The decrease in R_H at low temperatures for samples A and B are due to the superconducting transition. Whereas, the samples either in the low-doping region (sample A) or in the overdoped region (sample C) exhibit a temperature-independent R_H. These property changes as a function of doping are similar to those of other high-T_c systems, such as $La_{2-x}Sr_xCuO_4$ and $Tl_2Ba_2CuO_6+y$ systems.[3,4] From studying the Hall effect in Ni- and Co-doped 1:2:3 compounds, Ni-doped $La_{2-x}Sr_xCuO_4$ and other materials, Clayhold[23] proposed that the temperature dependence of R_H was correlated with the occurrence of superconductivity. The T dependence of R_H is suppressed whenever T_c is reduced by chemical doping. Our experimental results appear to support this view. Another point we should emphasize is that, although the TEP shows a sign change from positive to negative with increasing hole concentration, the Hall coefficient never goes negative. This is very different from the behavior of the La system, in which R_H becomes negative for $x > 0.3$.

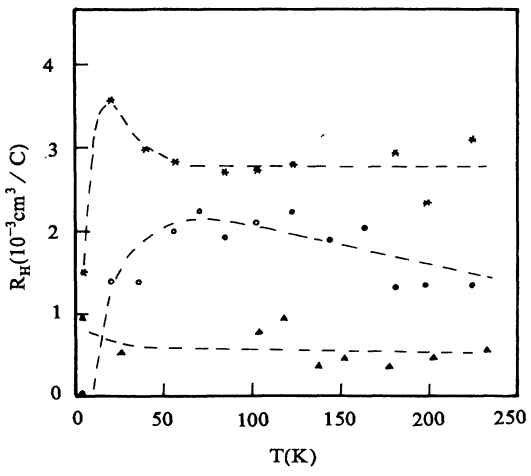

FIG. 6. Temperature dependence of R_H for $Bi_{2.1}Sr_{1.6}La_{0.3}CuO_y$ (A), $Bi_{2.1}Sr_{1.8}La_{0.1}CuO_y$ (B), and $Bi_{1.7}Pb_{0.3}Sr_2CuO_y$ (C) samples. The dashed lines are a guide to the eyes.

Usually a rapid decrease of R_H with increasing hole concentration is taken as signature of the tendency toward a Fermi-liquid-like state. But the question is to what extent the electronic states of the carriers in the CuO_2 layers have been developed as the system undergoes a change from superconducting to nonsuperconducting metal. Adopting the two-carrier model mentioned above, the change of R_H is indeed consistent with the picture in which the Cu $3d_{x^2-y^2}$ electrons become gradually delocalized with an increasing number of dopant O $2p$ holes. However, because R_H remains positive, we conclude that the Cu $d_{x^2-y^2}$ electrons are not fully delocalized even in such an overdoped region in the phase diagram. If the Cu d electrons were fully delocalized, the system would be nearly a half-filled-band metal, so that these electrons should dominate the transport properties and drive the Hall coefficient negative. In other words, electron-correlation effects are not negligible in the overdoped compound.

IV. CONCLUSION

We have prepared a number of $Bi_{2.1}Sr_{1.9-x}La_xCuO_y$ and $Bi_{2-x}Pb_xSr_2CuO_3$ samples with varying x and performed x-ray diffraction, transmission electron microscopy, electrical resistivity, thermoelectric power, and Hall measurements on these samples. The normal-state resistivity of these samples shows that the La- and Pb-doped Bi 2:2:0:1 systems span the whole insulator–superconductor–nonsuperconducting-metal transition. The metal-insulator transition is observed in La-doped compounds with $x = 0.4$. In the insulating samples with $x > 0.4$, the conduction may follow a 2D VRH, whereas for those with $x = 0.4$, it is 3D VRH in nature. On the other hand, when Pb is introduced into 2:2:0:1 compounds, it changes from a superconducting to overdoped nonsuperconducting metal. The resistivity changes from a linear temperature dependence to a power-law temperature dependence with exponent $n \sim 1.5$. This $n \sim 1.5$ behavior persists over a wide temperature range (from low temperatures to room temperature in our experiment). This is difficult to interpret on the basis of ordinary-Fermi-liquid theory. TEP measurements demonstrate that, accompanied by the gradual transition from insulator towards overdoped metal, the value of TEP decreases and becomes negative. Hall-effect measurements indicate that R_H also decreases with increasing doping but is never negative. In addition, the temperature dependence of R_H is weaker in 2:2:0:1 compounds. The R_H for samples near the M-I transition region as well as in the overdoped region is nearly temperature independent. We explain these experimental results on the basis of a two-carrier model which assumes that the Cu $3d_{x^2-y^2}$ electrons undergo a change from localized state to a partially delocalized state with increasing

number of dopant O $2p$ holes. Such a partially localized state (or, equivalently, a partially delocalized state) of Cu electrons and also the interaction between them and the O $2p$ hole state in the CuO_2 layers are very difficult to treat theoretically, which may hinder a fuller understanding of the high-T_c mechanism.

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