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**LETTER TO THE EDITOR**

# The anomalous thermal conductivity of $La_{2-x}Sr_xCuO_{4-y}$ at very low temperatures

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**Abstract.** We report measurements of thermal conductivity ($\kappa$) extending to 100 mK on a series of $La_{2-x}Sr_xCuO_{4-y}$ specimens with $0.10 \leq x \leq 0.25$. For two superconducting samples ($x = 0.20, x = 0.25$) the temperature dependence of $\kappa$ weakens below about 0.5 K, approaching a variation linear in $T$ near 0.1 K. A non-superconducting sample ($x = 0.10$) exhibits a $\kappa \propto T^3$ dependence below 1 K, characteristic of phonon boundary scattering. After annealing in a vacuum, the $x = 0.20$ specimen became insulating and had a thermal conductivity similar in magnitude and temperature dependence to that of the $x = 0.10$ sample. Thus superconducting and non-superconducting samples are clearly distinguished by the behaviour of their thermal conductivities at sub-kelvin temperatures. These results are shown to be consistent with the presence of a small number of free carriers well below $T_c$ in the superconductors. We suggest that a non-superconducting band of electrons is present in the highly doped materials.

Experiments [1, 2] on $La_{2-x}Sr_xCuO_{4-y}$ suggest that for low Sr concentrations ($x$) normal-state transport is characterised by a single band of holes. These carriers are believed to be responsible for high-$T_c$ superconductivity. For concentrations $x \geq 0.15$ a multi-carrier spectrum [3] is indicated. The respective roles of these carriers in superconductivity is difficult to ascertain from electrical measurements such as resistivity, Hall effect, and thermopower where voltage signals disappear below $T_c$. The possibility that some of the carriers remain normal below $T_c$ can be investigated by measurements of thermal conductivity at very low temperatures. In this Letter we report measurements of thermal conductivity in superconducting and insulating $La_{2-x}Sr_xCuO_{4-y}$ material ($0.10 \leq x \leq 0.25$) for temperatures extending down to 0.1 K. The temperature dependence of the thermal conductivity in the highly doped ($x = 0.20$, $x = 0.25$) superconducting material weakens below about 0.5 K, approaching a variation linear in $T$ at the lowest temperatures. Two non-superconducting specimens, one with lower Sr content ($x = 0.10$) and one obtained by vacuum annealing the $x = 0.20$ sample, exhibit a rapidly decreasing thermal conductivity below 1 K, typical of polycrystalline insulators. The behaviour of $\kappa$ in the superconductors can be interpreted as the signature of heat transport by a small number of uncondensed carriers. In view of the experimental record, our data suggest that the non-superconducting carriers are electrons.

The details of sample preparation have been described previously [4]. Specimens of nominal Sr content $x = 0.10, 0.20$, and 0.25 were cut from discs with a diamond saw into parallelepipeds of typical dimensions $0.2 \times 0.2 \times 1.5\ \mathrm{cm}^3$. The $x = 0.2$ and $x = 0.25$

compounds exhibit zero resistance at temperatures of 30 and 15 K, respectively. Below 16 K the resistivity of the $x = 0.10$ sample [5] obeys the Mott law [6] for variable-range hopping, a behaviour characteristic of disordered semiconductors. This sample did not show zero resistance down to 1 K; however, magnetoresistance measurements [5], which probe the connectivity of superconducting islands, suggest the presence of incipient superconductivity in this sample for temperatures up to about 36 K. Further evidence of small, isolated, high-$T_c$ regions in this specimen is evident in flux expulsion (Meissner effect) measurements (figure 1) where a weak diamagnetism is observed below about 30 K. As mentioned above, we have also remeasured the thermal conductivity of the $x = 0.20$ specimen after vacuum annealing at 900 °C for 4 h. The Meissner curves for this material before and after heat treatment are also shown in figure 1. No superconductivity is evident in the vacuum-annealed material above 2 K. Thermal conductivity was measured in a dilution refrigerator using a steady-state technique with two calibrated germanium thermometers.

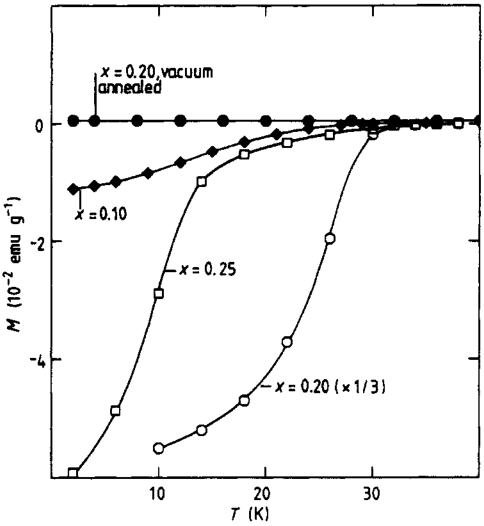

**Figure 1.** The field-cooled magnetisation (Meissner effect) of $La_{2-x}Sr_xCuO_{4-y}$ specimens. The measurement field is 30 Oe.

The thermal conductivity, $\kappa$, is shown in figure 2 for each of the three samples. While the temperature dependences in the range $2 \leqslant T \leqslant 15$ K are similar, a dramatic difference in behaviour is apparent at the lowest temperatures. The thermal conductivities for $x = 0.20$ and $x = 0.25$ show a weakening in their temperature dependences below about 0.5 K, while for $x = 0.10$ the conductivity decreases as $\kappa \propto T^3$. Consequently the heat conduction in the highly doped materials is larger than that of $x = 0.10$ by an order of magnitude or more at the lowest temperatures. This behaviour is surprising since for conventional superconductors well below $T_c$ condensed carriers are effectively removed from the heat conduction process, and one expects an insulating behaviour with $\kappa$ reflecting the rapidly decreasing lattice specific heat.

The $\kappa \propto T^3$ behaviour of the $x = 0.10$ sample is typical of polycrystalline insulators where phonon mean free paths are fixed by scattering from the microstructure. The

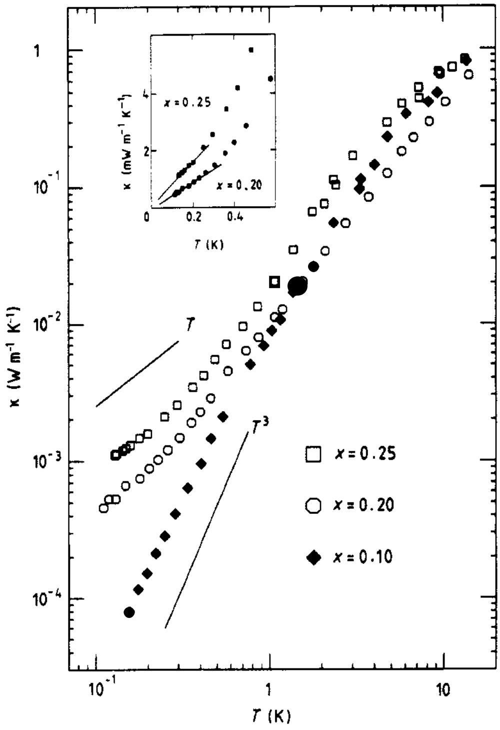

**Figure 2.** The thermal conductivity plotted against temperature for $La_{2-x}Sr_xCuO_{4-y}$ compounds. The inset shows the data for $x = 0.20$ and $x = 0.25$ replotted on a linear scale at the lowest temperatures. The full lines are guides to the eye.

lattice thermal conductivity, in the Debye model, can be expressed as

$$\kappa_L = \tfrac{1}{3}Cvl = (2\pi^2 k_B^4 l/15\hbar^3 v^2)T^3.$$

Here $C$ is the Debye heat capacity, $v$ is the velocity of sound, and $l$ is the phonon mean free path. Applying this formula to the data for $x = 0.10$ below 1 K with [7] $v = 5000$ m s$^{-1}$ yields $l \simeq$ 9–10 μm. This value is in good agreement with the range of grain and pore sizes evident in a scanning electron micrograph of these samples; see figure 3. One possibility that must be considered for these materials is that the weakened temperature dependence of $\kappa$ for $x = 0.20$ and $x = 0.25$ arises from a strongly frequency-dependent (e.g. Rayleigh) scattering of phonons from the microstructure. This phenomenon may occur at temperatures where the dominant phonon wavelength, $\lambda_{\text{dom}} \simeq hv/2.7\, k_B T$, exceeds the typical size of pores or grains. A plateau in $\kappa(T)$, which is characteristic of glassy [8] systems above 10 K, is the signature of such scattering. However, as is evident from a comparison of the micrographs (figure 3), the microstructure is not sufficiently different in these materials to account for the contrasting behaviour of their thermal conductivities below 0.5 K. Although the porosity† increases with Sr concentration, the typical grain and pore sizes for higher doping are 3–6 μm, comparable to that of $x = 0.10$. The data on the vacuum-annealed $x = 0.20$ sample provide the strongest argument

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† From microbalance measurements and a theoretical mass density of about 7.4 g cm$^{-3}$ we estimate porosities of about 0.30 for $x = 0.25$ decreasing to about 0.06 for $x = 0.10$.

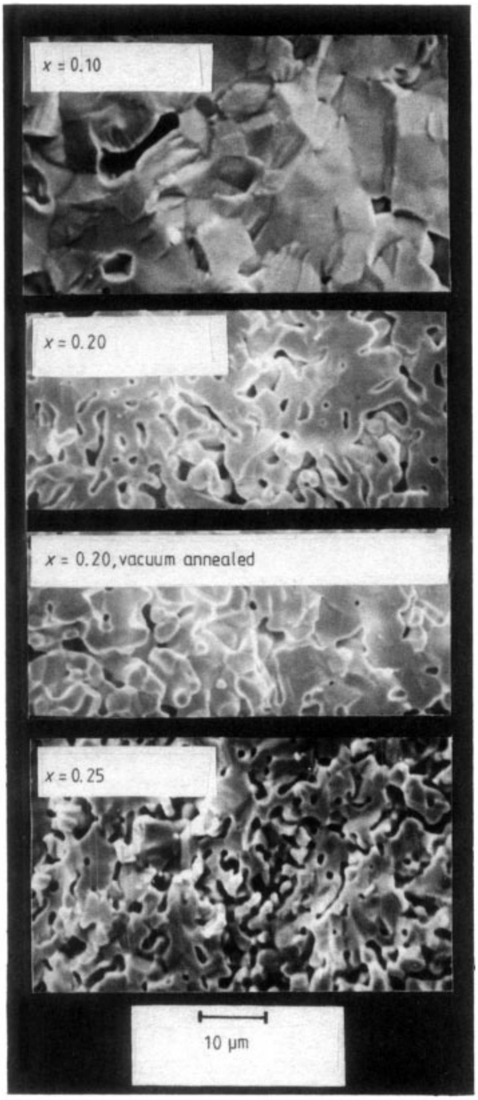

**Figure 3.** Scanning electron micrographs of the three $La_{2-x}Sr_xCuO_{4-y}$ compounds for which thermal conductivities are shown in figure 2, and of the vacuum-annealed $x = 0.20$ specimen.

against Rayleigh scattering in these materials. As indicated in figure 3, the microstructure is clearly unaffected by the heat treatment, yet the thermal conductivity shows no weakening in its temperature dependence (figure 4). This is in sharp contrast to its behaviour prior to heat treatment. In fact, the thermal conductivity for this vacuum-annealed material is very similar to that for $x = 0.10$. These results suggest that the weakened temperature dependence of $\kappa$ for the superconducting samples with $x = 0.20$ and $x = 0.25$ is associated with the high-$T_c$ phase. We propose that an additional heat conduction mechanism is operative in these superconducting samples.

The low-temperature thermal conductivity of the superconducting specimens is reminiscent of the behaviour observed in low-carrier-density systems such as semimetals [9, 10]. At very low temperatures where the phonon contribution decreases rapidly, even a small number of carriers may dominate the heat transport. A linear temperature

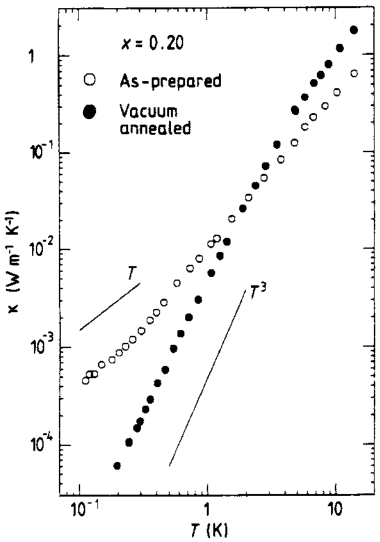

**Figure 4.** The thermal conductivity of the $x = 0.20$ specimen before and after vacuum annealing.

variation of the thermal conductivity is expected in the residual resistivity regime where carriers are scattered by impurities and defects. From the Wiedemann–Franz Law (WFL) the electronic thermal conductivity can be written as

$$\kappa_E = (L_0/\rho)T$$

where $L_0 \equiv (\pi^2/3)(k_B/e)^2 = 2.45 \times 10^{-8}\,V^2\,K^{-2}$ and $\rho$ is the electrical resistivity. Applying the WFL to the data at the lowest temperatures (see figure 2, inset) yields an 'effective residual resistivity', $\rho_0^{\rm eff}$, that would be associated with these carriers. For this analysis to be physically reasonable $\rho_0^{\rm eff}$ should reflect a fraction of the total carrier density inferred from normal-state measurements. Thus $\rho_0^{\rm eff}$ should be rather larger than the value estimated by making a linear extrapolation of the normal-state resistivity to zero temperature†, $\rho_0^{\rm extr}$. These values are $\rho_0^{\rm eff} \simeq 560\,\mu\Omega$ cm and $\rho_0^{\rm extr} \simeq 85\,\mu\Omega$ cm for $x = 0.20$, and $\rho_0^{\rm eff} \simeq 350\,\mu\Omega$ cm and $\rho_0^{\rm extr} \simeq 110\,\mu\Omega$ cm for $x = 0.25$. The ratios, $\rho_0^{\rm extr}/\rho_0^{\rm eff} \simeq 0.15$ and $0.30$, respectively, provide rough estimates of the fraction of normal carriers contributing to the low-temperature heat transport in the superconducting samples. These carrier fractions offer a plausible explanation for the widely observed [11] $T$-linear ($\gamma$) term in the low-temperature specific heat of these compounds. Using these fractions and normal-state values of the carrier density, inferred from Hall measurements [4] on these samples at 50 K, the experimental values [11] of $\gamma$ (approximately 5 mJ mol$^{-1}$ K$^{-2}$) can be reproduced‡ with a reasonable choice of effective mass (about 2–3 $m_e$).

We now address the origin of these carriers. One possibility is that they arise from compositional inhomogeneities, for example at interfaces between superconducting and

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† Here we use the experimental result $d\rho/dT \sim 3.6\,\mu\Omega$ cm K$^{-1}$ for both $x = 0.20$ and $x = 0.25$ as determined in [2].

‡ Here we use free-electron theory where $\gamma = \frac{1}{3}\pi^2 k_B^2 N(E_F)$ and $N(E_F) = (m^*/\pi^2\hbar^2)(3\pi^2 n)^{1/3}$ is the density of states at the Fermi level.

semiconducting regions. Providing an argument against this interpretation is the $x = 0.10$ compound which is undoubtedly inhomogeneous in this sense, yet shows no evidence for free-carrier transport in its thermal conductivity. A more intriguing possibility is that normal carriers well below $T_c$ are intrinsic to the superconducting phase in the $x = 0.20$ and $x = 0.25$ materials. This could be, in principle, a consequence of coexisting, superconducting and normal bands. Hall measurements [1, 2] indicate hole conduction in a single band for $x \leqslant 0.15$ with one hole introduced per Sr dopant. For higher Sr concentrations oxygen vacancies form, the hole concentration decreases, and multi-band conduction is evident [3]. The strong correlation of hole concentration [2] with $T_c$ supports a picture of superconductivity involving holes only. In this context our data could be understood if the electrons arising at higher Sr concentrations do not participate in superconductivity and thus contribute to heat transport below $T_c$. The lack of evidence for such an electronic contribution in the data for the $x = 0.10$ specimen would be consistent with the notion that free electrons are not present for low Sr concentrations. However, free carriers in isolated, unconnected regions would not contribute to the measured thermal conductivity. Thus we cannot rule out the possibility that free electrons are intrinsic to the high-$T_c$ phase regardless of Sr concentration. The insulating behaviour of the vacuum-annealed $x = 0.20$ sample is presumably a consequence of the enhanced oxygen deficiency, which is an effective source of disorder and also tends to reduce the hole density. In this regard a shift of the Fermi level to a region of localised electronic states [11] is one possible scenario. The similarity in behaviour of the thermal conductivities for the $x = 0.10$ and vacuum-annealed $x = 0.20$ materials would seem to support this interpretation.

In summary, the heat transport behaviours of superconducting and insulating $La_{2-x}Sr_xCuO_{4-y}$ are dramatically different at sub-kelvin temperatures. The enhanced thermal conduction of highly doped superconducting specimens provides evidence of normal free carriers well below $T_c$. These carriers might arise as a consequence of the higher Sr concentrations or could be intrinsic to the high-$T_c$ phase in this compound. In this regard we note that similar results† on the 90 K $YBa_2Cu_3O_{7-\delta}$ system suggest that the existence of normal carriers far below $T_c$ is a characteristic of high-$T_c$ ceramics in general.

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† See the footnote on p L961.

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