Thermoelectric power of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ and $Pr_{1.85}Ce_{0.15}CuO_{4-y}$

Z. S. Lim
Physics Division, Research Institute of Industrial Science and Technology, Pohang, 790-330, Korea

K. H. Han
Department of Physics, Pohang Institute of Science and Technology, Pohang, 790-330, Korea

Sung-Ik Lee, Yoon H. Jeong, and S. H. Salk
Department of Physics, Pohang Institute of Science and Technology, Pohang, 790-330, Korea and Physics Division, Research Institute of Industrial Science and Technology, Pohang, 790-330, Korea

Y. S. Song and Y. W. Park
Department of Physics, Seoul National University, Seoul, 151-742, Korea
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The temperature dependence of the thermoelectric power (TEP) for $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ and $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ is reported. The key features of the present measurements are as follows: (1) the signs of TEP for both samples are positive, in contrast to the previous results; (2) the TEP for both samples remains flat in the normal state below 250 K but decreases rapidly above 250 K; (3) the TEP of only $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ shows a peak near 50 K; (4) and, finally, the onset temperatures of the sudden drop of TEP are higher than those of the resistance drop.

Despite the unprecedented research activity after the discovery of the high-T_c superconducting ceramics, a proper understanding of the superconducting mechanism in these materials is still lacking. Most of the high-T_c materials discovered thus far contain Cu-O pyramids or octahedra in their structures, and the majority charge carriers are known to be holelike.[1-7] Among the numerous theories to explain the superconductivity, there exists some that may not even hold if the charge carriers are electrons.[8] In view of the present situation with no convincing theories, the recent discovery of the new class of oxide superconductors $L_{1.85}Ce_{0.15}CuO_{4-y}$ (L stands for Pr, Nd, Sm) (Ref. 9) is of great significance in the sense that these new materials could provide an important clue for reaching the correct theory. These materials have Nd_2CuO_4 (T'-phase) structures[9] and do not contain Cu-O pyramids or octahedra but contain only sheets of Cu-O squares. More importantly, these materials are claimed to be n-type, based on the fact that the Hall coefficient and the thermoelectric power (TEP) are negative.[9,10] Considering the impact of n-type superconductors on theory, it is quite important to test the consistency of n-type superconductivity with as many experimental data as possible.

In this paper we report the TEP measurements of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ and $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ as a function of temperature. The TEP is a powerful probe to study the electronic properties of conductors such as sign of charge carriers, carrier concentration, and carrier-phonon coupling, provided that the experimental result is properly interpreted. The TEP of $Nd_{2-x}Ce_xCuO_4$ has been briefly studied by Takagi and co-workers[9] and Uji, Aoki, and Matsumoto.[10] Their measurements showed the negative TEP and these results were cited along with the negative Hall coefficient to support n-type superconductivity. Contrary to their results, we discovered that the signs of the TEP for both samples are *positive*.

The superconducting materials $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ and $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ were prepared by solid-state reaction. In this method samples were quickly prepared by calcining a mixture of the constituent oxides (CeO_2, Pr_6O_{11}, Nd_2O_3, CuO) in air at 950 °C. Then the powder was pressed into pellets and sintered at temperatures of 1150 °C in air atmosphere for 12 h. These pellets were quenched to room temperature. The pellets were then annealed at 1000 °C inside the Ar atmosphere for 10 h and quenched to room temperature in the same atmosphere. To obtain the superconducting samples, oxygen deficiency is essential. Since annealing is achieved at high temperatures, a large amount of oxygen in the samples is liberated. To maintain the oxygen deficiency, we blocked the oxygen recombination with samples by quenching in Ar atmosphere. Investigation of chemical homogeneity using electron probe microanalysis (EPMA) has shown that the samples show quite homogeneous phase identity. Hereafter, we will call $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ ($Pr_{1.85}Ce_{0.15}CuO_{4-y}$) as Nd (Pr).

Hall coefficients at room temperature were measured by the low-frequency ac five-probe method using a lock-in amplifier. Our preliminary results show that the signs of Hall coefficients for Nd and Pr samples are negative consistent with the result of Tokura, Takagi, and Uchida.[9] The magnitudes are almost the same as those of Tokura, Takagi, and Uchida. Complete measurements as a function of temperature are in progress.

In Fig. 1, the temperature dependence of resistivities for Nd and Pr measured by the standard four-probe method is shown. While the resistivity of Pr above the onset temperature shows a semiconducting tendency, that of Nd remains relatively flat. For Nd, the resistivity drops near 24 K, but it does not go to zero at the lowest temperature

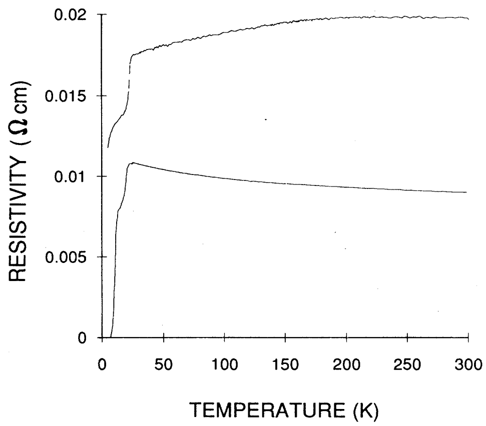

FIG. 1. Electrical resistivity of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (upper) and $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ (lower).

measured (4 K). Incomplete oxygen deficiency may be the prime reason for this particular Nd sample not having a complete zero resistance.[9] For Pr, the onset temperature of resistivity drop is 23 K and temperature of complete zero resistivity is 7 K. This onset temperature of 23 K is higher than the 17 K Tokura, Takagi, and Uchida obtained by susceptibility measurements.

In Fig. 2 we have plotted the results of the TEP measurements of Nd and Pr in the temperature range from 10 to 300 K. For the TEP measurements, samples were cut into pieces with dimensions $2\times1\times5$ mm^3. A sample was mounted on top of two copper blocks with silver paint. One of the copper blocks was heated by a nichrome wire to make temperature gradient across the sample. The temperature difference was monitored by a copper-constantan thermocouple and 50-μm gold wires were attached to the end of the sample to measure the thermal emf. Compared to the published TEP data of Y-Ba-Cu-O and La-Sr(Ba)-Cu-O which are in the range of 1 μV/K to several hundred μV/K, the TEP's of our samples are relatively small (less than 1 μV/K). For this small TEP, lead corrections were essential. Accuracy of our measurements is estimated to be about 0.1 μV/K.

The most evident feature in Fig. 2 is that the sign of TEP for both Nd and Pr is positive in contrast to the negative TEP results of the previous studies.[9,10] Another contrasting observation is that our TEP's show rapid decrease as the temperature increases above 250 K whereas that of Takagi, Uchida, and Tokura's Nd sample is almost temperature independent between 80 and 300 K. Although the different signs of TEP seem perplexing, this may indicate the presence of more than one type of charge carrier. Similar effects were also observed in the Y-Ba-Cu-O system. While most of the previous studies[1-7] showed the positive TEP in Y-Ba-Cu-O, there also exist some TEP measurements[11-13] which show the negative sign. Therefore extreme care must be exercised in determining the carrier type from the TEP measurements.

The flat nature of TEP is often found in Y-Ba-Cu-O as well as La-Sr(Ba)-Cu-O, and the same behavior is seen for Nd and Pr below 250 K. This flat nature is explained

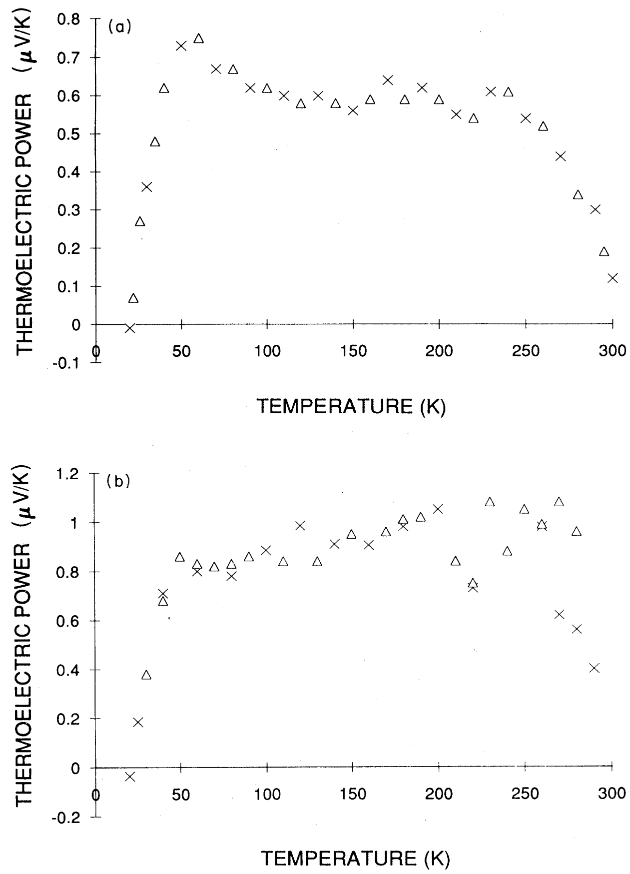

FIG. 2. Temperature dependence of thermoelectric power of (a) $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ and (b) $Nd_{1.85}Ce_{0.15}CuO_{4-y}$. Triangles (crosses) are measured while sample is warming (cooling).

by neither the diffusion mechanism of the carriers nor the phonon drag effect.[1,5,11,14] In Y-Ba-Cu-O and La-Sr(Ba)-Cu-O, some other mechanisms such as the magnon drag effect,[15] the variable range hopping,[16] the Coulomb-correlated hopping in the Hubbard model, and the combination effect of semiconductor and metal[6] were suggested. More work should be done to understand the behavior.

The rapid decrease of TEP above 250 K in Pr should be noted. Due to the rapid decrease of TEP, there might be a chance that TEP crosses over zero at some high temperature and becomes negative. TEP measurements at higher temperatures are currently under way to check this possibility.

Of particular interest in Fig. 2 is the appearance of a peak near 50 K only in Pr. The origin of this peak is not precisely known at this time, but probably related to the oxygen contents of samples. Similar peaks are also seen in the TEP measurements of Y-Ba-Cu-O.[2,5,7,15] Kang *et al.*,[15] for instance, investigated the behavior of the peak in the TEP of Y-Ba-Cu-O. They observed that the position and the shape of the peak strongly depended on the oxygen deficiency.

One final point worth mentioning is the fact that the onset temperatures of TEP drops are higher than those of the resistance drops. A possible explanation might be as follows. Since these materials are granular, one expects high electrical resistances between grains. On the other hand, the temperature drops between grains are expected to be small and consequently, the granular nature would have less effect on TEP than the electrical resistivity.

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