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Thermal conductivity of $YBa_2Cu_4O_8$ dominated by phonon-phonon interactions

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The thermal conductivity κ of dense sintered ceramic $YBa_2Cu_4O_8$ in the range 30–310 K has been measured. At 100 K, κ is 10 $W m^{-1} K^{-1}$, approaching the in-plane κ of single crystals of other high-T_c materials. κ decreases rapidly with increasing T to 7.4 $W m^{-1} K^{-1}$ at 300 K. Fitting standard models for $\kappa(T)$ to the data we find that κ is limited mainly by phonon-phonon interactions. Depending on the model used, the best fit is found for effective values of Θ_{Debye} between 155 and 185 K, characteristic for the acoustic phonon branches, indicating that such phonons carry most of the heat. Finally, we suggest a possible way to test the electron-phonon model for the electrical and thermal conductivities in high-T_c materials.

Since the thermal conductivity κ is one of the few transport properties that has a nonzero value in both the normal and superconducting states, studies of κ give valuable information on the interaction between electronic carriers and phonons and the scattering of both by defects and impurities. This has caused a recent surge of interest in κ data for high-temperature superconductors (HTS), and data for κ in the most common HTS materials, in particular $YBa_2Cu_3O_{7-\delta}$ (Y 1:2:3), are reviewed in Refs. 1–3. We present in this paper data for κ in $YBa_2Cu_4O_8$ (Y 1:2:4) as a function of temperature T. To our knowledge no previous data exist for Y 1:2:4, possibly because of the difficulty in producing this material as a high-density bulk material or as large single crystals.

The data for κ in Y 1:2:4 differ to a surprisingly large extent from those for Y 1:2:3, which has a very similar structure, and κ is dominated by phonon-phonon interactions. A more detailed report[4] containing further experimental and theoretical details will be published later.

Bulk material with a porosity $<2\%$ was produced by hot isostatic pressing CuO with Y 1:2:3 as described previously[5] and characterized by x-ray-diffraction analysis. κ was measured on a $0.7\times0.9\times13.8$ mm^3 rod, cut along the axis of the hot isostatic pressed cylinder. The resistivity ρ was 630 $\mu\Omega$ cm at 300 K, similar to reported single-crystal in-plane values,[6] and the resistive onset transition temperature T_c was 79 K with a transition width of about 4 K, somewhat larger than observed previously on material produced in the same way.[5,7]

The thermal conductivity data were obtained over the range 30–310 K by two different methods. The longitudinal steady-state method[8] was used in the range 30–160 K. At higher temperatures it is well known[1,8–11] that radiation heat losses may cause significant experimental errors, usually giving too large values for κ. In the range above 70 K we therefore measured instead the thermal diffusivity a using Ångström's method,[8,12] which in principle eliminates all effects of heat losses to the surroundings. κ was then calculated as $\kappa = a d c_p$, where d is the density and c_p the specific heat capacity. However, this method also had drawbacks: First, to get high accuracy we must use relatively large temperature signals, implying a large heater power and thus large temperature gradients in the sample. This will smear sharp changes in κ, such as often observed[1–3] at T_c, and the high power makes it difficult to reach temperatures below 70 K. Second, the accuracy in the calculated values of κ depends on the accuracy in the data for both a and c_p, and also on the accuracy of the measured T: For $T<150$ K the slope dc_p/dT is large and small errors in T might lead to incorrect values of κ. In our case, c_p was measured between 250 and 350 K and found to agree well with literature data,[13] and below 250 K we therefore used literature data,[13] scaled to match ours above.

All measurements were carried out in a vacuum $<10^{-5}$ mbar and T was measured using type K thermocouples. The steady-state data were corrected for Joule heating in, and heat conduction along, connection wires. For the measurements of a we used the equipment described in Ref. 14 with heater periods of 4 to 20 s. For both methods the dominating source of systematic experimental errors was the uncertainty in the measured sample dimensions and thermocouple distances, and we estimate maximum errors of ±8 and ±12 %, respectively, for the steady-state and Ångström's methods. The temperature-dependent parts of these errors are only 3 and 2 %, respectively, and the rms statistical scatter in both methods is below 2%. The measured T dependence is much more accurate than the magnitudes of κ.

Figure 1 shows κ as a function of T. Above 140 K the data have been calculated from a, and below this we show data measured by the steady-state method. In the region 70–160 K, where both methods were used, the data agreed to within the combined experimental errors, and the data shown have been multiplied by suitable constants above and below 140 K to match at this temperature. No discontinuity in $d\kappa/dT$ is observed at the boundary between the data sets.

There exist no previous data for Y 1:2:4 in the literature with which to compare our results for a and κ. As a comparison, we show in Fig. 2 literature data[10,11] for the in-plane κ in single-crystal Y 1:2:3 together with experimental data for κ in hot isostatic pressed ceramic Y 1:2:3, again obtained using Ångström's method and literature data[13] for c_p. The excellent agreement between our and literature data[1–3] verifies the accuracy of this method.

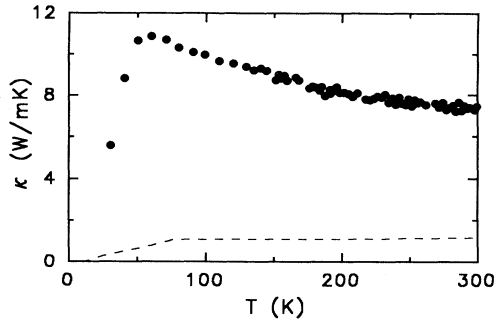

FIG. 1. Thermal conductivity κ of Y 1:2:4 as a function of T. The dashed curve shows electronic component $\kappa_e = TL_0/\rho$.

The T dependence of κ is very different in the two materials. For Y 1:2:3, κ depends weakly on T in the normal state and increases sharply below T_c, while for Y 1:2:4 κ decreases by 26% between 100 and 300 K, with only a small change in $d\kappa/dT$ near T_c. Very small anomalies at T_c have also been observed[1-3] for other high-T_c materials, but a large negative $d\kappa/dT$ in the normal state is unusual. The magnitude of κ in sintered Y 1:2:4 is higher than in sintered Y 1:2:3 below 300 K, approaching the in-plane κ of single-crystal Y 1:2:3 at 100 K. These features suggest the electron-phonon interaction is much weaker in Y 1:2:4 than in Y 1:2:3. We show below that this is not true.

The data are analyzed in terms of the relaxation time model.[1,8,15] The total thermal conductivity κ is decomposed into an electronic component κ_e and a lattice component κ_p, neglecting unusual mechanisms such as pair condensation-evaporation transport.[1] Above T_c we use as a first approximation the standard expression[8] $\kappa_e = TL_0/\rho$. Since ρ extrapolates to $\rho \approx 0$ at $T=0$, $\kappa_e \approx 1$ W m^{-1} K^{-1} is almost independent of T, as shown by the dashed curve in Fig. 1. However, we note that this is an upper limit only, and we return to this question below. In principle, we should also take into account superconducting fluctuations near T_c, but the magnitude of such effects is not well known. In the superconducting state, κ_e is found by extrapolating the normal-state values linearly to below T_c and using correction factors from Ref. 16, assuming that electron-phonon scattering dominates.

Since $\kappa_e \ll \kappa$ at all T, we concentrate our analysis on κ_p which is given by[1,8,15]

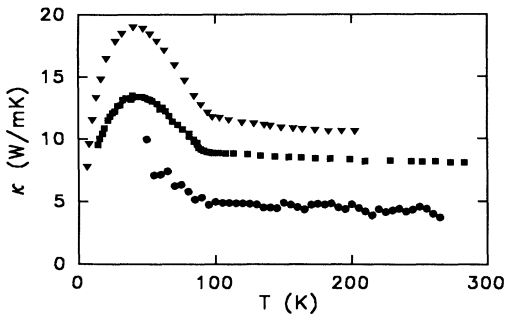

FIG. 2. Thermal conductivity κ for Y 1:2:3 vs T. ●: this work (sintered); ■: Ref. 11; ▼: Ref. 10 (in-plane κ of single crystals).

$$\kappa_p = T^3 \int_0^{\Theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x-1)^2} dx \ , \quad (1)$$

where $x = \hbar\omega/k_B T$ and τ is the relaxation time, given by

$$\tau^{-1} = \tau_b^{-1} + \tau_d^{-1} + \tau_e^{-1} + \tau_p^{-1} = A + BT^4 x^4 + CTxg(x, T/T_c) + DT^3 x^2 \exp(-\Theta_D/\alpha T) \ . \quad (2)$$

The terms describe scattering by boundaries, point defects, electrons, and phonons, respectively. We have excluded the effect of sheetlike faults[1,9,15] since Y 1:2:4 does not contain twins, and also the anisotropy correction[9,15] in Eq. (1) since we study a ceramic sample.

Initially, we used the standard[8,17,18] phonon-phonon scattering term DT^3x^2 in Eq. (2). However, although this gives the correct high-T limit $\kappa \propto T^{-1}$, it gives a constant κ_p below $0.25\Theta_D$ in contrast to the exponential increase due to freezing out of umklapp processes usually observed.[8] To improve the model we added the exponential factor in Eq. (2), as suggested in the literature.[8,17] Cohn *et al.*[11,19] and Peacor *et al.*[9,10] chose to use instead a term DT^4x^2, since this gave[19] the best fit to their data up to 180 K, but this implies $\kappa \propto T^{-1}$ at high T where they note that the term must be modified.[19] For Y 1:2:3 the difference is not very important, since the phonon thermal resistivity $W_p = \kappa_p^{-1}$ is dominated[9,19] by phonon-electron and phonon-defect scattering, but as shown below the phonon-phonon term dominates in Y 1:2:4.

We have fitted Eqs. (1) and (2) to our data for Y 1:2:4 after subtracting $\kappa_e = TL_0/\rho$, with and without the exponential term in Eq. (2), using values for T_c and the gap scaling parameter[1,15] χ in the ranges 75–79 K and 0.5–1.74, respectively, and using Θ_D as an adjustable parameter. For the exponential term, literature data for insulators suggest[8,17] $\alpha = 2.2$, but we also tried $\alpha = 1$, 5, and 10. To compare our results with those for Y 1:2:3 from Refs. 10 and 11, we have included in our fitting program subroutines written by Cohn. The results from the fitting procedure are shown in Table I and Fig. 3. Table I shows the values for Θ_D and the parameters A–D in Eq. (2) giving the best fit to the data for each type of phonon-phonon scattering term tried. We also show the relative rms difference $\Delta\kappa$ between the data and the fitted function, normalized such that $\Delta\kappa = 1$ corresponds to 0.23 W m^{-1} K^{-1} for the best fit. The statistically best fits were always obtained using $T_c = 79$ K and $\chi = 1$ (a BCS size gap), but in the range 50–80 K the slope $d\kappa/dT$ was best reproduced by $\chi = 0.7$. In Table I we also show the parameters given by Peacor *et al.*[9] for their two Y 1:2:3 samples, rescaled to correct for the different prefactors.

In Table I, two features are immediately apparent: First, for Y 1:2:4 the best fits are found using values for Θ_D significantly lower than those obtained from data for c_p; for Y 1:2:4, the average Θ_D between[13] 100 and 300 K is about 525 K, but using this value resulted in significantly larger differences between the data and the fitted functions, as shown also in Fig. 3. Also, the exponential phonon-phonon term with $\alpha = 5$ or 10 always gave the best results. Second, with an adjustable Θ_D the best fits were always found with $B = 0$. None of the fitted functions gave a perfect fit close to T_c (Fig. 3); this is a

TABLE I. Coefficients in Eq. (2) giving the best fit to our data for Y 1:2:4 and those from Refs. 9 and 10.

A (s^{-1})	B ($K^{-4}s^{-1}$)	C ($K^{-1}s^{-1}$)	D ($K^{-3}s^{-1}$)	Θ_D (K)	Relative $\Delta\kappa$	Phonon term
$YBa_2Cu_4O_8$						
76 991	0	309.5	5.0×10^{-2}	185	1.04	T^3x^2
79 631	0	326.9	1.0×10^{-4}	157	1.75	T^4x^2
87 258	0	282.6	4.5×10^{-2}	175	1	exp $\alpha=5$
41 391	3.76×10^{-4}	493.4	0.239	525	1.79	exp $\alpha=5$
$YBa_2Cu_3O_7$ single crystal (Refs. 9 and 10)						
159	1.18×10^{-3}	573.3	2.61×10^{-4}	380		T^4x^2 (sample 1)
108	2.30×10^{-3}	203.8	1.69×10^{-4}	380		T^4x^2 (sample 2)

common observation for high-T_c materials, and the deviations found are smaller than or similar to those observed in other works.[1-3,20] The model used seems unable to describe $\kappa(T)$ in this range, and more advanced models, such as that recently presented by Wermbter and Tewordt,[21] might give a T dependence closer to the observed behavior.

The fact that an exponential phonon-phonon term with a large α gives the best fit implies that in Y 1:2:4 umklapp scattering is important to very low temperatures, as also suggested by de Wette and Kulkarni[22] for Y 1:2:3. The model of Refs. 9–11 ($\tau_p^{-1}=DT^4x^2$) should[4] give results similar to those given by the exponential term at low T, but its stronger T dependence at high T does not agree with our experimental data. The fitted values of Θ_D, 155–185 K, are significantly lower than the value found from[13] c_p, which, however, takes into account all lattice modes, including high-energy optical phonons. Since most of the heat is carried by acoustical phonons[8] the effective Θ_D for heat conduction should be lower than 525 K. de Wette and Kulkarni[22] calculated an effective Θ_D of 140–185 K for the acoustical and the lowest optical branches for Y 1:2:3, and since dispersion curves for acoustical phonons in Y 1:2:3 and Y 1:2:4 are similar[23] the effective Θ_D for acoustical phonons should also be similar. We thus suggest that the low fitted values for Θ_D reflect the fact that acoustical phonons are responsible for the main part of κ_p. For comparison, we show in Table I the best result found using $\Theta_D=525$ K; the fitted parameters A–D still have physically acceptable values, but the rms deviation from the experimental data is 80% higher than that obtained with a low Θ_D.

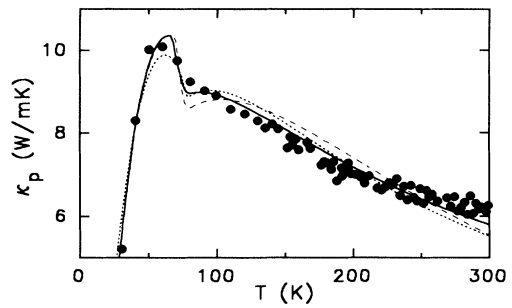

FIG. 3. Best fit for lattice thermal conductivity κ_p to Eq. (1) for Y 1:2:4. ●: experimental data; solid curve: $\Theta_D=175$ K; dotted curve: $\Theta_D=525$ K both with $\tau_p^{-1}=DT^3x^2\exp(-\Theta_D/5T)$; dashed curve: the best fit obtained with $\tau_p^{-1}=DT^4x^2$, $\Theta_D=157$ K.

The main difference between the fitted parameters for Y 1:2:3 and Y 1:2:4 is the size of the defect scattering term [parameter B in Eq. (2)]. For Y 1:2:3, this term dominates[9,19] κ_p and determines its magnitude at practically all temperatures, while for Y 1:2:4 we always found a best fit for $B=0$. Point defect scattering is thus much weaker in ceramic Y 1:2:4 than even in single-crystal Y 1:2:3, and we believe that this difference is due to the stable oxygen stoichiometry of Y 1:2:4 which makes oxygen defects very rare in Y 1:2:4 compared to Y 1:2:3. It has previously been observed[1,24] that κ_p decreases rapidly with increasing δ in Y 1:2:3 because of the increasing oxygen disorder. Since the point defect term in combination with electron or phonon scattering is very efficient[4] in reducing the magnitude of κ_p, the virtual absence of defects also explains why κ_p in Y 1:2:4 is much larger than in ceramic Y 1:2:3 and, near T_c, even larger than the in-plane κ_p of many single-crystal Y 1:2:3 samples.[1,11]

For phonon-electron coefficient C, Cohn *et al.*[19] state that neglecting the anisotropy term in (1) leads to values 40% higher than when this is included. Taking this into account, we find C is very similar in magnitude in Y 1:2:4 and Y 1:2:3, and the difference in $\kappa(T)$ is thus not due to a weak electron-phonon interaction in Y 1:2:4.

In principle, data for χ and the electron-phonon interaction parameter λ can be deduced from the κ measured near T_c, but the limited range between T_c and the boundary scattering regime, plus the small enhancement observed for our ceramic sample, make the analysis uncertain. As seen in Fig. 3, the true enhancement of κ_p is larger than shown in Fig. 1, since it is partly masked by the simultaneous drop in κ_e. It is thus important that accurate values for κ_e are used in the analysis. The values calculated from the Wiedemann-Franz law above are upper bounds only, and we have tried to improve upon this model. As a first step, we replaced the linear fit with a Bloch-Grüneisen electron-phonon resistivity term ρ_{ep} plus a residual resistivity term ρ_0, fitted as described before.[7] We then calculated κ_e from these data, using the Sommerfeld value for L_0 together with ρ_0 and a theoretical electronic Lorenz number L_e, calculated[4] from the Bloch-Grüneisen expression[8] for ρ_{ep} and the Motakabbir-Grimvall[25] expression for κ_e, together with ρ_{ep}, and found a significantly lower κ_e as shown in Fig. 4. However, reanalyzing our data for κ_p after subtraction of the modified data for κ_e we obtained results[4] very similar to those shown above.

As a result of this calculation, however, we suggest that in single-crystal samples κ_e might give rise to a measurable anomaly in κ below 120 K. We illustrate this by the third curve in Fig. 4, calculated for a hypothetical Y 1:2:4 material with electrical properties identical to those for our sample except for a strongly reduced ρ_0 (by 90%). With this small ρ_0, κ_e increases rapidly at low T according to the standard formula[8] $\kappa_e^{-1}=aT^{-1}+bT^2$. Although L_e also decreases rapidly with decreasing T the two effects balance, and the net result after multiplication by Geilikmann's correction factor [15] is a fairly sharp "step" anomaly in κ_e at about 25 K. The deviation from the almost linear $\kappa_e(T)$ in the standard model (see Fig. 4) is fairly large and might be observable in high-precision data for κ. In the case studied, the difference between a linear interpolation of the data and the true behavior is a peak of up to 0.4 $\mathrm{W\,m^{-1}\,K^{-1}}$ near 25 K. We suggest that this opens a possible way to test theories for electronic transport in high-temperature superconductors: If an anomaly of this type is observed at low T, with a magnitude and location that can be calculated from the measured electrical resistivity, this would be very strong evidence that the standard electron-phonon mechanism is operating in these materials. We note that unexplained cusplike anomalies have sometimes been observed[1] in this region for many HTS materials but have usually been ascribed to other mechanisms or to experimental errors. Unfortunately, Fig. 4 also shows that the residual resistivity of our sample is not low enough for us to carry out this simple test.

In conclusion, our measurements of κ in Y 1:2:4 show that its T dependence is unusual among high-T_c superconductors in being dominated by phonon-phonon interactions above T_c. Both phonon-phonon and phonon-electron interaction strengths are similar to those in Y 1:2:3, and the very different behavior is ascribed to the near absence of phonon-defect scattering in Y 1:2:4. The very low effective Θ_D indicates that acoustic phonons carry most of the heat current in these materials, and we show that agreement with theory can be much improved by taking umklapp scattering into account in the fitted phonon-phonon term. Finally, we have suggested a simple way to test available theories for charge and energy transport in high-T_c single-crystal material.

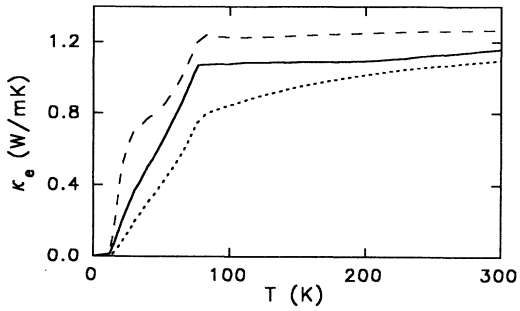

FIG. 4. Calculated electronic thermal conductivity κ_e. Solid curve: $\kappa=TL_0/\rho$ (same as in Fig. 1); dotted curve: calculated from fitted Bloch-Grüneisen model with theoretical L_e; dashed curve: same as dotted curve, but with a reduced ρ_0.

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