Anisotropic thermal conductivity of superconducting lanthanum cuprate

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We have measured the thermal conductivity of a single crystal of $La_{1.96}Sr_{0.04}CuO_4$ in directions both parallel and perpendicular to the copper-oxygen planes. While the effects of electron scattering for in-plane heat transport are strong, the transfer of heat across the CuO_2 planes is limited primarily by sheetlike faults with spacings on the order of 100 Å. The resulting very high out-of-plane thermal resistivity masks the effects of electron scattering in this direction and prevents a careful study of the anisotropy of the electron-phonon coupling in this superconductor.

We have undertaken the first study of the directional dependence of the thermal conductivity κ of a high-temperature superconductor, in this case a lanthanum cuprate compound. Though members of this family have comparatively low transition temperatures (0–40 K, depending on Sr, Ba, or Ca doping content), they have proven to be the easiest to grow into the large single crystals required for these thermal measurements. Studies of the directional dependence of the thermal conductivity in single crystals can yield important information about the anisotropy of the electron-phonon interaction and energy gap in these compounds.[1]

The earliest studies of the thermal conductivity[2–7] on sintered compounds showed that κ is very small in magnitude, is dominated by phonon conduction with charge carriers playing little direct role, and exhibits a very noticeable upturn at T_c. This upturn in κ has been ascribed to a decrease in scattering of phonons by charge carriers as the latter condense into the Cooper pairs responsible for superconductivity. The magnitude of the thermal conductivity depends strongly on the porosity of the sintered material. Thus these studies have provided little other than qualitative information about the electron-phonon interaction, and in particular could not address the issue of anisotropy of the thermal transport. Thus the need for measurements on single-crystal high-T_c materials is clear and immediate. The only measurements reported in the literature are those of Graebner *et al.* on the $YBa_2Cu_3O_7$ system,[8] and Zhu *et al.* on $Bi_2Sr_2Ca_2Cu_2O_8$.[9] Both of these studies considered only the in-plane conduction and were confined to temperatures below 8 K. The questions of anisotropy and effects near T_c in single crystals have not yet been addressed.

We report here our study of thermal conductivity of a single crystal of $La_{1.96}Sr_{0.04}CuO_4$ in both the in-plane and out-of-plane directions from room temperature down to liquid-helium temperatures. We find that while κ parallel to the CuO_2 planes ($\kappa_\parallel$) is very similar to the sintered materials, conduction across the planes ($\kappa_\perp$) is very poor and shows no anomalous behavior near T_c. We present an analysis of these results based on a modified Bardeen-Rickhayzen-Tewordt (BRT) model of lattice thermal conductivity of a superconductor, which allows us to draw conclusions about the nature of scattering in this material.

The single crystal used in this study was grown at the Massachusetts Institute of Technology (MIT) Crystal Physics Laboratory using a top-seeded growth technique. Dopant content was not experimentally determined; the value of 0.04 is a nominal stoichiometry derived from the concentrations of the starting materials. The [001] and [100] crystallographic axes were determined by Laue x-ray backscattering. The sample was cut into a parallelepiped of approximate dimensions $1 \times 4 \times 8$ mm^3, with the [100] direction along the longest axis and the [001] direction along the shortest. To measure the in-plane thermal conductivity (i.e., along the longest crystal dimension), we used a steady-state two-heater, one-thermometer technique,[10] which is essentially a "four-probe" measurement of the sample's thermal conductance. In order to measure κ across the CuO_2 planes, the sample was sandwiched between two pieces of copper. While the temperature of one copper block was held constant, the other block was heated with a known amount of power, and the temperature rise between the two pieces of copper was monitored using a chromel-constantan thermocouple. This technique thus measures the thermal resistance of the sample and any thermal contact resistance between it, the silver paint, and the copper blocks. Unless the thermal resistance of the sample is much larger than the sum of the contact resistances, the latter must be corrected for in the measurement. At room temperature we measure a value of 56 K W^{-1} (corresponding to a value of $\kappa \approx 1.7$ W m^{-1} K^{-1}) for the thermal resistance of our sample across the planes. In order to check whether contact resistance is important, we then replaced the sample with a piece of microscope slide of identical geometry, and measured $\kappa \approx 1.1$ W m^{-1} K^{-1}. A second piece of microscope slide was then measured using a four-probe technique (microscope slide glass is an amorphous and isotropic material), with the result of $\kappa \approx 1.2$ W m^{-1} K^{-1}. Thus, in view of the very good agreement between the two-probe and four-probe techniques on the microscope

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slide, and the similar magnitudes of thermal resistance of our sample and the slide, we conclude that thermal contact resistances have only a very small effect on the measurement perpendicular to the planes. We estimate the absolute error in our measurement at about 20% and the relative error about 5%.

Figure 1 shows the in-plane electrical resistivity of our sample. After falling below room temperature, ρ reaches a shallow minimum and begins a slight upturn before superconductivity begins to set in near 25 K. The transition is very broad and becomes complete near 9.5 K. This is consistent with studies in the literature, which show that T_c is a strong function of dopant content.[11]

Figure 2 shows our measurements of the thermal conductivity of single-crystal $La_{1.96}Sr_{0.04}CuO_4$, as well as measurements on a sintered sample of 20% Sr content.[3] In the CuO_2 plane direction (hereafter called the in-plane direction) the thermal conductivity is very similar to the sintered material, but differs in being somewhat larger in magnitude and having a stronger upturn near T_c. Perpendicular to the planes, κ is very small and shows no hint of an anomaly at the transition temperature. From the magnitude of the electrical resistivity and using the Wiedemann-Franz law, it can be shown that, as in the case of the sintered compounds, virtually all of the heat is carried by phonons both in and out of the CuO_2 planes.

The most striking feature of the curves in Fig. 2 is the anisotropy of the thermal conductivity, which is a factor of 3 at room temperature and increases to 16 at 10 K. Such a large anisotropy is normally not observed in most crystalline materials, because in a three-dimensional solid, most of the heat is carried by transverse phonons which have very little anisotropy in their velocity vector. This suggests that the anisotropy arises from differences in phonon scattering for the two crystal directions.
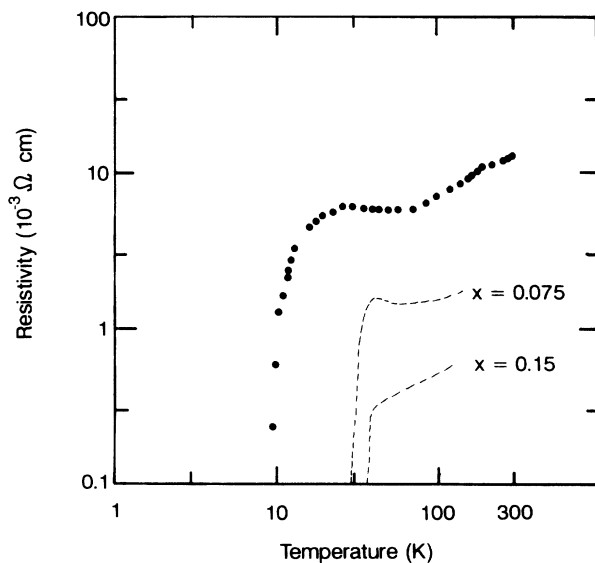
A unified description of the lattice thermal conductivity of superconductors was given in 1959 by Bardeen, Rickhayzen, and Tewordt (BRT).[12] This so-called BRT model considers only scattering of phonons by electrons and derives expressions for the thermal conductivity in the normal and superconducting states. An extension of the BRT model to high-temperature superconductors which includes scattering by crystal defects as well as electrons was recently given by Tewordt and Woelkhausen (TW).[1] In order to quantify the understanding of our data, we will apply this TW model to the present case.

Within the Debye framework of lattice dynamics, the thermal conductivity can be written as

$$\kappa = (k_B/2\pi^2 v)(k_B/\hbar)^3 T^3 \int_0^{\Theta/T} \tau(z)[z^4 e^z/(e^z - 1)^2]dz ,$$

where Θ is the Debye temperature, v is a suitably averaged phonon velocity, $z = \hbar\omega/k_B T$, ω is the phonon frequency, and $\tau^{-1}(z)$ is the sum of the scattering rates of all types of scattering processes. In any crystal of finite dimensions, the crystal boundaries are capable of scattering phonons and yield a scattering rate of

$$\tau_b^{-1} = v/L ,$$

where L is essentially the smallest crystal dimension or the crystallite size. In a real crystal, interstitials and/or vacancies contribute a point defect scattering rate of

$$\tau_p^{-1}(z) = A\omega^4 = A'z^4 T^4 ,$$

where A is related to the fractional concentration of point defects c_p of fractional mass difference $\Delta M/M$ by

$$A = c_p a^3 (\Delta M/M)^2/4\pi v^3 ;$$

here a is the lattice constant. A third scattering mechanism which the TW model considers is scattering from

FIG. 1. Electrical resistivity in the CuO_2 planes of single-crystal $La_{1.96}Sr_{0.04}CuO_4$. Also shown are data (Ref. 11) for other dopant concentrations x on sintered compounds, for comparison.
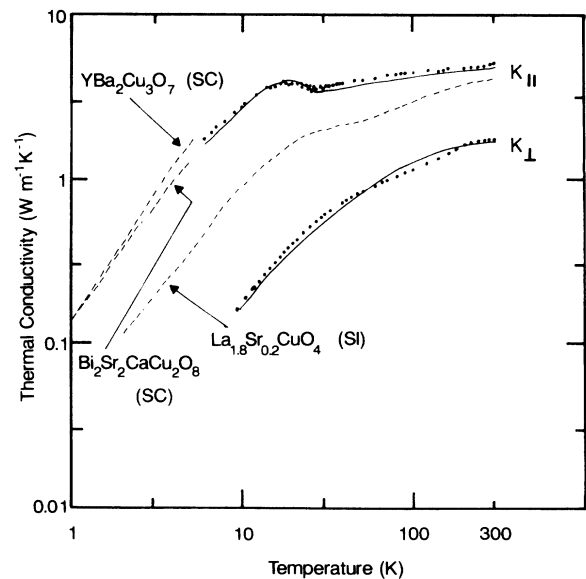
FIG. 2. Thermal conductivity parallel and perpendicular to the CuO_2 planes. Dashed lines are literature data for sintered material (SI) and single crystals (SC), and solid lines are fits discussed in the text.

sheetlike faults (i.e., stacking faults), and is given by

$$\tau_s^{-1}(z) = B\omega^2 = B'z^2T^2 ,$$

with $B = 0.7(6\pi^2)^{2/3}\gamma^2N_s$, where N_s is the number of stacking faults per unit length, and γ is the Grueneisen constant. Finally, the effect of electron scattering is accounted for using

$$\tau_e^{-1}(z) = Cg(z,y)\omega = C'g(z,y)zT ,$$

where the function $g(z,y)$ is the ratio of phonon-electron scattering times in the normal and superconducting states, and depends on both the energy gap and temperature through the parameter $y = \Delta(T)/k_BT$; the form of $g(z,y)$ is discussed in detail in Refs. 1 and 12. The coefficient C is given by

$$C = (\pi/2)(k_BT_c/t)\lambda/a ,$$

where t is the effective hopping matrix element for a two-dimensional tight-binding band of electrons, and λ is the phonon-electron coupling constant.

A fit to our data using these expressions is given by the solid lines in Fig. 2. We fitted $\kappa_{\parallel}$ using boundary, point-defect, and electron scattering rates, and we fitted $\kappa_{\perp}$ by adding a stacking fault term. The parameters of the fit are given in Table I. While the electron scattering term plays an important role for the in-plane heat conductivity, we find that for $\kappa_{\perp}$ the scattering from stacking faults overwhelms all other scattering processes. In particular, the electron scattering term is found to have virtually no effect on the resulting fit, even if C is allowed to vary over an order of magnitude. The strength of the stacking fault scattering for out-of-plane transport yields a sheet fault spacing on the order of 100 Å. It is natural to associate such sheets with misaligned CuO_2 planes; the magnitude of N_s thus suggests that approximately every tenth CuO_2 sheet is not in registry with the crystal structure. The anisotropy in point-defect concentration is at first surprising, but may result from a fitting artifact: Firstly, the effect of anisotropic strain fields should be considered, and secondly, the fit to the out-of-plane data is quite insensitive ($\sim 20\%$) to the value of $c_p(\Delta M/M)^2$.

Finally, the overwhelmingly large stacking fault scattering rate for out-of-plane transport unfortunately precludes us from drawing any conclusions with regard to the anisotropy of the electron-phonon coupling. For in-plane conduction we find $\lambda \sim 0.6$, which is nearly the same as that found by TW for sintered compounds.[13] A similar study on a Bi- or Y-based sample would thus be quite interesting, in order to see if larger λ's are associated with

TABLE I. Parameters relevant to the fit of the thermal conductivity. The question mark denotes unavailable data.

Parameter	Value	
	Parallel	Perpendicular
v (m/s)	5000	5000
Θ (K)	380	380
$L(\mu m)$[a]	40	40
$c_p(\Delta M/M)^2$ [a]	~ 0.1	~ 0.01
γ	1	1
N_s (m^{-1})[a]	0	7×10^7
t (K)	5000	5000
a (Å)	4	10
λ[a]	~ 0.6	?

[a]Fitted parameter.

higher T_c's.

To summarize, we have presented the first measurements of the anisotropy of thermal conductivity in a single-crystal high-temperature superconductor, $La_{1.96}$-$Sr_{0.04}CuO_4$. We find that the heat conduction in the CuO_2 plane direction is very similar to that of the sintered material, being only weakly temperature dependent in the normal state and showing a small upturn at T_c. Across the planes, the thermal conductivity is much smaller and shows no corresponding anomaly at the transition. These results are understood in terms of a modified Bardeen-Rickhayzen-Tewordt model in which heat carrying phonons are scattered primarily by point defects and electrons in the plane and predominantly by sheetlike faults of spacing ~ 100 Å across the planes. This extremely strong stacking fault-phonon scattering is the principal reason for the large anisotropy in κ, and prevents a detailed study of the anisotropy in electron-phonon coupling in this compound. We hope to extend these measurements to materials of higher transition temperature in the near future.

Note added in proof. During preparation of this paper we became aware of a work of similar nature which recently appeared in print [S.J. Hagen, Z.Z. Wang, and N.P. Ong, Phys. Rev. B **40**, 9389 (1989)]. These authors find a similar anisotropy but provide a somewhat different explanation of its origin.

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[13]It should be noted that the TW model calculates κ in the weak-coupling limit. Different expressions for the electron-phonon scattering time would be operative in a strongly coupled superconductor, and this problem has not yet been considered.