Thermal Conductivity of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ Single Crystals and Signatures of Stripes in an Electron-Doped Cuprate

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It was recently demonstrated that the anisotropic phonon heat transport behavior is a good probe of the stripe formation in $La_{2-x}Sr_xCuO_4$ (LSCO) [X. F. Sun *et al.*, Phys. Rev. B **67**, 104503 (2003)]. Using this probe, we examined an electron-doped cuprate $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (PLCCO) and found that essentially the same features as those in LSCO are observed. Moreover, the in-plane resistivity ρ_{ab} of lightly doped PLCCO shows metallic behavior ($d\rho_{ab}/dT > 0$) in the Néel ordered state with a mobility comparable to that in LSCO. It is discussed that these peculiar properties in common with LSCO signify the existence of stripes in electron-doped cuprates.

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High-T_c superconductivity shows up when either holes or electrons are doped to parent Mott-insulating cuprates. The essential features of the phase diagram, such as the Néel ordering in the lightly doped regime and superconductivity in the moderately doped regime, are approximately symmetric [1,2] for hole- and electron-doped sides, with the undoped Mott insulator sitting in the middle, and this leads to a key paradigm in the study of the high-T_c cuprates: the electron-hole symmetry. However, there are also disparities between the two sides, and understanding the similarities and differences between the hole- and electron-doped cuprates would be crucial for elucidating the fundamental nature of these materials. Of particular interest is whether the "stripes" [3] (a sort of quasi-one-dimensional charge/spin density wave) exist in the electron-doped cuprates [4], since such self-organized structures have been observed in the hole-doped cuprates [5] and are discussed to be relevant to the occurrence of superconductivity [3].

The most convincing evidence for the stripes in the hole-doped cuprates had been obtained by neutron scattering in the form of "incommensurate" superstructure peaks [6–9]; on the other hand, neutron scattering experiments on an electron-doped material $Nd_{2-x}Ce_xCuO_4$ (NCCO) found only commensurate magnetic peaks to coexist with the superconductivity [10]. Such commensurate peaks would naturally suggest that there is no superstructure in the spin system; however, if the stripes are "in-phase" domain boundaries of the spin system that leave strong commensurate peaks (as opposed to antiphase boundaries that give rise to only incommensurate peaks), the neutron data on NCCO can be consistent with such stripe structures [11]. Thus, it is still an open question whether the stripes exist in the electron-doped cuprates. Here we show that the transport properties of an electron-doped cuprate demonstrate peculiar features that are similar to those in the hole-doped cuprates, where such features [12,13] have been shown to be naturally understood as consequences of the stripe formation. Therefore, it is most likely that the stripes exist in electron-doped cuprates and that there is an approximate electron-hole symmetry not only for the occurrence of superconductivity but also for the stripe formation.

Recently, we demonstrated [13] that the c-axis phonon heat transport is a good probe of the stripe formation in lightly hole-doped $La_{2-x}Sr_xCuO_4$ (LSCO); namely, the spin stripes in this system are well ordered in the CuO_2 planes but are disordered along the c axis [8], which (perhaps through the strong spin-lattice coupling [14]) causes the c-axis phonons to be strongly scattered. We also demonstrated [12] that the in-plane resistivity ρ_{ab} of lightly doped LSCO crystals shows metallic behavior ($d\rho_{ab}/dT > 0$) even in the long-range-ordered Néel state, where the hole mobility is virtually the same as that in optimally doped samples; such an unusual metallic behavior can naturally be understood if doped holes form self-organized "rivers" whose distance changes with doping [12,15]. Taking these features as signatures of stripes, we set out to examine the transport properties of the $(Pr, La)_{2-x}Ce_xCuO_4$ (PLCCO) system, for which Fujita *et al.* reported [16] that high-quality single crystals can be grown by the traveling-solvent floating-zone (TSFZ) technique. We choose the composition of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$, which is structurally stable in the lightly Ce-doped region [17].

High-quality $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ single crystals ($x =$ 0, 0.01, 0.03, 0.05, 0.08, 0.10, and 0.13) are grown by the TSFZ technique in flowing oxygen. The crystals are cut into rectangular platelets with a typical size of $2.5 \times 0.5 \times 0.1$ mm^3, where the c axis is perpendicular or parallel to the platelets within an accuracy of better than 1°. The ab-plane and c-axis thermal conductivities (κ_{ab} and κ_c) are measured by a steady-state technique [13]. Several samples are measured for each Ce concentration to check for the reproducibility, resulting in the uncertainties in the reported values of less than 10%. The standard ac four-probe method is employed to measure the resistivity [18]. Note that the properties of the electron-doped

cuprates are very sensitive to oxygen nonstoichiometry [19,20]; reduction annealing is necessary to remove excess (apical) oxygen from oxygenated (as-grown) crystals and to introduce electrons into the CuO_2 planes. For this work, to remove sufficient apical oxygens while creating only a small amount of oxygen vacancies in the reduced samples, we performed thermogravimetry analyses and settled on the annealing at 850–875 °C for 24 h under Ar gas flow [21]. With this condition, the difference in the oxygen content between the oxygenated and reduced samples (measured by the weight change after the Ar annealing) is rather small (for example, the difference is 0.1% for the $x = 0.05$ sample).

To begin with, let us discuss the temperature dependences of κ_{ab} and κ_c of undoped $Pr_{1.3}La_{0.7}CuO_4$ (PLCO) crystals shown in Fig. 1, where the data for La_2CuO_4 (LCO) [13] are also included for comparison. The LCO crystals exhibit a pronounced phonon peak at low temperature in both κ_{ab} and κ_c, while at high temperature close to the Néel temperature T_N ($\simeq$300 K) another peak appears in κ_{ab}, and this has been attributed to the magnon heat transport [13,22,23]. One can see that PLCO shows a much higher low-T peak in both κ_{ab} and κ_c, suggesting an intrinsically better phonon transport in PLCO [24]; also, these data testify the high-quality of our crystals. In the $\kappa_{ab}(T)$ data, one can further see that the magnon contribution to the heat transport is evident in PLCO, where the larger phonon contribution turns what was a clear peak in LCO into a hump; note that the position of this hump is consistent with T_N ($\simeq$260 K in Pr_2CuO_4 [25]). It is fair to note that this is not the first time a signature of the magnon heat transport in the so-called T' phase is observed, since a similar hump profile was reported for polycrystalline Pr_2CuO_4 samples [26]. However, only by using single crystals can one confirm that the hump appears only in the ab plane, which is essential for attributing this hump to the magnons in two-dimensional (2D) spin systems.

Figure 2 shows how $\kappa_{ab}(T)$ and $\kappa_c(T)$ of PLCCO change with doping. With increasing x, the high-T hump in κ_{ab} becomes weaker and almost disappears at $x = 0.05$ [which can be better seen in the inset of Fig. 2(a)], even though the Néel temperature shows just a weak x dependence up to $x = 0.08$ in PLCCO [16]. This behavior is somewhat similar to that in LSCO, where the magnon peak is completely suppressed with only 1% Sr doping, for which T_N is still as high as 240 K [13].

The main finding in Fig. 2 is that the low-T phonon peak shows very anisotropic evolution upon electron doping; namely, the low-T peak of κ_c is dramatically suppressed with slight Ce doping, while the doping effect on κ_{ab} is much more modest. The inset of Fig. 2(b) shows a plot of the x dependence of the peak height relative to that of $x = 0$; here, similar data for LSCO [13] are also shown. One can see that the drastic suppression of the c-axis phonon peak upon slight carrier doping is common to LSCO and PLCCO. Note that the contribution of electronic heat transport is negligibly small at low temperatures in these insulating crystals [13], so the doping

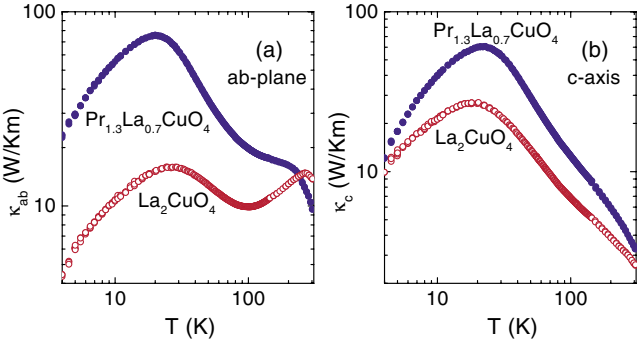

FIG. 1 (color online). Thermal conductivity of parent cuprates $Pr_{1.3}La_{0.7}CuO_4$ and La_2CuO_4 (taken from Ref. [13]) along (a) the ab plane and (b) the c axis.

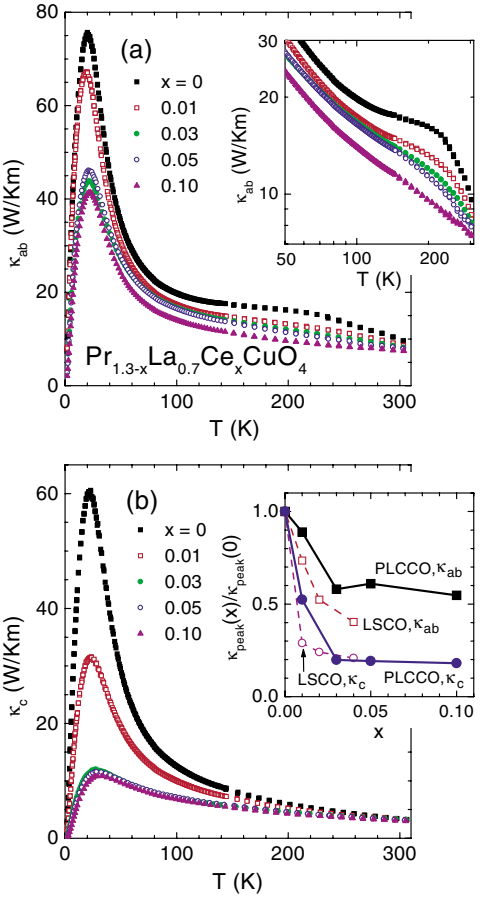

FIG. 2 (color online). Thermal conductivity of reduced single crystals of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ along (a) the ab plane and (b) the c axis. Insets: (a) $\kappa_{ab}(T)$ data near the high-T hump in a log-log plot. (b) Doping dependences of the peak values of κ_{ab} and κ_c, normalized by the values at $x = 0$, for PLCCO and LSCO (data for LSCO are taken from Ref. [13]).

dependence in the low-T heat transport is solely due to some doping-induced scattering of phonons.

There are several possibilities for this strong doping-induced phonon scattering, such as the usual impurity-phonon scattering, electron-phonon scattering, and local structural distortions induced by ion substitutions. For PLCCO, thanks to the peculiar role of oxygen nonstoichiometry [16,19], a good way to clarify the phonon scattering mechanism is to compare the behavior of the reduced crystals to that of oxygenated ones, where the charge carrier density in the CuO_2 planes is depleted [20].

Figure 3 shows such a comparison for $x = 0$ and 0.05 crystals, which gives us useful pieces of information: First, it is clear that the removal of oxygen little changes the low-T phonon heat transport in undoped crystals [Figs. 3 and 3(b)], which implies that the apical oxygen and/or the oxygen vacancies [19] scarcely scatter phonons in both the ab-plane and the c-axis directions. Second, the peak height in $\kappa_{ab}(T)$ for $x = 0.05$ shows no difference between the oxygenated and reduced samples [Fig. 3(c)], which suggests that it is the structural distortion due to the Ce doping, rather than the charge carriers, that is mainly responsible for the scattering of the in-plane phonons and for the ~40% damping of the κ_{ab} peak compared to $x = 0$; this structural distortion seems to scatter phonons isotropically, because the κ_c peak of the oxygenated samples is also reduced by ~40% with 0.05 Ce doping [see Figs. 3(b) and 3(d)]. Third, the dramatic

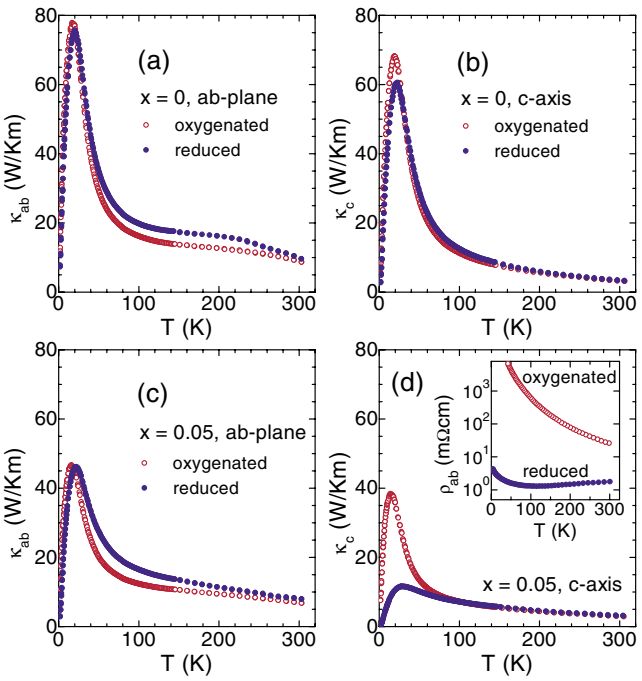

FIG. 3 (color online). Comparison of the thermal conductivity of oxygenated and reduced $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ single crystals for (a),(b) $x = 0$ and (c),(d) $x = 0.05$. Inset of panel (d) shows $\rho_{ab}(T)$ data of oxygenated and reduced samples for $x = 0.05$.

suppression of the phonon peak in κ_c with Ce doping is observed only in the reduced sample, which means that the strong phonon scattering is definitely related to the electrons in the CuO_2 planes, even though the electrons have little c-axis dispersion and are not normally expected to scatter c-axis phonons significantly. [The inset of Fig. 3(d) shows a comparison of $\rho_{ab}(T)$ for oxygenated and reduced $x = 0.05$ samples, which demonstrates how starkly the mobile carrier density changes upon reduction.]

As was discussed in Ref. [13] for the case of LSCO, the lattice distortions induced by the stripes can naturally provide the anisotropic phonon scatterings, when the stripes are well ordered in the planes but are disordered along the c axis (which is actually the case for the spin stripes in LSCO [8]). Given the striking similarities in the suppression of the κ_c peak between LSCO and PLCCO [and also the additional evidence in Fig. 3(d) that the strong phonon damping must be related to the doped electrons], it is most reasonable to conclude that the peculiar thermal conductivity behavior in PLCCO is due to the stripes that have been previously undetected, and the data suggest that the stripes are not established for $x < 0.03$. As mentioned in the introduction, since the neutron scattering has found commensurate magnetic peaks for NCCO [10], the stripes that are to be formed in the electron-doped cuprates should be in-phase antiferromagnetic domain boundaries, which do not frustrate the spin periodicity and are benign to the Néel order. We note that existence of the in-phase stripes has been suggested for the weak-ferromagnetic state of LSCO at $x = 0.01$ under a high magnetic field [18], not to mention the theoretical predictions for them in the literature [27].

It is useful to note that some of the unusual features recently found in NCCO might be related to the anomalous thermal conductivity behavior: An optical phonon at ~70 meV was found to soften upon slight Ce doping [28], and rather mysterious 2D superlattice structure was observed when NCCO ($x = 0.15$) was reduced [29]. While it is possible that these features are also coming from some form of spin/charge texture, much remains to be sorted out about the exact roles of Ce doping and reduction in electron-doped cuprates.

In passing, we note that Hess *et al.* recently argued [30] that the scattering by soft phonons associated with the lattice instability of the low-temperature-orthorhombic (LTO) phase, rather than the scattering by stripes, is the source of the damping of the phonon peak in LSCO. However, this picture clearly falls short in explaining the drastic suppression of the κ_c peak in the *lightly doped* LSCO, where the LTO-transition temperature does not change much from La_2CuO_4 [2]. Furthermore, PLCCO has no LTO instability (this system is tetragonal irrespective of Ce doping and temperature) and yet shows the anomalous damping of the phonon peak, which gives another good reason to dismiss the soft phonon scenario.

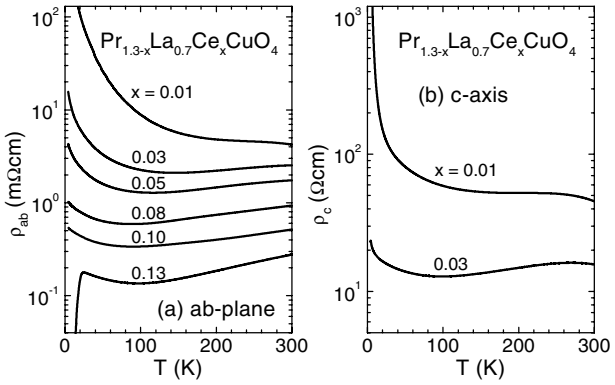

FIG. 4. (a) Temperature dependences of ρ_{ab} of the reduced single crystals of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ ($x = 0.01$–0.13) that are Ar annealed at 850–875 °C. (b) Temperature dependences of ρ_c of the reduced single crystals at $x = 0.01$ and 0.03.

The temperature dependences of ρ_{ab} are shown in Fig. 4(a) for $x = 0.01$–0.13. It is intriguing to see that the $x = 0.01$ sample is weakly insulating ($d\rho_{ab}/dT < 0$) at room temperature, while the $x = 0.03$ sample shows a metallic behavior; this seems to be correlated with the behavior of κ_c, where the anomalous damping of the low-T peak saturates above $x = 0.03$, and suggests that the metallic behavior in ρ_{ab} is also due to the stripe formation. As was discussed for LSCO, observation of a metallic in-plane transport in the long-range Néel ordered state (T_N should be around 200 K at $x = 0.03$–0.08 in PLCCO [16]) is anomalous [15], and it is even more peculiar that the hole mobility in the Néel state is similar to that at optimum doping [12]. It was proposed that the self-organization of charges into stripes gives a plausible picture to understand this doubly unusual metallic behavior in the Néel state [12,15]; apparently, the same discussion is applicable to the lightly electron-doped PLCCO, where the electron mobility is calculated to be around 5 $cm^2/V\,s$ at 300 K, which is surprisingly similar to that in LSCO and is suggestive of the transport mechanism being the same. Therefore, the ρ_{ab} data give additional support to the conjecture that the stripes are formed in PLCCO at $x \geq 0.03$. Intriguingly, the temperature dependence of the c-axis resistivity (ρ_c) also shows a qualitative change between $x = 0.01$ and 0.03 [Fig. 4(b)].

In summary, two peculiar features in the transport properties, which are considered to signify the existence of stripes in the lightly hole-doped LSCO, are both observed in the lightly electron-doped PLCCO: anomalous damping of the c-axis phonons and the "high mobility" metallic transport in the Néel ordered state. A natural conclusion of these observations is that the stripes are formed not only in the hole-doped cuprates but also in the electron-doped cuprates. Thus, there seems to be an approximate electron-hole symmetry for the stripe formation, though the detailed structure of the stripes is likely to be different.

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