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Low-temperature phonon thermal conductivity of single-crystalline Nd_2CuO_4: Effects of sample size and surface roughness

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The effect of sample size and surface roughness on the phonon thermal conductivity κ_p of Nd_2CuO_4 single crystals was studied down to 50 mK. At 0.5 K, κ_p is proportional to $\sqrt{A}$, where A is the cross-sectional area of the sample. This demonstrates that κ_p is dominated by boundary scattering below 0.5 K or so. However, the expected T^3 dependence of κ_p is not observed down to 50 mK. Upon roughing the surfaces, the T^3 dependence is restored, showing that departures from T^3 are due to specular reflection of phonons off the mirrorlike sample surfaces. We propose an empirical power law fit to $\kappa_p \sim T^\alpha$ (where $\alpha < 3$) in cuprate single crystals. Using this method, we show that recent thermal conductivity studies of Zn doping in $YBa_2Cu_3O_y$ reaffirm the universal heat conductivity of d-wave quasiparticles at $T \rightarrow 0$.

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To understand the pairing mechanism in a superconductor, it is essential to know the symmetry of the order parameter. In this context, measurements of low-temperature thermal conductivity κ, which probes the low-energy quasiparticle excitations, has emerged as a powerful probe of the order parameter in superconductors. For conventional s-wave superconductors with a fully gapped excitation spectrum, the linear-temperature electronic contribution to thermal conductivity is zero at $T \rightarrow 0$, i.e., the residual linear term $\kappa_0/T = 0$. This can be seen in the single-gap s-wave superconductor Nb,[1] multiband s-wave superconductors MgB_2 (Ref. 2) and $NbSe_2$,[3] and two newly discovered superconductors C_6Yb (Ref. 4) and Cu_xTiSe_2.[5]

For unconventional superconductors with nodes in the gap, the nodal quasiparticles will contribute a finite κ_0/T. For example, $\kappa_0/T = 1.41$ mW K^{-2} cm^{-1} in the overdoped cuprate Tl2201, a d-wave superconductor with $T_c = 15$ K,[6] and $\kappa_0/T = 17$ mW K^{-2} cm^{-1} for the ruthenate Sr_2RuO_4, a p-wave superconductor with $T_c = 1.5$ K.[7] The fact that κ_0/T is universal,[8] in the sense that it is independent of scattering rate, allows for a measurement of the gap maximum Δ_0 via[9]

$$\frac{\kappa_0}{T} \simeq \frac{k_B{}^2}{6} \frac{n}{c} \kappa_F \frac{v_F}{\Delta_0}, \qquad (1)$$

where n is the number of CuO_2 planes per unit cell, c is the c-axis lattice constant, and k_F and v_F are the Fermi wave vector and velocity at the node, respectively. This has been used to map out the gap as a function of doping in $YBa_2Cu_3O_y$ (Ref. 10) and Tl2201.[9]

The measured thermal conductivity is the sum of two contributions, respectively, from electrons and phonons, so that $\kappa = \kappa_e + \kappa_p$, where κ_e/T is a constant as $T \rightarrow 0$. Therefore, the key issue for these low-temperature thermal conductivity studies is how to extrapolate κ/T to $T = 0$, i.e., to extract the residual linear term κ_0/T. This requires a good understanding of the phonon conductivity $\kappa_p(T)$. In the regime $T \rightarrow 0$, the phonon mean free path becomes limited only by the physical dimensions of the sample. At the surface of a crystal, the phonon may either be absorbed and remitted with an energy distribution given by the local temperature (diffuse scattering) or it may be reflected elastically (specular reflection). In the case of diffuse scattering, the phonon is reradiated in a random direction, resulting in a temperature independent phonon mean free path l_0, given by the cross-sectional area A of the sample: $l_0 = 2\sqrt{A/\pi}$. From simple kinetic theory, the conductivity of phonons is given by[11]

$$\kappa_p = \frac{1}{3} \beta \langle v_p \rangle l_0 T^3, \qquad (2)$$

where β is the coefficient of phonon specific heat and $\langle v_p \rangle$ is a suitable average of the acoustic sound velocities. The electronic linear term is then naturally extracted by plotting thermal conductivity data as κ/T vs T^2, and interpreting the intercept as the residual linear term at $T = 0$ and the slope as the phonon contribution governed by Eq. (2).

However, as the temperature of a crystal is reduced and the average phonon wavelength increases, a surface of a given roughness appears smoother, which may increase the occurrence of specular reflection and result in a mean free path which varies as some power of temperature, so that $\kappa_p \propto T^\alpha$. We would, thus, expect a deviation from the diffuse scattering limit of T^3 temperature dependence for samples with sufficiently smooth surfaces. Such an effect has been previously observed in many studies of low-temperature phonon heat transport in high quality crystals, such as Al_2O_3,[12] Si,[13] KCl and KBr,[14] LiF,[15] and diamond.[16]

For the high-T_c cuprate superconductors, the extrapolation of κ_0/T has been a controversial issue, particularly in the underdoped regime where κ_0/T is small. Some authors fit their data to $\kappa/T = a + bT^2$ below about 120 mK, assuming that boundary scattering of phonons only occurs below 120 mK and there is no specular reflections.[17,18] Others consider that sample size and specular reflections do affect κ_p,

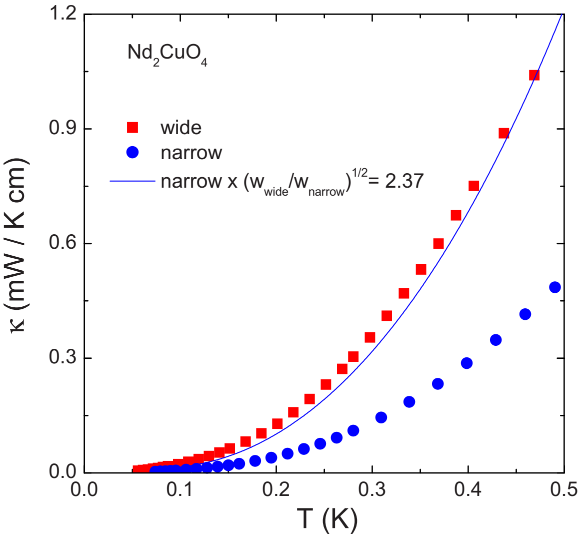

FIG. 1. (Color online) In-plane thermal conductivity κ of the undoped insulating cuprate Nd_2CuO_4 below 0.5 K, for an as-grown single crystal before ("wide," red squares) and after ("narrow," blue circles) it was cut along the length. By cutting, the width w was reduced by a factor of 5.6. At $T=0.5$ K, κ is reduced in direct proportion to the reduction in $\sqrt{w}$, as indicated by the solid line.

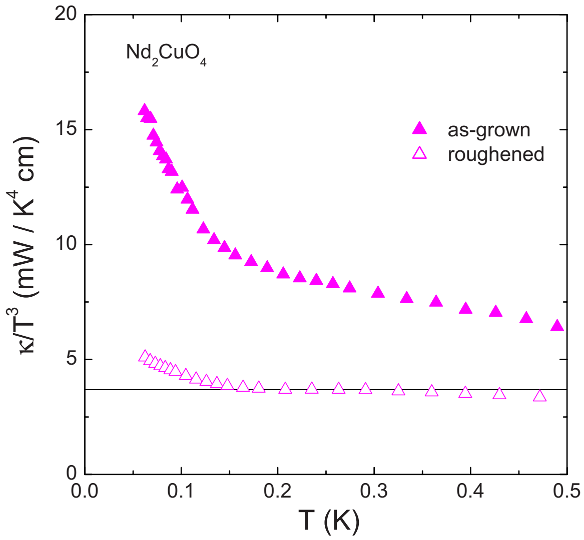

FIG. 2. (Color online) In-plane thermal conductivity κ of an as-grown single crystal of Nd_2CuO_4 before ("as-grown," full triangles) and after ("roughened," empty triangles) its smooth mirror-like surfaces were roughened by sanding. As indicated by the horizontal line, roughening allows one to recover the diffusive regime at low temperature, characterized by a constant κ/T^3, at least down to 150 mK.

and fit their data to $\kappa/T=a+bT^\alpha$ below about 0.5 K.[10,19,20] Disagreement on extrapolation procedure has fueled a debate[21,22] on whether $YBa_2Cu_3O_y$ is a thermal metal below the doping level of $p=0.05$,[17,19,20] and possible breakdown of the universal thermal conductivity in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.5}$.[18]

In this paper, we investigate the low-temperature phonon thermal conductivity of cuprate single crystals by measuring the insulating (undoped) parent compound Nd_2CuO_4, for which $\kappa_0/T=0$. First, by reducing the sample width w, we show that κ_p is proportional to $\sqrt{wt}$ at 0.5 K, with t the unchanged sample thickness. This clearly demonstrates that κ_p is dominated by boundary scattering below 0.5 K. Second, we show that a sample with rough surfaces has a temperature dependence much closer to T^3 than one with smooth surfaces, which is apparently caused by the reduced specular reflections at the rough surfaces. Finally, based on this understanding of κ_p, we discuss how to extract κ_0/T in cuprate single crystals at finite doping (where $\kappa_0/T>0$).

Single crystals of Nd_2CuO_4 were grown by a standard flux method. The as-grown samples are platelike with very smooth surfaces in the *ab* plane. In-plane thermal conductivity κ was measured in a dilution refrigerator down to 50 mK using a standard one heater–two thermometer steady-state technique. Note that in zero field, magnons are gapped and the thermal conductivity of insulating Nd_2CuO_4 only comes from phonons: $\kappa=\kappa_p$.[23]

Boundary scattering. To study the boundary scattering of phonons, an as-grown Nd_2CuO_4 single crystal with dimensions $1.5\times0.90\times0.086$ mm^3 (length$\times$width$\times$thickness) was measured first. Then it was cut along the length so that its width w was reduced (by a factor of 5.6) to 0.16 mm, and measured again. Figure 1 shows κ vs T for the wide (before cutting) and narrow (after cutting) samples below 0.5 K. It is clear that the narrow sample has a much smaller κ than the wide sample in this temperature range. Actually, at $T=0.5$ K, κ of the narrow sample is precisely $\sqrt{5.6}=2.37$ times smaller than the wide sample. This means κ is reduced in direct proportion to the reduction in $\sqrt{A}=\sqrt{wt}$, where t is the unchanged sample thickness. This is strong evidence that κ is limited by sample size, and boundary scattering is unambiguously the dominant mechanism for phonon conductivity below 0.5 K.

Specular reflection. Having demonstrated that phonons are scattered by sample surfaces below 0.5 K, we proceed to study the effect of surface roughness on the temperature dependence of κ. An as-grown Nd_2CuO_4 single crystal with dimensions $1.0\times0.43\times0.086$ mm^3 was measured first. Afterwards, both its mirrorlike *ab*-plane surfaces were roughened by sanding, then it was remeasured. During sanding, the thickness of the sample was reduced. The geometric factor for the roughened sample was set to be such that κ(rough)$=\kappa$(smooth) at high temperature (e.g., 50 K), which gives the estimated thickness of 0.062 mm, with unchanged width of 0.43 mm. In Fig. 2, the data of the smooth and roughened samples are plotted as κ/T^3 vs T to reveal the deviation from the T^3 dependence expected if the phonon mean free path $l_p\propto\kappa/T^3$ were constant, independent of T. l_p is clearly not constant for the smooth sample, while for the roughened sample, roughening has made l_p much more constant, at least down to 150 mK. This is unambiguous proof that specular reflection is important in these crystals. Below 150 mK, the phonon wavelength becomes long enough to average over the roughness and produce some specular reflections.

From the data of Fig. 2, we can estimate the phonon mean free path l_p for the roughened sample. Equation (2) can be written as[24]

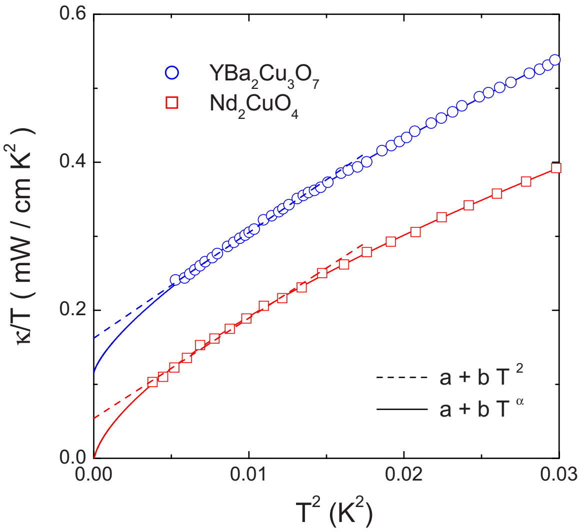

FIG. 3. (Color online) In-plane thermal conductivity κ of undoped Nd_2CuO_4 (data from Ref. 23) and slightly overdoped $YBa_2Cu_3O_7$ (data from Ref. 18) single crystals, plotted as κ/T vs T^2 below 175 mK. The dashed and solid lines represent two extrapolation procedures: (1) $\kappa/T=a+bT^2$ below 120 mK and (2) $\kappa/T=a+bT^{\alpha}$ below 175 mK. The former yields a spurious residual linear term ($\kappa_0/T>0$) in the insulator Nd_2CuO_4, and thus, overestimates κ_0/T in the superconductor $YBa_2Cu_3O_7$.

$$\kappa_p=\frac{2}{15}\pi^2 k_B\left(\frac{k_BT}{\hbar}\right)^3\langle v_p^{-2}\rangle l_0. \tag{3}$$

The in-plane sound velocities of Nd_2CuO_4 (along [100]) were reported to be $v_L=6050$ m/s (longitudinal), $v_{T1}=4220$ m/s (transverse with [010] polarization), and $v_{T2}=2460$ m/s (transverse with [001] polarization).[25] Taking an approximate average value for $\langle v_p\rangle$ equal to 4000 m/s and using the horizontal line in Fig. 2 for the value of κ_p/T^3 in the roughened sample, Eq. (3) yields a phonon mean free path $l_p=0.16$ mm, in good agreement with the idealized value of $l_0=2\sqrt{wt/\pi}=0.18$ mm obtained from the sample dimensions. This confirms that the T^3 behavior seen below 0.5 K in the roughened sample is, indeed, due to boundary scattering.

Extracting κ_0/T. From Figs. 1 and 2, it is clear that for typical cuprate single crystals with smooth surfaces, phonon thermal conductivity will reach the boundary scattering regime below 0.5 K and κ is expected to deviate from the standard T^3 dependence due to specular reflections. Considering together previous studies of other conventional insulators,[12–16] a reasonable way to extract κ_0/T of cuprate single crystals is to fit the thermal conductivity data to $\kappa/T=a+bT^{\alpha}$. In Fig. 3, we reproduce two sets of published data: one on undoped Nd_2CuO_4 (from Ref. 23), the other on fully doped $YBa_2Cu_3O_7$ (from Ref. 18). For Nd_2CuO_4, fitting κ/T to $a+bT^{\alpha}$ below 175 mK gives $\kappa_0/T=-0.004\pm0.006$ mW K^{-2} cm^{-1} and $\alpha=1.29\pm0.04$. In contrast, a fit to $\kappa/T=a+bT^2$ below 120 mK gives $\kappa_0/T=0.054\pm0.003$ mW K^{-2} cm^{-1}. For this insulator, the negligible κ_0/T obtained from the first fit is physically more reasonable than the finite κ_0/T from the second fit. This shows that a textbook fit overestimates κ_0/T.

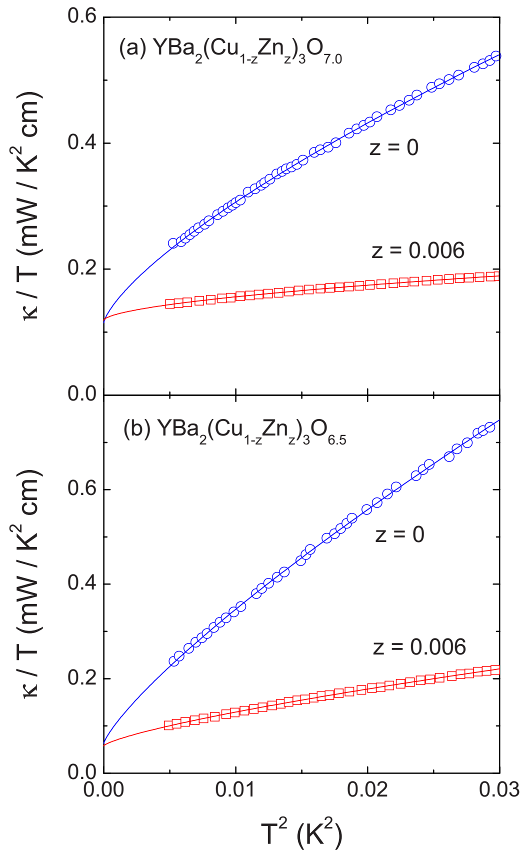

FIG. 4. (Color online) Thermal conductivity of pure and Zn-substituted $YBa_2Cu_3O_y$ with (a) $y=7.0$ and (b) $y=6.5$ (data from Ref. 18). The solid lines are fits to $\kappa/T=a+bT^{\alpha}$ below 175 mK, used to extract κ_0/T, seen to be universal in both cases (i.e., unchanged by Zn substitution).

Applying the same two fits to $YBa_2Cu_3O_7$ (dashed and solid lines in Fig. 3) gives $\kappa_0/T=0.162\pm0.001$ and 0.115 ± 0.004 mW K^{-2} cm^{-1}, respectively. Based on our findings of Nd_2CuO_4 (Fig. 3), the lower estimate ($\kappa_0/T=0.115$ mW K^{-2} cm^{-1}) is expected to be closer to the true value for $YBa_2Cu_3O_7$.

Let us now turn to the controversial issue of whether thermal conductivity is universal in $YBa_2Cu_3O_y$. In a *d*-wave superconductor, κ_0/T is due to nodal quasiparticles, and standard theory shows κ_0/T to be "universal,"[26,27] i.e., independent of impurity concentration, in the limit of weak scattering ($\Gamma\ll\Delta_0$). Upon increasing the scattering rate Γ so that it becomes a significant fraction of the gap maximum Δ_0, κ_0/T is expected to increase slightly[26,28] (assuming the normal state is a metal). Experimentally, it was first observed in optimally doped cuprates: in $YBa_2Cu_3O_y$ ($y=6.9$) as a function of Zn doping[8] and in $Bi_2Sr_2CaCu_2O_{8-x}$ as a function of radiation damage.[29] It was later verified in the layered nodal superconductor Sr_2RuO_4.[7]

Repeating the original experiment, Sun *et al.*[18] reported κ data for a pure and a Zn-doped crystal of $YBa_2Cu_3O_y$ with $y=7.0$, reproduced in Fig. 4(a). The main effect of Zn doping is to cause a dramatic suppression of the *slope* of κ/T as a function of T^2. The authors extrapolate the data using a fit to $\kappa/T=a+bT^2$, restricted to a very small interval (70–120 mK). The value of κ_0/T thus extrapolated turns out to be 20% lower in the sample with 0.6% Zn. Based on this slight difference, Sun *et al.* go on to claim a breakdown of universal transport in $YBa_2Cu_3O_y$.

However, the determination of κ_0/T depends on the extrapolation procedure, as seen in Fig. 3. Using a fit to $\kappa/T=a+bT^{\alpha}$ below 170 mK for pure and 0.6% Zn-doped $YBa_2Cu_3O_7$ [solid lines in Fig. 4(a)] yields $\kappa_0/T=0.115$ and 0.119 mW K^{-2} cm^{-1} with $\alpha=1.45$ and 1.12, respectively. The error in this kind of experiment, mainly coming from the uncertainty in sample dimensions, is usually of order $\pm10\%$. The error from the data fitting is usually of order $\pm5\%$. Therefore, the total error is of order $\pm15\%$. This means that within error bars, their data confirm the validity of the standard theory of universal transport in this archetypal cuprate. In Fig. 4(b) a similar result is found in underdoped $YBa_2Cu_3O_{6.5}$, where $\kappa_0/T=0.063$ and 0.058 mW K^{-2} cm^{-1} for pure and 0.6% Zn doped, with $\alpha=1.60$ and 1.50.

Any variation in κ_0/T with Zn doping should be put in proper context: with 0.6% Zn doping, the inelastic scattering rate was estimated to increase by roughly a factor of 10 in $YBa_2Cu_3O_{6.9}$.[8] Hence, the normal-state κ/T in the zero-temperature limit should decrease by a factor of about 10. Therefore, the change in quasiparticle conductivity measured in the superconducting state, if any, is seen to be at most a few percent of the change expected in the normal state. This is precisely what is meant by universal transport.

In contrast to $YBa_2Cu_3O_y$, the breakdown of standard theory for $La_{2-x}Sr_xCuO_4$ (LSCO) (Ref. 18) appears to be fairly unambiguous (a rigid shift in κ/T caused by a small change in scattering rate) and consistent with a prior report of breakdown in underdoped LSCO.[10] This is presumably a consequence of the fact that suppressing the superconducting state in LSCO leads to an insulating (and magnetic) state, rather than the metallic state assumed by standard theory.[30,31]

In summary, by studying the effect of sample size and surface roughness on the phonon thermal conductivity of Nd_2CuO_4 single crystals, we show that phonon heat conduction in cuprates is dominated by boundary scattering below 0.5 K. In as-grown (or polished) single crystals, specular reflection alters the T dependence away from the expected T^3 dependence. As a result, in no range of temperature down to $T=0$ is a T^3 fit to the phonon part of κ appropriate. A better, but by no means exact, fit is obtained by allowing the power to adjust away from 3, toward 2, as found in conventional insulators. In the absence of a good theoretical treatment of specular reflection, this is probably the best one can do.

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