Thermal conductivity of polycrystalline $YBa_2Cu_4O_8$

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We have measured the thermal conductivity κ and the thermal diffusivity a of a dense bulk ceramic polycrystalline sample of $YBa_2Cu_4O_8$ (1:2:4) in the temperature range 30–300 K. We find $\kappa \approx 10$ $W m^{-1} K^{-1}$ at 100 K, significantly higher than in ceramic $YBa_2Cu_3O_{7-\delta}$ (1:2:3) and approaching the in-plane value for single-crystal 1:2:3, and decreasing to 7.6 $W m^{-1} K^{-1}$ at 300 K. The data for this sample can be described by standard theories for phonon thermal conductivity of crystalline materials with boundary, phonon, and electron scattering. The higher κ in 1:2:4 as compared to 1:2:3 is, in this model, due to the smaller point defect scattering in the former. The fitted parameters for the three scattering mechanisms all agree with independent estimates based on simple models; inserting data for electric resistivity, grain size, carrier density, and lattice properties we can predict κ and its T dependence to within about 20%. We also discuss models for the phonon and electron thermal conductivities in some detail, including some second-order effects such as inelastic electron scattering and a T-dependent carrier density.

I. INTRODUCTION

Studies of the thermal conductivity κ give valuable information on the interaction between charge carriers and phonons and on the scattering of both by defects and impurities. Since κ is also unusual in having a nonzero value in both normal and superconducting states there has recently been a surge of interest in data for κ in high transition temperature superconductors (HTS). Abundant data now exist for κ in both ceramic, polycrystalline material, and in single crystals of most HTS materials, in particular for $YBa_2Cu_3O_{7-\delta}$ (1:2:3), as discussed in several recent reviews.[1,2] However, because $YBa_2Cu_4O_8$ (1:2:4) is difficult to produce as a high-density bulk material or as large single crystals we know of no previous data for this material. We have, therefore, recently presented[3] data for κ in dense, bulk, ceramic, polycrystalline 1:2:4 as a function of temperature T over the range 30–310 K. The data were briefly discussed in terms of available theories, and we showed that $\kappa(T)$ was surprisingly different in 1:2:4 and 1:2:3 in spite of the very similar crystal structure. At all T, phonon-phonon interactions give rise to a much larger thermal resistivity in 1:2:4 than do electron-phonon interactions, while point-defect scattering was found to be negligible, probably because of the stable oxygen stoichiometry of 1:2:4. In contrast, point-defect scattering dominates κ completely[4,5] in 1:2:3, even for single crystals.

We give here a more complete analysis of our data. Our most important conclusion is that, contrary to several recent reports,[6,7] the BCS-based semiclassical theory[1] used here is able to describe $\kappa(T)$ for our 1:2:4 sample very accurately; even the magnitudes of the three dominating scattering terms agree with those given by simple estimates. Although we show that the agreement between theory and experiment can be improved even further by taking into account second-order effects such as inelastic electron scattering, fluctuations, and a possible change in carrier density with T, we believe that the basic thermal transport properties of our sample can be well described by this theory, particularly if realistic phonon data are used.

The paper is structured as follows: In Sec. II we describe the sample and the experimental methods used. This is followed by a brief account of our experimental results in Sec. III. Section IV describes the theoretical model used, in particular models for the phonon-phonon interaction and Umklapp scattering, and we discuss the interaction of point-defect scattering with other scattering mechanisms. In Sec. V we then discuss our experimental results in terms of the theory just presented. The results for each scattering mechanism are discussed separately, and we compare the results with the simplest possible theoretical models for phonon and electron transport. Finally, we present our conclusions in Sec. VI.

II. EXPERIMENTAL DETAILS

A. Material synthesis and characterization

Dense bulk polycrystalline ceramic material was produced by hot isostatic pressing (HIPing) a mixture of CuO and 1:2:3 powders in Ar, using a glass container to avoid losing oxygen as described previously.[8] The material was characterized by x-ray diffraction and the diffraction spectrum was in excellent agreement with literature data.[9] No peaks attributable to unreacted starting materials were found, but optical micrography indicated the possible presence of small CuO inclusions and showed the sample to be an aggregate of randomly

oriented grains with typical dimensions $20\times20\times2$ μm^3. The porosity was less than 2%, in agreement with the measured density d which was indistinguishable from the theoretical value. Near the surface of the HIPed cylinder macroscopic cracks opened during cooling because of the difference in thermal expansivity between the glass and the 1:2:4. For the measurements of κ, a rod with dimensions $0.7\times0.9\times13.8$ mm^3 was therefore cut along the axis of the cylinder where the homogeneity was best. The measured electrical resistivity ρ was 630 $\mu\Omega$ cm at 300 K, in excellent agreement with our previous data for nominally identical material.[10] The onset transition temperature T_c was 79 K with a transition width of about 4 K.

B. Measurements of thermal conductivity and thermal diffusivity

To obtain the best possible accuracy in κ over the range 30–310 K two different methods were used. Below 160 K we measured κ by the standard longitudinal steady-state method.[1,11,12] However, in this method thermal radiation can lead to serious overestimates of κ at high T (Refs. 1, 4, and 11–14), and above 70 K we therefore used instead the standard version of Ångström's temperature wave method, which, in principle, eliminates heat-loss effects. This method actually measures the thermal diffusivity a, but κ can be found from $\kappa=adc_p$, where c_p is the specific-heat capacity.

All measurements were carried out in a vacuum of about 2×10^{-5} mbar near 300 K and very much better near 100 K. The sample was provided with a heater in one end and was attached at the other to a copper heat sink to which all wires were thermally anchored, and which could be screwed to the inside of a Cu chamber in the cryostat. In the steady-state method, κ was measured over a distance of 5.3 mm on the sample using calibrated type-K thermocouples, 50 μm in diameter. The heater power was calculated from measured currents and voltages, and the data were corrected for Joule heating in, and heat conduction along, connecting wires. A theoretical estimate showed radiation losses to be negligible ($<1\%$) below 100 K. To eliminate a small apparent background in ΔT the heater was switched periodically with a period of several minutes, much larger than the observed time constant of the sample. Measurements with different input powers gave practically identical results, and the data shown below were obtained with $\Delta T\approx2$ K between the thermocouples. Below 50 K, the corrections were more than 20% of the measured values and we believe the data in this region to be the least accurate.

The thermal diffusivity a was measured using Ångström's method,[11,12,15] i.e., calculating a from the attenuation and phase shift of a temperature wave between two points on the sample. In this experiment the two points were separated by about 1 mm, the signal period was in the range 4–30 s, and we used equipment and methods described by Jacobsson and Sundqvist.[16] Because of the high power used we could not reach $T<70$ K with this method, and the resulting large dT/dx might also smear the sharp changes in $d\kappa/dT$ often observed[1,2] near T_c. With this method the experimental error in κ increases at low T, since dc_p/dT increases with decreasing T and small errors in T can then give large errors in κ. c_p was measured between 250 and 350 K, in which range our data differed by a factor of 1.040 ± 0.002 from literature data.[17] Below 250 K we therefore used the data of Ref. 17, multiplied by this constant to match ours. In some experiments we found a to depend on signal frequency and the surrounding medium (air or vacuum). This problem was expected[18] because of the small sample and its low a, but the magnitude of the problem was unexpectedly large which was traced to heat storage effects in the adhesive holding the thermocouples in place. Using the theory of Ref. 18 we could reproduce qualitatively the errors and show them to be below 1% under the conditions used in later runs. One set of measurements was also made using a related two-frequency method[19] with the sample immersed in solidified castor oil, and thus completely different boundary conditions; both methods gave the same results. In the final runs, heater periods of 4–20 s gave indistinguishable results, and we believe that this method gives a significant improvement in experimental accuracy above 200 K compared to the steady-state method.

For both methods the dominating source of systematic experimental error was the uncertainty in sample dimensions and thermocouple distances. We estimate maximum errors of ±5 and ±10% from geometrical errors for the steady-state method and Ångström's method, respectively. To these figures should be added T-dependent errors smaller than ±3% for the steady-state method, while for κ obtained using Ångström's method we estimate a maximum T-dependent error of ±2% at 300 K and ±4% near 150 K. As shown below, the rms statistical scatter in both methods is below 2% and the measured T dependence is therefore much more accurate than the magnitudes of κ.

III. EXPERIMENTAL RESULTS

Figure 1 shows ρ as a function of T for our sample. The data are very similar to previous data[10] and, as be-

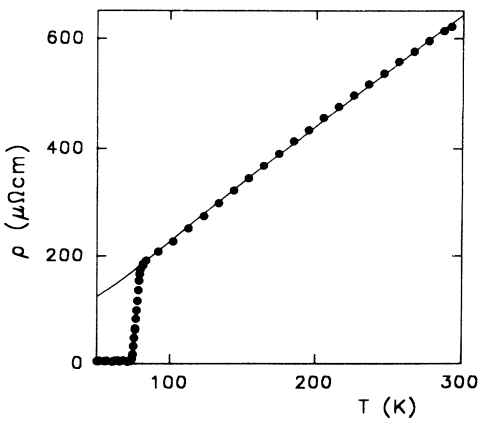

FIG. 1. Electric resistivity ρ vs T. Solid curve is a Bloch-Grüneisen function fitted to the data.

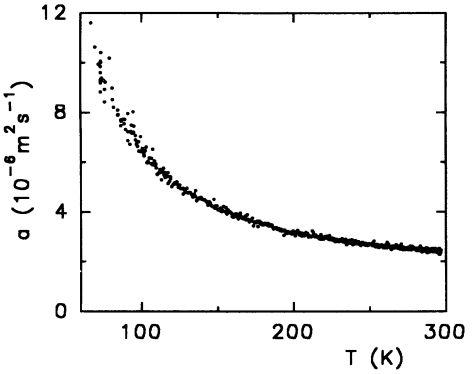

FIG. 2. Thermal diffusivity a as a function of T from one experiment.

fore, a Bloch-Grüneisen expression for phonon limited resistivity could be fitted to the data with excellent results. With an effective Debye temperature $\Theta_D=276$ K and a residual resistivity $\rho_0=99.3$ $\mu\Omega$ cm the rms deviation between the data and the fitted function (shown in the figure) was 2.5 $\mu\Omega$ cm. As before, the addition of a parallel resistivity term[10] $\rho_{\rm par}=4.4$ mΩ cm significantly improved the fit. In the present case we attribute this term to conduction through c-axis-oriented grains in the polycrystalline sample, but an intrinsic saturation behavior cannot be ruled out.[20] With $\rho_{\rm par}$ included, the other fitted parameters become $\Theta_D=389$ K and $\rho_0=132$ $\mu\Omega$ cm, and the fit became visibly better with an rms deviation of 1.6 $\mu\Omega$ cm. The measured ρ at 300 K corresponds[10] to an in-plane resistivity near 400 $\mu\Omega$ cm, in reasonable agreement with single-crystal[21] and thin-film[22] data.

In Fig. 2 we show a as a function of T, while final data for κ were given in Fig. 1 of Ref. 3. Below 140 K we used data obtained by the steady-state method, while above 140 K we calculated κ from a. In the region 70–160 K, where both methods were used, the magnitudes of κ agreed to within the combined errors while the average $d\kappa/dT$ differed by about 10%. Data from the two sets were multiplied with suitable constants to match at 140 K. We know of no other data for either a or κ in 1:2:4 and we refer to Ref. 3 for a comparison with data for 1:2:3, in both single-crystal and sintered, polycrystalline form. We note that the magnitude of κ in our ceramic 1:2:4 sample is very similar to the in-plane κ of 1:2:3 near 100 K, while for sintered 1:2:3 κ is significantly lower, 3–5 $\mathrm{W\,m^{-1}K^{-1}}$. Also, for 1:2:4 κ decreases by 26% in going from 100 to 300 K, while for single crystal 1:2:3 κ depends weakly on T for $T>T_c$. (For melt-processed 1:2:3 a decrease in κ similar to that found here has been observed.[5]) The differences between the data for κ in 1:2:3 and 1:2:4 are also reflected in similar differences between the data for a in 1:2:4 (Fig. 2) and those for 1:2:3 (for example, from Refs. 23).

IV. THEORETICAL MODEL

A. Lattice thermal conductivity

Neglecting unusual mechanisms, such as vortex convection or pair condensation-evaporation transport believed to exist[1] in the superconducting state, κ can be written as the sum of an electronic thermal conductivity κ_e, discussed in the next section, and a phonon thermal conductivity κ_p. In HTS materials κ is dominated by κ_p, and we analyze our data for κ_p using a model based on BCS theory,[24] applied to HTS materials by Tewordt and Wölkhausen[25] and used in most works since.[1–5] In this model,

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

where $x=\hbar\omega/k_BT$ and $\tau(x,T)$ is a relaxation time. We have included the usual prefactors[1,4,25] in τ, which we write

$$\begin{aligned}\tau^{-1}&=\tau_b^{-1}+\tau_d^{-1}+\tau_e^{-1}+\tau_p^{-1}+\tau_s^{-1}\\&=A+BT^4x^4+CTxg(x,T/T_c)\\&\quad+Df(x,T)+ET^2x^2\ .\end{aligned} \tag{2}$$

The terms describe phonon scattering by boundaries, point defects, electrons, phonons, and sheet defects, respectively, and $g(x,T/T_c)$ is the ratio between the relaxation times in the normal and superconducting states. We neglect the effects of sheetlike faults[1,25] since 1:2:4 does not contain twins, although it might contain stacking faults. We tried several times to add such a term to the fitted functions but always found a best fit with $E=0$. We also exclude the anisotropy correction[1,4] to the electron-phonon term, since we study a polycrystalline sample, and effects of unusual scattering centers such as

TABLE I. Limiting low- and high-T behavior of the lattice thermal conductivity λ_p for the different scattering mechanisms and models discussed in the text.

Scattering agent	Inverse relaxation time τ^{-1}	Low-T limit	High-T limit
Boundaries	A	$\lambda_p=26T^3/A$	$\lambda_p=\theta_D^3/3A$
Electrons	CTx	$\lambda_p=7.2T^2/C$	$\lambda_p=\Theta_D^2/2C$
Phonons (standard model)	DT^3x^2	$\lambda_p=3.3/D$	$\lambda_p=\Theta_D/DT$
Phonons (Peacor *et al.*[a])	DT^4x^2	$\lambda_p=3.3/DT$	$\lambda_p=\Theta_D/DT^2$
Phonons (Umklapp freeze)	$DT^3x^2\exp(-\Theta_D/\alpha T)$	$\lambda_p=3.3[\exp(\Theta_D/\alpha T)]/D$	$\lambda_p=\Theta_D/DT$
Sheet defects	ET^2x^2	$\lambda_p=3.3T/E$	$\lambda_p=\Theta_D/E$

[a]Reference 4.

tunneling states.[1] Fluctuation effects may be important near T_c, since a decrease in carrier density decreases the electron scattering rate and thus increases κ_p above that given by the model, but as discussed by Cohn *et al.*[14] no theory yet exists for such effects on κ_p.

To illustrate the effects of various scattering terms we define phonon thermal resistivities W_{pi} ($i=b$, d, e, p, and s) as the resistivity $W_{pi}=\kappa_p^{-1}(\tau=\tau_i)$ found from (1) if only a single scattering mechanism is active. We show in Table I the low- and high-T behavior of four of these terms, excluding the point-defect term which can only dominate at intermediate T. (We define W_p as the total phonon thermal resistivity $W_p=\kappa_p^{-1}$.)

For the phonon-phonon interaction term $f(x,T)$ we tried several models which we discuss in some detail, since this mechanism dominates[3] κ in 1:2:4. The standard model[11,26,27] $f=T^3x^2$ gives $\kappa_p \propto T^{-1}$ at $T>\Theta_D$, but below about $\Theta_D/4$ it gives a constant κ_p, while experiments show[11] an exponential increase due to freezing out of Umklapp processes. We have thus added a factor $\exp(-\Theta_D/\alpha T)$ as suggested in the literature;[11,26] the constant α varies the effective Umklapp cutoff temperature, and data for insulators[11,26] suggest $\alpha\approx 2.2$. Instead of an exponential term, Cohn *et al.*[5,13] and Peacor and co-workers[4,28] use $f=T^4x^2$ since this gave[5] the best fit to the low-T data. However, such a term gives $\kappa_p \propto T^{-2}$ at high T which does not agree with experiments. Florent'ev *et al.*[29] even use $f=T^5x^2$, giving $\kappa_p \propto T^{-3}$ at high T.

We illustrate the differences between the terms in Fig. 3, showing calculated values for W_{pp} vs T/Θ_D for the "classical" term $\tau_p^{-1}=DT^3x^2$, the modified term DT^4x^2 used by Peacor *et al.*,[4] and two terms $DT^3x^2\exp(-\Theta_D/\alpha T)$, one with $\alpha=2.2$ as for insulators[11,26] and one with $\alpha=5$ to shift the Umklapp cutoff to $T\ll\Theta_D$, thus giving $W_{pp}\propto T$ down to very low T. Data are shown for $0\le T\le 2\Theta_D$ and normalized such that $W_{pp}=1$ at $T=\Theta_D$. The behavior observed experimentally, $W_{pp}\propto T$ at high T and an exponential decrease below, is only shown by the exponential terms, but Fig. 3 suggests a reason why Peacor and co-workers[4,28] and Cohn and co-workers[5,13] could successfully use $\tau_p^{-1}=DT^4x^4$: Below $0.5\Theta_D$ this term has a T dependence very similar to that of the exponential term.

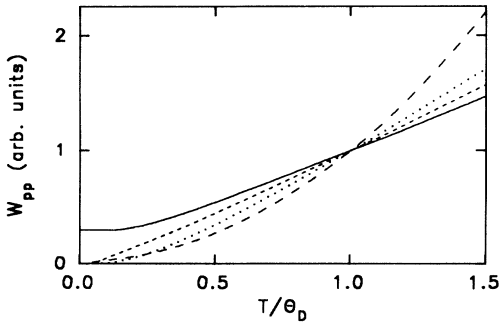

FIG. 3. Calculated phonon-phonon thermal resistivity W_{pp} vs T/Θ_D for different models of the function $f(T,x)$. Solid curve: $f=T^3x^2$, long dashes: $f=T^4x^2$, dotted and short dashes: $f=T^3x^2\exp(-\Theta_D/\alpha T)$, dotted with $\alpha=2.2$ and short dashes with $\alpha=5$.

For ρ we can assume that terms due to different scattering mechanisms add to give $\rho=\rho_{ep}+\rho_0$ (Matthiessen's rule). This is *not* true for W, except[11] in the rare case that normal phonon-phonon scattering dominates κ. We illustrate this in Figs. 4(a)–4(c) which show calculated data for W_{pi}, as defined above, vs T/Θ_D. Figure 4(a) shows $\kappa_{pe}=W_{pe}^{-1}$ and $\kappa_{pp}=W_{pp}^{-1}$, both normalized to 1 at $T=\Theta_D$ by a suitable choice of the parameters C and D. If Matthiessen's rule is valid we can calculate κ_p by adding thermal resistivities, such that $\kappa_p=(W_{pe}+W_{pp})^{-1}$ (dashed curve in the figure), i.e., $\kappa_p=0.5$ at $T=\Theta_D$. Carrying out the calculation using

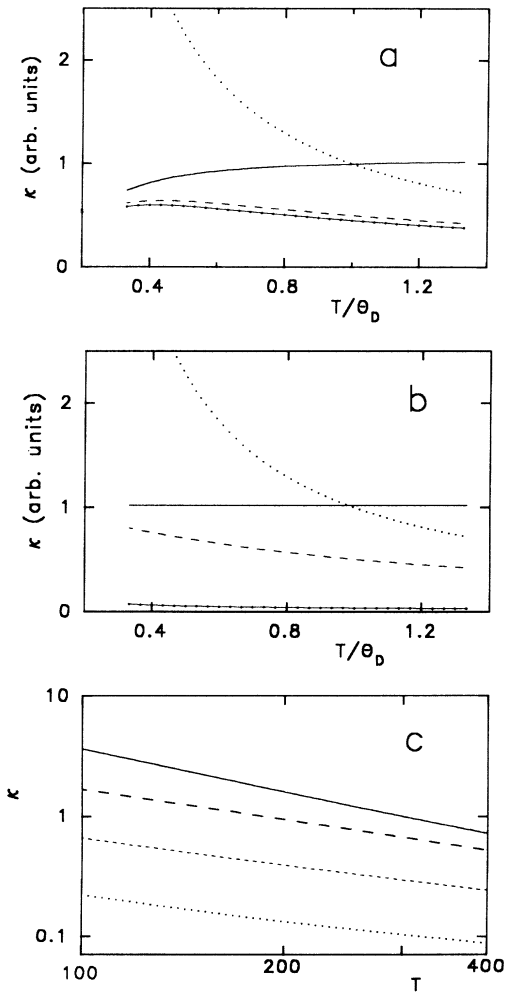

FIG. 4. Calculated data for relative κ_p vs T/Θ_D. (a) Solid curve: W_{pe}^{-1}, dotted: W_{pp}^{-1}. Dashed curve is $(W_{pe}+W_{pp})^{-1}$ while dot-dashed is calculated from Eq. (1) using $\tau^{-1}=\tau_e^{-1}+\tau_p^{-1}$. (See text for details.) (b) Same as (a), but with point-defect scattering instead of electron scattering. (c) Full curve: W_{pp}^{-1}. The curves below show the effect of adding increasing amounts of point-defect scattering, from the top down corresponding to $W_{pd}=0.1$, 1, and 10% of W_{pp} at 300 K. Note logarithmic axes.

(1) we find $\kappa_p = 0.45$ at this T, and the result thus agrees with Matthiessen's rule to within about 10%. This is not so if we replace W_{pe} by W_{pd} [Fig. 4(b)]. The dashed curve shows the result expected from Matthiessen's rule, but adding point-defect scattering to phonon scattering actually cuts κ_p down to 0.035 at Θ_D, hardly distinguishable from zero on the scale of the figure. Adding W_{pd} to W_{pe} in the same way we find an even smaller $\kappa_p = 0.009$. The effect is *not* a simple scaling effect, in which case we could still use an "effective" Matthiessen's rule. From a large number of calculations with $W_{pd} \leq W_i$ we find that the addition of point-defect scattering can be approximated by functions of the type $W_{\text{tot}} = W_i[1 + G(W_{pd})^{\varepsilon}/W_i]$, with $G = 109$ and $\varepsilon = 0.66$ for $i = pe$ and $G = 28$, $\varepsilon = 0.53$ for $i = pp$. The total W is strongly nonlinear in W_{pd} and when we combine defect scattering with a T-dependent scattering mechanism not only the magnitude of W but also the slope dW/dT are changed. This is illustrated by Fig. 4(c) showing the effect of adding increasing amounts of point defects to a sample initially dominated by phonon-phonon scattering. We use a log-log plot to underline that the initial T^{-1} dependence of κ_p is transformed into a $T^{-\beta}$ dependence, with $\beta < 1$. Small amounts of impurities or defects can thus have very large nonlinear effects on the total κ and depress its value much more than a naively expected, even modifying its expected functional dependence on T, as recently found[30] for solid C_{60}. We thus cannot write $W = W_{pd} + W_{pe} + W_{pp}$ when strong defect scattering is present, and the analyses of κ in 1:2:3 by Yu *et al.*[6] and others[31] along these lines are of doubtful value.

B. Electronic thermal conductivity

In the normal state, κ_e is 10–15 % of the total κ for our sample. Although we shall devote most of our analysis to the dominant term κ_p, it is necessary to have an accurate model for κ_e in order to find the true magnitude of κ_p.

Although other models have been suggested,[6,7] it is usually assumed that κ_e can be calculated reasonably accurately from ρ, using Wiedemann-Franz' law. As a first approximation we have thus used the expression[11] $\kappa_e = TL_0/\rho$ above T_c. Since ρ extrapolates to $\rho \approx 0$ at $T = 0$, $\kappa_e \approx 1$ W m^{-1} K^{-1} is then[3] almost independent of T. Below T_c, κ_e is found by extrapolating ρ and using correction factors from Geilikman, Dushenat, and Chechetkin.[32] However, as shown previously[3] this procedure gives an upper limit only, since we have not taken inelastic electron scattering into account,[11] and we showed[3] that the exclusion of such an effect leads to significant errors. Depending on the model used, our calculations showed that κ_e may be up to 40% lower at T_c than given by the standard model. We also predicted that 1:2:4 samples with a very low ρ_0 may show a small but detectable anomaly in κ_e near 30 K, whose existence might be used as a tool to distinguish between different theories for κ in HTS's. However, Jiang and Carbotte[33] recently found a very similar anomaly in κ_e arising from anisotropic scattering in layered materials, and if such an anomaly is found it might thus be difficult to identify the mechanism responsible.

In principle we should also take into account superconducting fluctuations near T_c, but this is a small effect: Cohn *et al.*[14] find its magnitude to be $< 1\%$ of the total κ even for single crystal 1:2:3 with κ_e twice as large as that of our sample. Finally, we note that the BCS-based model used here is not generally accepted, and that other models exist. Geilikman, Dushenat, and Chechetkin[32] predict that pair condensation decreases κ_e, but both experimental[6] and theoretical[7] studies exist which claim that the peak observed in κ below T_c is due, at least in part, to an increase in κ_e.

V. DISCUSSION

A. Fitting procedure and general results

We have fitted Eqs. (1) and (2) to our data for κ_p, found by subtracting κ_e from the total κ. Several models were used: We have used both models for κ_e discussed above, all three models for τ_p discussed in Sec. IV A (with $\alpha = 1$, 2.2, 5, and 10), and values for T_c and the gap-scaling parameter[1,25] χ in the ranges 75–79 K and 0.5–1.74, respectively. We have also used Θ_D as an adjustable parameter because, first, the effective Θ_D found from the fit to $\rho(T)$ was much lower than the average value 525 K found from[17] c_p between 100 and 300 K, prompting us to look for similar effects in κ_p, and second, the standard model for W_{pp} could not describe κ_p vs T well with $\Theta_D = 525$ K. The latter effect was traced to the constant low-T W_{pp} given by this model (see Table I and Fig. 3), and to improve the fit we tried a lower Θ_D.

Since the number of data points per unit temperature varies with T (Fig. 1 of Ref. 3), a fit to all points overestimates the importance of the high-T data and forces the fitted function to agree with these at the expense of the data near and below T_c. We have thus fitted Eq. (1) to a data set where most of the high-T data have been deleted. The fitting routine was based on a nonlinear gradient search method, forcing all parameters to remain nonnegative. When the best fit was found with one parameter equal to zero we deleted the corresponding term in (2) to speed up the final fitting procedure. To ensure that our results would be directly comparable with those of Peacor *et al.*[4] for 1:2:3 we used in our program subroutines for $g(x, T/T_c)$ written by Cohn of this group and communicated by Uher at the University of Michigan.

The results from this procedure are shown in Table II and in Fig. 5. Table II lists the values for Θ_D and parameters A–D found to give the best fit to the data for each model. (Data for the exponential τ_p with $\alpha = 10$ were almost identical to those for $\alpha = 5$.) The quality of the fit is indicated by the relative rms differences $\Delta\kappa$ between our data and the fitted functions. Since we used a reduced data set, $\Delta\kappa$ does not relate directly to the data shown in Ref. 3, but $\Delta\kappa = 1$ as given for the best fit corresponds to a difference of 0.23 W m^{-1} K^{-1} rms between the experimental data and the fitted function. We made several attempts to include a sheet-defect term but always found

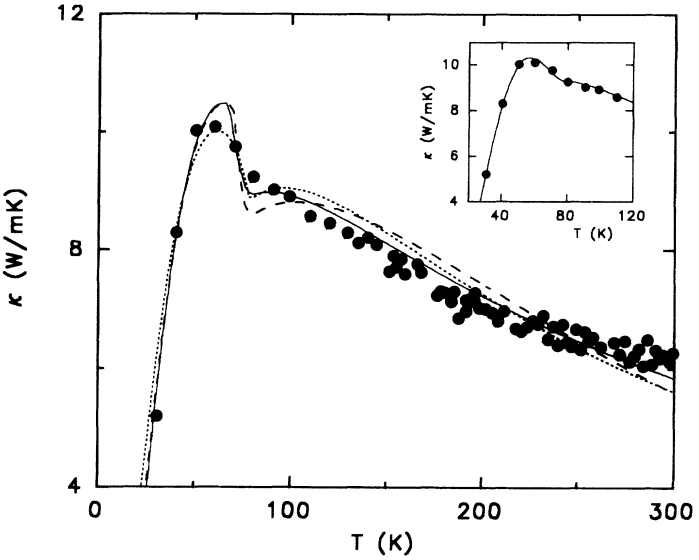

FIG. 5. Lattice thermal conductivity κ_p of $YBa_2Cu_4O_8$ vs T. Dots are experimental data and curves show fitted functions: Dashed curve — best fit with $f=T^4x^2$ ($\Theta_D=156$ K), solid curve — best fit with $f=T^3x^2\exp(-\Theta_D/5T)$ ($\Theta_D=176$ K). As a comparison, dotted curve shows result with same f as solid curve but with $\Theta_D=525$ K. Inset shows an alternative fit over a smaller range in T (see text).

the best fit for $E=0$. Also, the best fits were always found with $T_c=79$ K and $\chi=1$, i.e., a BCS gap, and except for one case all data in the table were found using these parameters in the fit. Since we used Θ_D as a free parameter, we also show for several of the models corresponding results for $\Theta_D=525$ K (as found from c_p) for comparison.

For comparison we have also fitted single-crystal 1:2:3 data given by Peacor and co-workers[4,28] (sample 1, data read from figures) to our model, i.e., excluding the anisotropy correction, but including sheet-defect scattering. Table II shows both the parameters given by Peacor

TABLE II. Parameters Θ_D and A–E in Eqs. (1) and (2) for different models and data sets, as obtained from the fitting procedure. $\Delta\kappa$ is the relative rms difference between data and the fitted function; as discussed in the text, for 1:2:4 $\Delta\kappa=1$ corresponds to about 0.23 $W\,m^{-1}\,K^{-1}$ rms. Except stated otherwise, all data for 1:2:4 were found using $T_c=79$ K and $\chi=1$. Data given here differ slightly from the preliminary results in Ref. 3, since different sets of data points were used.

Θ_D (K)	A	B	C	D	E	$\Delta\kappa$	Model for $f(x,T)$
$YBa_2Cu_4O_8$, our sample, with $\kappa_e=TL_0/\rho$:							
156	7.7×10^4	0	3.3×10^2	9.9×10^{-5}		1.76	T^4x^2
187	7.7×10^4	0	3.4×10^2	5.0×10^{-2}		1.06	T^3x^2
156	7.9×10^4	0	3.0×10^2	4.7×10^{-2}		1.35	$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=1$
163	8.2×10^4	0	2.7×10^2	4.2×10^{-2}		1.09	$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=2.2$
176	8.7×10^4	0	3.1×10^2	4.5×10^{-2}		1.02	$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=5$
525[a]	1.7×10^4	8.1×10^{-4}	3.5×10^2	4.1×10^{-4}		2.56	T^4x^2
525[a]	8.1×10^3	3.3×10^{-4}	59	0.18		2.76	T^3x^2
525[a]	3.8×10^4	4.0×10^{-4}	5.1×10^2	0.23		1.75	$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=5$
230[b]	1.1×10^5	0	3.9×10^2	0.12			$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=5$
145[c]	6.7×10^4	0	2.7×10^2	2.3×10^{-2}		0.91	$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=5$
$YBa_2Cu_4O_8$, our sample, with inelastic corrections in κ_e:							
150	6.9×10^4	0	2.5×10^2	1.0×10^{-4}		1.80	T^4x^2
193	7.4×10^4	0	3.0×10^2	5.6×10^{-2}		1.05	T^3x^2
182	8.8×10^4	0	2.8×10^2	5.0×10^{-2}		1.00	$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=5$
525[a]	4.1×10^4	3.3×10^{-4}	4.6×10^2	0.25		1.73	$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=5$
$YBa_2Cu_3O_{7-\delta}$ (Sample 1 of Ref. 4):							
380[a,d]	159	1.2×10^{-3}	5.7×10^2	2.6×10^{-4}	0.54		T^4x^2
370	26	1.1×10^{-3}	4.2×10^2	2.5×10^{-4}	1.26	(1.15)	T^4x^2
220	50	9.3×10^{-4}	4.9×10^2	2.2×10^{-2}	0.95	(1.77)	T^3x^2
285	31	1.6×10^{-3}	2.3×10^2	8.3×10^{-2}	1.06	(1.0)	$T^3x^2e^{-\theta_D/\alpha T}$, $\alpha=2.2$

[a]Constant Θ_D, not optimized for best fit.
[b]Curve shown in the inset of Fig. 5; fitted with $\chi=0.95$.
[c]Model with a T-dependent carrier density as shown in Fig. 7.
[d]Data taken from Ref. 4 and rescaled with the corresponding prefactor in Eq. (1).

et al.[4] and those obtained here. Excluding the anisotropy term does not significantly change the results for the point-defect and phonon scattering, while the electron-phonon term changes by about 30%.

From Table II we find several interesting results: (i) For 1:2:4, the best fits are found with Θ_D significantly *lower* than 525 K; a similar, but smaller Θ_D reduction is found for 1:2:3; (ii) the best fits were found using $f=T^3x^2\exp(-\Theta_D/5T)$, but with a variable Θ_D, $f=T^3x^2$ gives very similar results; (iii) with a variable Θ_D the best fits were always found *without* point-defect scattering ($B=0$); (iv) taking inelastic scattering into account in κ_e improves the fit very little and does not change the fitted parameters much, and (vi) with a variable Θ_D the parameters obtained in different models are surprisingly similar, with variations rarely larger than $\pm 15\%$ from the average values. These results are discussed in detail below. However, none of the best fits reproduced the data well close to T_c, as shown in Fig. 5. That a global "best" fit deviates rather strongly from the data close to T_c is observed in many studies, and deviations similar to those shown are found in other recent works.[4,34] However, we found that very good fits could be found over smaller ranges in T with the same model by choosing different parameter values, as shown in the inset in Fig. 5. Here, a lower χ and a higher Θ_D than those giving the global best fit were used, and $\Delta\kappa$ was large because of large high-T deviations (Table II). However, the fitted function is in excellent agreement with the data near and below T_c.

The fitted parameters are very stable with respect to the choice of model, and different selections of data points in the set gave very similar results. That the results for the two models for κ_e agree so well is surprising, considering that the magnitudes of κ_e differ by up to 40% in the sensitive range near T_c and give rather different $d\kappa_p/dT$:s in this range. The large number of free parameters give shallow minima in $\Delta\kappa$, particularly for the five-parameter fit for 1:2:3, and it was possible to co-vary two or more parameters by fairly large amounts without a large increase in the residual. For the three-parameter fits for 1:2:4 at low Θ_D, however, the minima were well defined. The uncertainties in the fitted $A-E$ might be as large as 10–50 % depending on parameter and the functions used, but the repeatability was excellent and repeating a fit the same final parameters were obtained. In the sections below, we discuss results for each parameter separately.

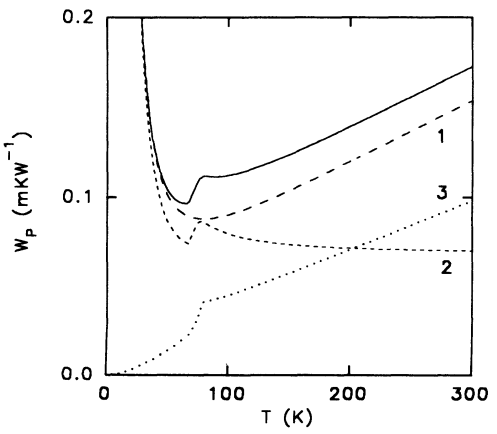

FIG. 6. Phonon thermal resistivity W_p vs T (full curve). Lower three curves show results obtained by removing one scattering mechanism at a time: 1—no electron scattering, 2—no phonon scattering, 3—no boundary scattering.

B. Phonon-phonon scattering

The relative importance of the different scattering terms can be found from Fig. 6. Inspired by Fig. 3 of Ref. 4 we show the total thermal resistivity W_p plus the results obtained when removing one scattering mechanism at a time from the fitted function. Boundary scattering clearly dominates κ_p up to 200 K, above which phonon scattering becomes more important, while electron scattering has only a small effect except near 100 K, where it is comparable with phonon scattering in importance. Different models for τ_p give very similar results, with the exception of the term $f=T^4x^2$, which always gives the worst fit (Table II). With low values for Θ_D, all functions except T^4x^2 give the same T^{-1} dependence for κ_p above the peak and the exponential Umklapp cutoff at low T cannot be observed. However, with $\Theta_D=525$ K as originally used, the Umklapp cutoff starts above T_c, and in this case the addition of an exponential term does give a significant improvement (Table II). The high optimum value for $\alpha(=5)$ might indicate that Umklapp scattering is important to very low T in the complicated lattice of 1:2:4, as recently suggested by de Wette and Kulkarni[35] for 1:2:3.

The fact that the fitted values for Θ_D (150–195 K) are significantly lower than data from c_p (Ref. 17) was discussed in Ref. 3, and we concluded that since most of the heat is carried by acoustical phonons,[1,11,36] the effective Θ_D for heat conduction should be lower than that obtained from c_p which includes high-energy optical modes. This is partly verified by de Wette and Kulkarni,[35] who calculated Θ_D for the acoustical branches for 1:2:3 and found values in the range 140–185 K, significantly lower than those (330–460 K) found taking all modes into account. Θ_D varies strongly with T, since the actual phonon spectrum[37] of 1:2:4 is anything but Debye-like, and we note again that we can obtain an excellent fit to our data over limited ranges in T by an appropriate choice of Θ_D (see inset in Fig. 5). For comparison, we show in Table II results for $\Theta_D=525$ K; the fitted $A-D$ are still physically acceptable, but the rms deviation from the experimental data is more than 50% higher than that obtained with a low Θ_D.

One should be very cautious trying to deduce physical results from statistical fits with several independent parameters, and we must ask whether the present results are significant. First-principles calculations of κ_p using realistic models are possible for simple materials[27] but not for such complicate structures as those for HTS's. Slack[36] gives a simple expression for W_{pp} in crystals with a complicated lattice,

$$W_{pp} = A_o \gamma^2 n_c^{2/3} T (M a_0 \Theta_D^3)^{-1} , \quad (3)$$

where M is an average atomic weight, a_0 is the cube root of the atomic volume, n_c is the number of atoms per unit cell, A_o is a constant, and γ the Grüneisen parameter. Here, γ is usually approximated by $\gamma = \beta V K / c_v$, where β is the volume thermal expansivity, V is the atomic volume, and K is the bulk modulus, while for Θ_D we take the high-T limit. The model takes only longitudinal acoustic phonons into account, and for $n_c > 3$ calculated values may differ by a factor of 5–8 from experimental data even for cubic materials.[36] For 1:2:4 at 300 K we have[38] $\beta = 35 \times 10^{-6}$ K^{-1} and[39] $K = 112$ GPa, and approximating c_v by c_p we find $\gamma = 1.43$. From the fitted value for D and Eqs. (1)–(2) we find an "experimental" value for W_{pp} of approximately 2.7×10^{-4} T mK W^{-1}, while inserting the high-T limit[17] $\Theta_D = 545$ K into Eq. (3) we find 3.4×10^{-4} T. Alternatively, we should perhaps use $\Theta_D \approx 200$ K for acoustic phonons at high T, giving an order-of-magnitude change in W_{pp}, but we must then also use the correct γ for these phonons, which we have not found in the literature. Considering the simplicity of the theory, the fitted value for D is physically reasonable and actually in surprisingly good agreement with theory.

C. Defect and boundary scattering

The main difference between 1:2:3 and 1:2:4 in terms of the fitted parameters is the size of the defect-scattering term. In 1:2:3, this term[4,5] dominates κ_p and determines its magnitude at practically all T. Such strong defect scattering will also depress the slope $d\kappa_p/dT$ below that expected when phonon-phonon scattering is present [see Fig. 4(c)], as observed for $d\kappa_p/dT$ in 1:2:3. For our 1:2:4 sample we always found a best fit for $B = 0$, except when using high, fixed values of Θ_D giving a low-quality fit. As discussed before,[3] we believe that the stable oxygen level in 1:2:4 gives a weaker point-defect scattering in sintered 1:2:4 than even in single-crystal 1:2:3, in agreement with the fact[14,40] that κ_p decreases with increasing δ in 1:2:3. Since point-defect scattering interacts with electron or phonon scattering to reduce strongly the magnitude of κ_p (Sec. IV A), the virtual absence of oxygen defects thus explains both why κ_p in our sintered 1:2:4 sample is larger than in sintered 1:2:3 and, near T_c, even larger than the in-plane κ_p for many single crystal 1:2:3 samples,[1,13] and why $d\kappa_p/dT$ is different in the two materials.

Because of the small grains, boundary scattering dominates κ_p over a large range in T. In Fig. 6 we see that the importance of boundary scattering equals or exceeds that of phonon-phonon scattering at $T < 200$ K, and that it is always more important than the electron-phonon term. No large increase can thus occur in κ_p below T_c. To check our model we have calculated an average grain size L from the fitted value for A in Eq. (2). A comparison with expressions given by Tewordt and Wölkhausen[25] shows that

$$A = 2\pi (4\pi/3)^{-1/3} \hbar a^2 (\Theta_D / k_B)^2 L^{-1} ,$$

where a is an average lattice constant. Inserting a typical value $A = 7 \times 10^4$ we find an effective grain diameter of 6 μm, in agreement with the experimental value (Sec. II A). Because of the small point-defect term, κ should be very high in single crystal 1:2:4 below T_c. This should be important in technical applications where the high-T stability of 1:2:4 would be an added bonus.

D. Phonon-electron scattering

Our results for C differ from those given by Peacor *et al.* for 1:2:3, but the difference is mainly due to the different models. Cohn *et al.*[5] state that neglecting the anisotropy term in (1) leads to values for C 40% lower than when this is included, in good agreement with our result. C is similar in magnitude in 1:2:4 (250–340) and in single crystal 1:2:3 (230–490), and the difference in $\kappa(T)$ is thus *not* due to a weaker electron-phonon interaction in 1:2:4, as might be naively inferred from the data. In theory, D should be independent of sample processing, while C should vary with carrier density (or δ). In terms of W_{pe} the free-electron model predicts[11]

$$W_{pe} T/\rho = \pi^2 n_a^2 / 3 L_0 . \quad (4)$$

W_{pe}/ρ should thus increase with the number n_a of free carriers per atom (i.e., with increasing carrier density n or decreasing δ), but data[5] for single-crystal and melt-processed 1:2:3 tend to show the inverse behavior, with W_e/ρ increasing with increasing δ. We might argue that free-electron theory cannot describe 1:2:4 or 1:2:3, but even in better models we expect $\rho \propto n^{-1}$ and $W_{pe} \propto n$, and the deviations from the proportionality $W_{pe}/\rho \propto n^2$ are thus difficult to explain. Possibly, the use of a better approximation than $\tau_p^{-1} = T^4 x^2$, as used by Cohn *et al.*, might give C values that agree better with theory. We expected the high ρ of our sample (compared to single crystal 1:2:3) and the higher carrier density[41] in 1:2:4 to give a higher W_{pe} for 1:2:4, but this is not found, probably because the free-electron model is too crude to allow comparisons between materials. However, applying (4) to our data gives $n_a = 0.081$ holes per atom or $n = 6 \times 10^{21}$ cm^{-3}, in excellent agreement with $n = 0.27$ (CuO$_2$ unit)$^{-1} = 5.4 \times 10^{21}$ cm^{-3} found from band-structure calculations.[41] The fitted magnitude of D is thus quite reasonable.

Hall-effect measurements show a strong T dependence[42] of the Hall coefficient R_H below 150 K in 1:2:4, sometimes interpreted as an increased in n by a factor of 2–3 from T_c to 150 K. This would imply a similar increase in W_{pe} which, if true, should cause a more rapid decrease in κ_p with T than predicted by (1) and a smaller $d\kappa_p/dT$ above 150 K. Such an effect is, in fact, observed (Fig. 5). To test this we added an "adjustment factor" $F(T)$ to the electron-phonon term such that $\tau_e^{-1} = CFTxg(x, T/T_c)$; F simulated $n(T)$ as given by $R_H(T)$ by taking $F = 1$ for $T > 150$ K, then decreasing linearly from 1 to 0.2 between 150 and 70 K. As shown in Fig. 7 and Table II this modification gave an improvement in $\Delta\kappa$ by about 11% and, in fact, gave the best fit observed to the data. Surprisingly, it thus seems that the T dependence of n is real and has a measurable effect on

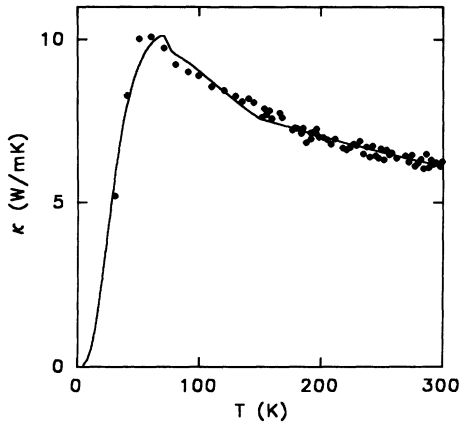

FIG. 7. Same as Fig. 5, except that a model with a T-dependent carrier density was used in the fit (see text for details).

κ_p. However, there are strong arguments against this interpretation: (i) The carrier density $(1-4)\times10^{22}$ cm^{-3} given[42] by R_H is much larger than that found from theory.[41] Since there are several bands at E_F in 1:2:4 there is no simple relation between n, $R_H(T)$, and dn/dT. (ii) Even without this modification $\Delta\kappa$ is similar in magnitude to the experimental uncertainty, and, as for the effect of inelastic scattering on κ_e, it is questionable whether we can take the result at face value, and (iii), a T-dependent n should also modify ρ, which is fitted very accurately by a (constant-n) Bloch-Grüneisen model. On the other hand, anomalies in ρ *are* observed[21] in this range of T, there *is* recent optical[43] evidence for a T-dependent n in 1:2:3 and Bi 2:2:1:2, a combination of hole-hole scattering and a linear increase in n with T *might* give $\rho \propto T$, and if band-structure effects give a T-dependent R_H, such effects might also modify $W_{pe}(T)$. Weighing the evidence, however, we prefer to view this interesting result as a probable coincidence.

Near T_c, finally, fluctuation effects might give important effects on the electron-phonon term since the formation of hole pairs would reduce the scattering rate and thus decrease W_{pe}. As shown by Fig. 5, the model gives too low values for κ_p near T_c and a fluctuation correction would improve the fit. However, we have not pursued this question for lack of theoretical models for the effect of fluctuations on κ_p.

E. Thermal conductivity under high pressure

Very recently, we have also measured[44] κ as a function of p for the same sample. Our measurements show that κ increases slowly with p above 150 K, but decreases below. We estimated the p dependence of the three scattering terms in κ_p from simple theories, finding that the boundary scattering term should vary slowly with p and that the phonon-phonon scattering term W_{pp} should decrease by about 6% per GPa (i.e., κ_p should increase). For the electron-phonon term the situation is more complicated: For a "normal-metal"-type model, C should decrease with increasing p, but if the rapid drop in ρ is due to an increase in n with p due to charge transfer, C should increase. $d\kappa_e/dp$ was calculated from $d\rho/dp$ through the Wiedemann-Franz law, as before. These estimates turned out to predict the p dependence of κ very accurately in the high-T range, where phonon and boundary scattering dominate, and if we assumed a strong charge transfer with p we could also explain qualitatively the negative $d\kappa/dp$ found below 150 K.

VI. CONCLUSIONS

We have shown that κ in a sample of dense, bulk $YBa_2Cu_4O_8$ is surprisingly different from that found in the very similar material $YBa_2Cu_3O_{7-\delta}$. Analyzing the data in a semiclassical model, we attribute this difference mainly to the fact that oxygen vacancies are much less common in 1:2:4 than in 1:2:3 because of the well-defined oxygen stoichiometry of the former.

Fitting the data for κ_p to our model we obtain a very good fit from 30 to 300 K, with rms differences between data and the fitted function of 2–3 %, similar to the estimated maximum T-dependent measurement errors. The parameters obtained in the fit are very stable with different choices of terms in the model and with different selections of data points. Even more important, all parameter values obtained are in surprisingly good agreement with the results of simple estimates: From the fitted values, we calculate a theoretical grain size which is within 20% of the observed value and a carrier density within 10% of the band-structure value, and the phonon-phonon thermal resistivity obtained from the fit agrees with Slack's theoretical model to within 20%. Stating this in another way, the results show that we could have *predicted* κ and its T dependence to within better than 20%, using this model and known parameters such as n, Θ_D, γ, grain size, etc. The model is also able to predict[44] the correct p dependence of κ, and to explain the change in sign of $d\kappa/dp$ near 150 K.

However, the difference between the data and the fitted function shows a systematic trend with T, and the fitted function predicts a sharper anomaly at T_c than seen experimentally. Originally we attributed this to the model, and assumed that a better fit could only be obtained using a more advanced model, by including the effect of superconducting fluctuations near T_c, or perhaps even using models based on other types of excitations. However, the fit in this region could be significantly improved by small modifications of the fitting parameters (see inset in Fig. 5); in fact, an excellent fit could be obtained in this way over any "small" range in T with $\Delta T = 50-150$ K. We now believe that the problem lies on a more basic level: The Debye lattice model used is not a good approximation for either 1:2:3 or 1:2:4, as evident from the real problem spectrum[37] and from the strong T dependence of Θ_D given by data[17] for c_p. We believe that an even better agreement with theory would be obtained if we either used the real phonon spectrum or allowed Θ_D to vary with T. A small fluctuation term might also be present very close to T_c and, as shown above, an improved fit

could also be obtained by assuming that the carrier density varied with T below 150 K, or by improving the treatment of κ_e by including inelastic scattering. However, we believe that the main source for the deviations observed is the simplified treatment of the lattice properties of 1:2:4.

Our most important conclusion is thus that our data for κ as a function of T and p can be explained by semiclassical theory, with no need for alternative models.[6,7] This may be due to the fact that κ_p in our sample is limited mainly by boundary and phonon scattering, for both of which a good theory exists. A more severe test of the theory would be measurements on a single crystal, in which case electron-phonon scattering would be much more important. Such a study would give interesting information on the carrier-phonon interaction in HTS's, especially since the effects of point defects on κ_p should be much smaller than in 1:2:3. Also, as shown in Ref. 3, such a study might also help solve other basic questions regarding transport in high transition temperature superconductors.

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