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Influence of the pseudogap on the thermal conductivity and the Lorenz number of $YBa_2Cu_3O_x$ above T_c

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Systematic and detailed experimental data for the *a*-axis thermal conductivity $\kappa_a(T,x)$ of $YBa_2Cu_3O_x$ with $6.13 \leqslant x \leqslant 6.98$ are compared with the electrical resistivity $\rho_a(T,x)$ up to $T=300$ K. For wide ranges of T and x the overall behavior of $\kappa_a(T,x)$ follows that of $L_0T/\rho_a(T,x)$ (where $L_0=2.45\times10^{-8}$ W Ω K^{-2} is the standard value of the electronic Lorenz number L). This shows that the pseudogap causes an increase in $\kappa_a(T)$, comparable to that in $L_0T/\rho_a(T,x)$. A model calculation, in which a triangular pseudogap in the electron density of states causes a novel enhancement of L/L_0, is also compared with the data.

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The normal-state gap or pseudogap (PG) has been observed in most hole-doped high-T_c superconductors by various experiments,[1,2] but there is no consensus as to its origin, nor that of the superconducting pairing mechanism, although they may well be closely related. The PG is observed as a downward deviation from linear-T dependence in the in-plane resistivity $\rho(T)$ (Ref. 3) but experimental evidence for its effect on the thermal conductivity κ is contradictory, partly because it is difficult to separate the electron (κ^{el}) and phonon (κ^{ph}) contributions to κ and determine the electronic Lorenz number $L=\kappa^{el}\rho/T$. In Ref. 4 a strong increase in $\kappa(T)/\kappa(300)$ below 200 K for twinned $YBa_2Cu_3O_x$ crystals with $x=6.44$ to $x=6.77$ was ascribed to the spin gap, but in Ref. 5, κ^{el} of $YBa_2Cu_3O_{6.68}$ shows little T dependence, while ρ falls, giving a *decrease* in L below 190 K. This last result is more consistent with a claim[6] that L can fall to zero at very low T because of the breakdown of Fermi-liquid theory. In Ref. 7, L was found to be equal to the standard value, $L_0=2.45\times10^{-8}$ WΩ K^{-2} for $x\approx7.0$ and $T_c<T<200$ K, with both ρ_a and $\rho_b\sim T^1$.[7] However our analysis of more recent resistivity data[8] gives $\rho_{chain}\sim T^2$. In an effort to clarify these questions and to minimize the influence of the Cu-O chains, we have measured the *a*-axis thermal conductivity $\kappa_a(T)$ and $\rho_a(T)$ of detwinned $YBa_2Cu_3O_x$ crystals for many closely spaced values of x.

Single crystals of $YBa_2Cu_3O_x$ were grown by a self-flux method using a $BaZrO_3$ crucible[9] and were detwinned at Oxford by annealing under a uniaxial stress of 120 N/mm^2 at 300 °C in flowing oxygen for 8 h. A detwinned crystal was then cut into several pieces using a 15-μm-diameter wire saw and etched with 2% Br in ethanol. A single sample ($0.96\times0.24\times0.04$ mm^3 in *a*, *b*, and *c* directions, respectively) was used for the superconducting compositions. The oxygen content was decreased in small steps from $x=6.93$ to 6.38 by changing the annealing conditions,[10] and finally increased to $x=6.98$. Annealing was done without applying uniaxial stress, but the absence of twinning was always checked using a polarizing optical microscope.[11] Another crystal was used without detwinning to measure $\kappa(T)$ for the nonsuperconducting compositions, $x=6.13$–6.30, where the crystal structure is tetragonal and twinning is absent. A modified steady-state method that minimizes the effect of radiation losses, was used to measure $\kappa(T)$ (Ref. 12) as sketched in the inset of Fig. 1. A single crystal is mounted between two constantan wires (C) of diameter 125 μm, which act as heat links to the sapphire platforms (S) holding the heaters and thermometers. The heat flow in and out of the crystal is determined from the thermoelectric voltages across the heat links, and the known $\kappa(T)$ of constantan.[13] The temperature gradient along the crystal was measured using a small differential thermocouple (D). It was attached to an *a-c* face of crystal, because if it is on an *a-b* face, some layers can be torn off the surface when it is removed. Both positions gave the same results for $\kappa_a(T)$ within the relative experimental error of ±3%. After each annealing step, the crystal was etched with 2% Br in ethanol for a few minutes, the absence of twinning was checked, dimensions measured, and the

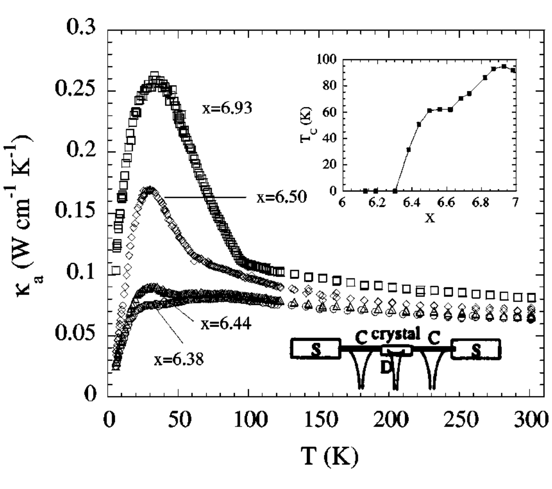

FIG. 1. Temperature dependence of the *a*-axis thermal conductivity $\kappa_a(T,x)$ of detwinned $YBa_2Cu_3O_x$ for $x=6.93$, 6.50, 6.44, and 6.38. The upper inset shows T_c vs x determined from the kink in $\kappa_a(T)$ and the lower one a sketch of the method used for thermal-conductivity measurement.

thermocouples were attached using Dupont 6838 epoxy. Then, after measurement of $\kappa_a(T)$, the thermocouples and silver paint were removed using a new blade, and the crystal was etched again before the next annealing treatment. Resistivity measurements were performed using the Montgomery method[14] on other pieces of the same crystal annealed simultaneously.

Figure 1 shows examples of the *a*-axis thermal conductivity $\kappa_a(T,x)$ of detwinned $YBa_2Cu_3O_x$ at $x=6.93$, 6.50, 6.44, and 6.38 from 6 to 300 K. For clarity not all our data are shown here. For $x=6.98$ to 6.50, $\kappa_a(T)$ increases gradually as T approaches T_c, but for $x=6.44$ and 6.38, $\kappa_a(T)$ has a weak maximum above T_c at $T=80$ K. The peak in $\kappa_a(T)$ near 30 K is observed for all superconducting compositions, but it suddenly becomes very small between $x=6.50$ and 6.44 where there are also drastic changes in the normal state.

For all superconducting compositions, there is a clear kink in $\kappa_a(T)$ at T_c. The values of x were obtained from the annealing conditions using published data[10] and previous work in our laboratory. The resulting $T_c(x)$ curve shown in the inset to Fig. 1, agrees reasonably with Ref. 15, where changes in x were obtained from the weight loss of a polycrystalline sample, but we did not attain such low values of T_c on the overdoped side. For the same values of T_c our $\rho_a(T)$ data agree with those in Ref. 8, but our x values are all $\simeq 0.12$ smaller. We have used some of the data in Ref. 8 for comparison with our $\kappa_a(T)$ results, because of technical problems with the Montgomery method between $x=6.56$ and 6.38.[16]

Figure 2(a) compares $\kappa_a(T)$ in the normal state with $L_0T/\rho_a(T)$ for many values of x. For $x=6.93$ the flat T dependence of $L_0T/\rho_a(T)$ confirms that $\rho_a(T)\propto T^1$; here the difference between $\kappa_a(T)$ and $L_0T/\rho_a(T)$ near T_c is caused by superconducting fluctuations and will be discussed elsewhere. The strong increase in $L_0T/\rho_a(T)$ below 150 K for $x\sim 6.5$ arises from the well-known effect of the PG on $\rho_a(T)$. However for lower values of x, $\rho_a(T)$ rapidly becomes larger and less T dependent, so the $L_0T/\rho_a(T)$ curves for $x\geqslant 6.5$ and $x\leqslant 6.38$ are very different. The corresponding effect in $\kappa_a(T)$, i.e., the different behavior for $x\geqslant 6.5$ and $x\leqslant 6.44$, is clearly visible in the upper part of Fig. 2(a) and moreover the magnitudes of the changes in $\kappa_a(T)$ and $L_0T/\rho_a(T)$ are very similar. Hence we can conclude that the PG *does* increase $\kappa_a(T)$ and that $L/L_0\sim 1$.

However as discussed below, there is a strong possibility that the PG actually causes a T-dependent enhancement of L/L_0. In order to test this experimentally we need to know $\kappa^{ph}(x,T)$, which is limited by phonon-defect scattering at low T and phonon-phonon Umklapp scattering at higher T.[7] There are several optical phonon modes with appreciable dispersion, so the T dependence of $\kappa^{ph}(T)$ is not known *a priori*. The x dependence of $\kappa^{ph}(T)$ is also not known, it will depend on the phonon-defect scattering rate and over what range of x the O defects act as independent scattering centers. In this paper we consider the two scenarios, $L=L_0$ and $L>L_0$ on an equal footing, but note that they could be distinguished by similar experiments on Ca-doped $YBa_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_{8+x}$ crystals where the overdoped region is wider. The variation of $\kappa^{ph}(T)$ with x corresponding to $L=L_0$ is shown in the upper part of Fig. 2(b), while the lower part shows the behavior of $\kappa^{ph}(T)$ when $L=L_{PG}$. For $x=6.99,6.98$ and $x=6.93$, the PG is small and has little effect. The reproducibility of the data for the two crystals with $x=6.99$ and $x=6.98$ suggests that $\kappa^{ph}(T)$ is already substantially reduced by oxygen-defect scattering at $x=6.93$. This point, and the fact that taking $L=L_{PG}$ makes $\kappa^{ph}(T)$ similar for $x=6.73$ and $x=6.38$ and very flat, tend to favor the $L=L_{PG}$ scenario. Although discrimination between $L=L_0$ and $L\gtrsim L_0$ is difficult, there is absolutely no evidence for a very small value of L, such as that reported at low T.[6] Our analysis also implies that the unusual behavior of the Hall Lorenz number L_{xy} for $YBa_2Cu_3O_{6.95}$ crystals, $L_{xy}\propto T$ and $L_{xy}\approx 0.15L_0$ just above T_c,[17] does not arise from a low value of L_{xx} but that it must be connected with the anomalous Hall effect in the cuprates.

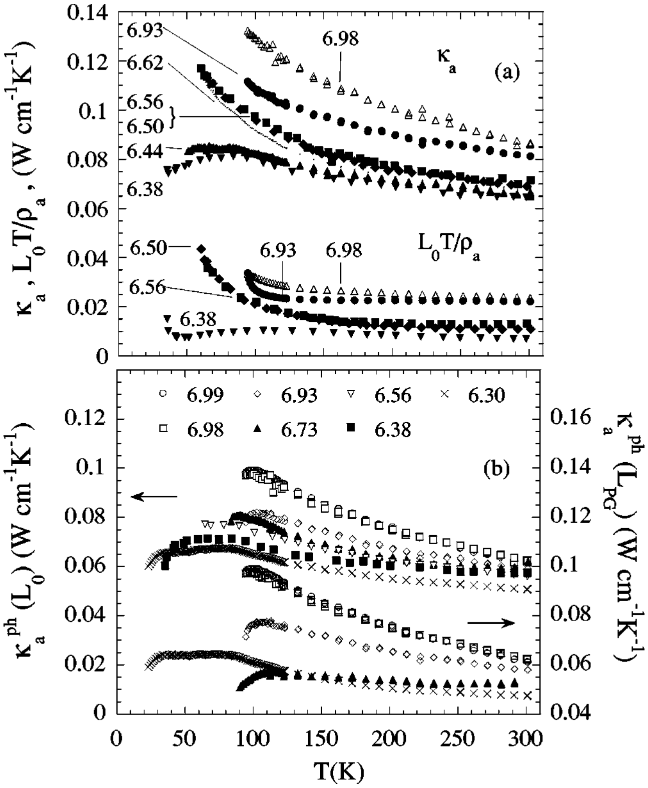

FIG. 2. (a) $\kappa_a(T)$ in the normal state for the x values shown, compared with $L_0T/\rho_a(T)$, where L_0 is the standard Lorenz number, 2.45×10^{-8} W Ω K^{-2}. Electrical resistivity data $\rho_a(T)$ from Ref. 8 are used for $x=6.38$, 6.50, 6.56 (in our notation, see Ref. 16), and our own data for $x=6.98$ and 6.93. (b) The upper plots show the difference κ_a-L_0T/ρ_a, denoted as $\kappa_a^{ph}(L_0)$, for the values of x shown, using our own $\rho_a(T)$ data for $x=6.99$, 6.98, 6.93, and 6.73, and those of Ref. 8 for lower values of x. The lower curves show $\kappa_a^{ph}(L_{PG})$ for the triangular PG model (see text).

In standard transport theory for a Fermi liquid, $L\leqslant L_0$ because small-angle inelastic scattering processes reduce κ_a^{el} without affecting $1/\rho_a$.[18] So for a reasonably conventional picture of the cuprates, for example, the nearly antiferromagnetic Fermi liquid, our results point towards the predominance of large-angle processes over a wide range of T and x,

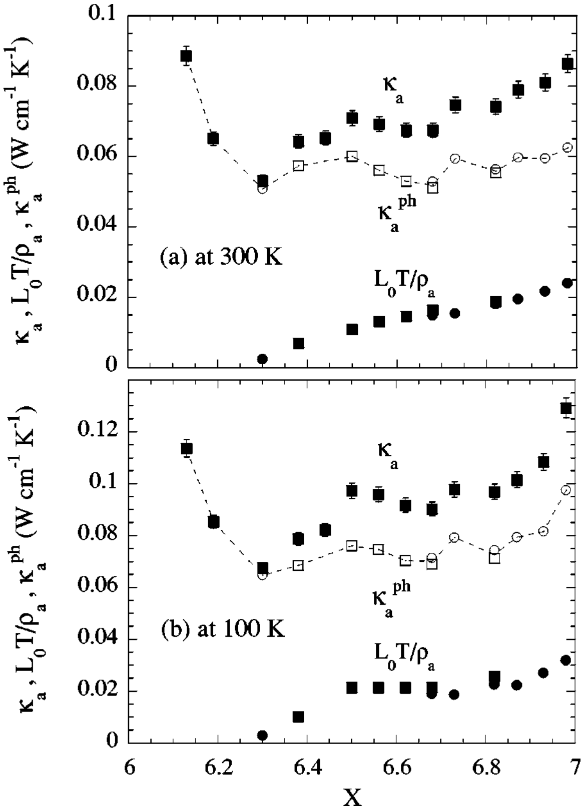

FIG. 3. κ_a, L_0T/ρ_a, and $\kappa_a^{\rm ph}$ ($\equiv \kappa_a - L_0T/\rho_a$) vs x at (a) $T = 300$ K and (b) $T=100$ K. Solid squares show $\rho_a(T)$ data from Ref. 8 for $x=6.38$ to 6.82 (see text). Our own resistivity data taken using the Montgomery method are shown by solid circles.

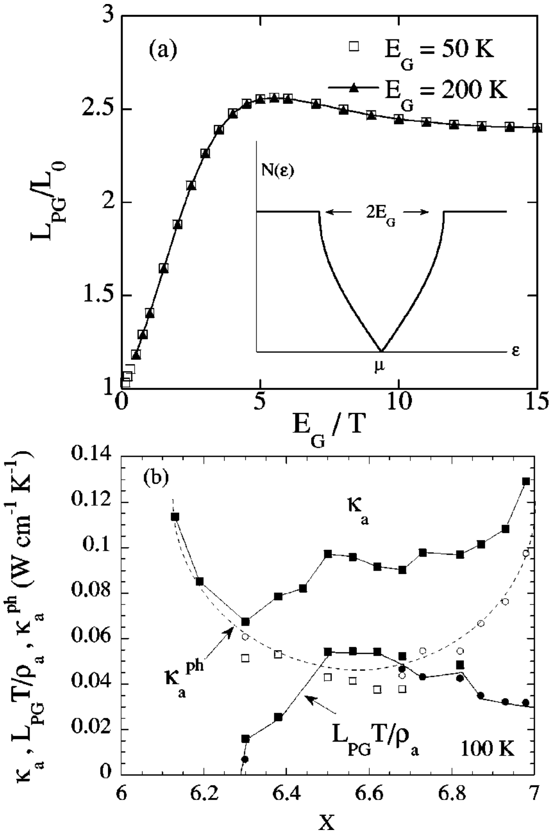

FIG. 4. (a) Lorenz number $L_{\rm PG}/L_0$ vs $E_{\rm G}/k_{\rm B}T$, calculated for the PG model (see text), with a cylindrical Fermi surface, the chemical potential $\mu=6000$ K and the values of $E_{\rm G}$ shown. The inset shows the corresponding density of states with a triangular gap of width $2E_{\rm G}$ centered at μ. (b) κ_a, $L_{\rm PG}T/\rho_a$, and $\kappa_a^{\rm ph}$ ($\equiv \kappa_a - L_{\rm PG}T/\rho_a$) vs x at $T=100$ K. Solid squares show $\rho_a(T)$ data from Ref. 8 for $x=6.38$–6.82 (see text). Our own resistivity data taken using the Montgomery method are shown by solid circles. All lines are guides to the eye.

e.g., scattering from spin fluctuations with large $\vec{Q}$ values. Values of $L \geqslant L_0$ would be most unusual but could arise if the carriers transported more entropy than expected for a Fermi liquid,[2] for example, spin entropy.[19]

Figures 3(a) and 3(b) show $\kappa_a(x)$ and $L_0T/\rho_a(x)$ at 300 K and 100 K using both our own $\rho_a(T,x)$ data and those of Ref. 8, with modified x values that give the same values of T_c. For $x \geqslant 6.3$, the $\kappa_a(x)$ curves are roughly parallel to $L_0T/\rho_a(x)$ at both temperatures, which is consistent with the preceding analysis. The phonon contributions $\kappa_a^{\rm ph}(x)(\equiv \kappa_a - L_0T/\rho_a)$ are also plotted in Figs. 3(a) and 3(b), they are only weakly dependent on x, in the range $x=6.3$–6.9, but rise towards the more ordered states at $x=6.0$ and 7.0. There is also a small peak in $\kappa_a^{\rm ph}(x)$ near $x=6.5$ where various studies suggest an ordered state with alternate full and empty Cu-O chains.[20] The plateau in L_0T/ρ_a from $x=6.8$ to 6.5 in Fig. 3(b) corresponds to the mysterious but well-established[8,16] merging of the $\rho_a(T,x)$ curves near $T=100$ K.

The other scenario considered here involves a fermion density of states (DOS) with a triangular gap $2E_{\rm G}$ at the chemical potential μ, where $E_{\rm G}$ is the pseudogap energy.[2] This gives a good empirical description of specific heat, entropy, and static susceptibility data for several series of cuprates[2] as well as c-axis $\rho(T)$ and magnetoresistance data.[21] We therefore calculated L for a cylindrical Fermi surface with a **k**-dependent PG, using the standard Boltzmann procedure[18] involving integrals of the form

$$K_n = \Sigma_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} . \mathbf{v}_{\mathbf{k}} (\varepsilon - \mu)^n \tau(\varepsilon) \frac{\partial f}{\partial \varepsilon}, \qquad (1)$$

where $\mathbf{v}_{\mathbf{k}}$, ε, and $\tau(\varepsilon)$ are the electron velocity, energy, and scattering time, n = 0, 1, or 2 and the Lorenz number $L \equiv \kappa\rho/T = K_2/(e^2T^2K_0)$. Following Ref. 2 all **k** states within an energy range $\mu \pm E_{\rm G} \cos 2\theta$ where $\tan\theta = k_y/k_x$, are omitted from the sum, giving the DOS shown as an inset in Fig. 4(a). A plot of L/L_0 vs $E_{\rm G}/k_{\rm B}T$, calculated with this model is shown in Fig. 4(a) for the case where $\tau(\varepsilon)$ is constant for $|\varepsilon - \mu| \lesssim 2k_{\rm B}T$, as expected for inelastic electron-electron scattering. The physical reason for the enhancement of L/L_0 is robust, namely when the DOS increases rapidly between $\varepsilon = \mu$ and $\varepsilon = \mu \pm 2k_{\rm B}T$; the usual Sommerfeld expansion leading to $L \approx L_0$ is no longer valid and the ratio of heat to charge transport is enhanced. But for elastic electron-impurity scattering, Fermi's golden rule gives $1/\tau(\varepsilon) \propto N(\varepsilon)$, the DOS factors would then cancel out, so the PG would have little effect on K_2 and $L \approx L_0$.[22]

We used the results in Fig. 4(a) taking $E_G(x)$ from Ref. 23, to replot Fig. 3(b) using L_{PG} rather than L_0. This is shown in Fig. 4(b), where it can be seen that $\kappa_a^{ph}(x)$ becomes more x dependent with a broad minimum near $x=6.5$. The T dependence of κ_a^{ph} was shown already in the lower part of Fig. 2(b). If the model does indeed apply to *a*-axis transport in under-doped cuprates, then it affects analysis of the Nernst effect,[19] because the Sondheimer cancellation would break down. On the other hand if phonons in YBCO are only weakly scattered by oxygen defects,[4] and $\kappa_a^{ph}(x)$ is only weakly dependent on x, as in Fig. 3, the model does not apply and other scenarios with $L \geqslant L_0$ are favored.

In summary, by making a systematic study of the *a*-axis thermal conductivity of $YBa_2Cu_3O_x$, we have shown in a reasonably direct way that the PG *does* cause an increase in κ^{el}. This shows that the PG does not arise from superconducting fluctuations, which are expected to increase $1/\rho_a(T)$ with no increase in $\kappa_a^{el}(T)$, since Cooper pairs do not contribute to $\kappa^{el}(T)$.[24] The data also suggest that over wide ranges of T and x, $L \gtrsim L_0$. This is difficult to understand within certain scenarios for the normal-state gap. For example, in the bipolaron picture, L would be reduced by a factor 6.6 mainly because the carriers have a charge $2e$.[25] More experiments and model calculations are required to determine κ^{ph} more precisely and thereby distinguish between various possible scenarios that can give $L \gtrsim L_0$.

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[11] The crystal had several twin boundaries near each end, that did not influence the measurement of $\kappa_a(T)$ and provide a convenient reference when verifying that the central area remained untwinned. After deoxygenating from $x=6.50$ to 6.44, the twin boundaries disappeared. On reoxygenating the crystal to $x=6.98$, a small amount of twinning did appear in the central region, but this did not affect $\kappa_a(T)$ for $T>40$ K because data for another detwinned crystal from the same batch with $x=6.99$ are identical above 40 K. This also shows that the effects of oxygen treatment on $\kappa_a(T)$ were reversible except below 40 K where the results suggest a slightly larger number of point defects in the reoxygenated crystal.

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