Journal of Alloys and Compounds, 195 (1993) 655–658
JALCOM 7551

Defects and the thermal conductivity of $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_4O_8$.

B.M. Andersson and B. Sundqvist

Department of Experimental Physics, Umeå University, S-90187 Umeå, Sweden*.

Abstract

We present below the first measured data for the thermal diffusivity and the thermal conductivity, λ, of dense, sintered ceramic $YBa_2Cu_4O_8$ (1-2-4) as a function of temperature T between 40 and 310 K. At 300 K, λ is 6.3 $Wm^{-1}K^{-1}$, increasing with decreasing T to about 9.5 $Wm^{-1}K^{-1}$ near T_c. This T dependence is much stronger than in $YBa_2Cu_3O_{7-\delta}$ (1-2-3). Only a very small enhancement is observed in λ below T_c. As in 1-2-3, λ is mainly limited by phonon scattering by defects.

1. Introduction*

The thermal conductivity λ is one of the few physical properties of a material that has a non-zero value in both the superconducting and the normal state and thus can be studied in both cases. Since λ also carries information on both the charge carriers and the phonons, and the scattering of both by each other, by defects, and by other excitations, it is not surprising that a large number of studies of λ have recently been carried out [1] on high transition temperature superconductors (HTS).

Most studies of λ have been carried out on $YBa_2Cu_3O_{7-\delta}$ (1-2-3) in either ceramic or single crystal form. We present below the first data for $YBa_2Cu_4O_8$ (1-2-4) which is more difficult to produce in the form of large, dense samples, and which has thus not been studied previously. These data are analysed here in terms of accepted theories, and it is shown that λ is mainly limited by phonon scattering by defects in the normal state. Since low-T measurements are still in progress, we postpone the discussion of the superconducting state to a more complete report published elsewhere [2].

2. Experimental details and results

The 1-2-4 material was produced by hot isostatic pressing a mixture of 1-2-3 and CuO powders as described previously [3]. The sample was cut along the axis of a hot pressed cylinder and had approximate dimensions 0.7x0.9x13.8 mm^3. As before, its porosity was smaller than 1.5%, and both T_c (79 K) and the measured electrical resistivity ρ (600 μΩcm at 295 K) were in good agreement with the results found in a previous study [4].

λ was measured directly using a steady state longitudinal ("four probe") method at low T (< 100 K). At higher temperatures, where radiation errors can be very large for this method, we measured instead the thermal diffusivity *a*, defined as $a = \lambda/dc_p$, where d is the density and c_p the specific heat capacity. The method used was Ångström's classical temperature wave method [5] and the experimental setup has been described in detail elsewhere [6]. λ was then calculated from the measured data for *a* using literature data [7] for c_p versus T. This method gives a very high accuracy for *a*, but the accuracy in the data for λ also depends on the accuracy of the data for c_p used, and since *a* varies rapidly with T (figure 1) a careful temperature calibration is very important. In the present case the experimental error is estimated to be below ±5% for both methods. More details will be given in Ref. 2.

Figure 1 shows typical experimental data for *a* as a function of T, and figure 2 shows data for λ calculated from *a*. Because of the very large number of data points collected in each run a random selection only is shown. For comparison we also include data for single crystal 1-2-3 from Ref. 8 in figure 2. We note that at 100 K, λ in our ceramic 1-2-4 sample equals the in-plane value for this particular 1-2-3 single crystal, and that the T dependence of λ is stronger in 1-2-4 than in 1-2-3. We have also measured *a* and λ for dense, sintered 1-2-3, produced by a similar hot pressing procedure but with a larger porosity. In that case we find a practically constant λ = 4.5 $Wm^{-1}K^{-1}$ from 100 to 300 K, then rapidly rising below 90 K, in excellent agreement with literature data for ceramic material with similar structure [1]. Only a very small enhancement of λ is found below T_c in 1-2-4;

* This work was financially supported by the Swedish Natural Science Research Council and by the Swedish National Board for Technical Development.

0925-8388/93/$06.00

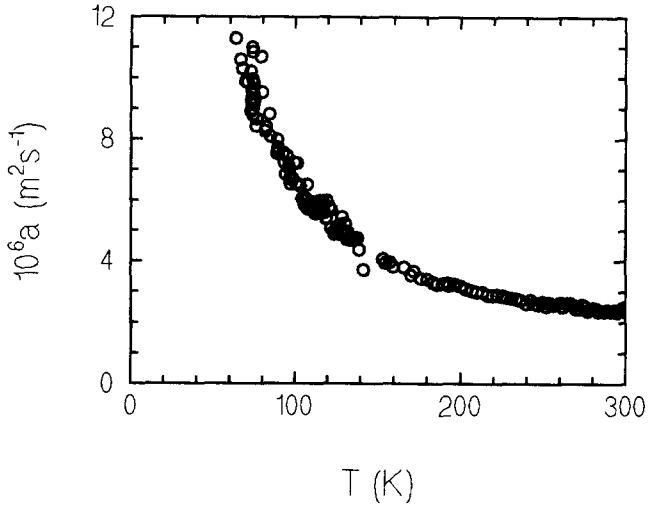

Figure 1. Thermal diffusivity a versus T for 1-2-4.

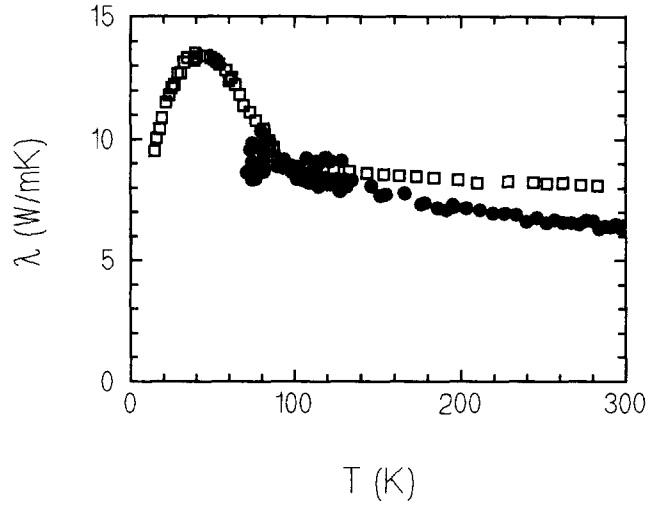

Figure 2. Thermal conductivity λ versus T. ● - 1-2-4 , (this work), □ - single crystal 1-2-3 (from Ref. 8).

figure 3 shows preliminary data obtained by the steady state method in this range. Further data for 1-2-4 in the superconducting state will be shown in Ref. 2.

3. Discussion

3.1. Theoretical model

We discuss the results for λ presented above in terms of accepted models. Both phonons and electrons (holes) carry thermal energy, and transport by phonons usually dominates λ in HTS [1]. The total λ can be written $\lambda = \lambda_p + \lambda_e$, where p denotes phonons and e electrons. It is usually assumed that λ_e can be calculated approximately

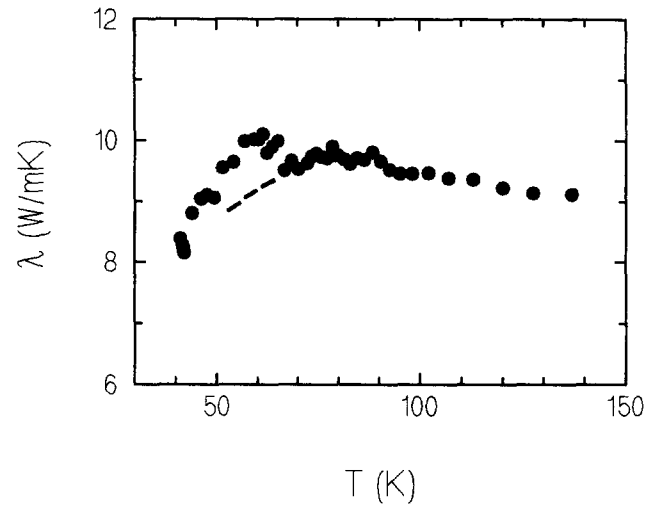

Figure 3. Thermal conductivity vs. T near T_c. Dashed line extrapolates the normal state behaviour.

from the standard expression $\lambda_e = L_0 T/\rho$, where L_0 is the Lorenz number and ρ the electrical resistivity. However, this expression will overestimate λ_e at low temperatures because of the neglect of inelastic scattering [9].

The lattice thermal conductivity can be written [1,10]

$$\lambda_p = T^3 \int_0^{\Theta/T} \frac{\tau(x,T) x^4 e^x dx}{(e^x - 1)^2}, \qquad (1)$$

where Θ is the Debye temperature, $x = \hbar\omega/kT$ and the total relaxation time τ is given by

$$\tau^{-1} \equiv A + BT^4x^4 + CTxg(x,y) + DT^3x^2\exp(-\Theta/\alpha T). \qquad (2)$$

All numerical prefactors have been included in Eq. (2), in which the four terms describe scattering by boundaries, defects, electrons (holes), and phonons, respectively; g is a function describing the ratio of electron-phonon scattering in the normal and superconducting states, and α is a numerical constant. The phonon-phonon term given above differs from that given by Uher [1] and coworkers [8,11,12]: The standard approximation is [13] DT^3x^2 giving $\lambda_p \propto 1/T$ at high T. In Refs. 8,11 and 12, a term DT^4x^2 is used, because this is found to give the best fit close to T_c, but this form gives $\lambda_p \propto 1/T^2$ at high T. The standard expression, on the other hand, leads to a constant λ_p as $T \to 0$, in contrast to the exponential increase actually observed [9]. The exponential factor is often introduced to solve these problems, and fits to experimental data for insulators

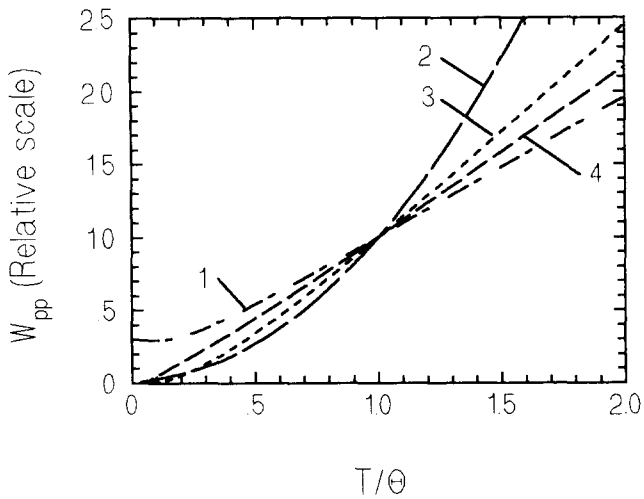

Figure 4. Calculated phonon-phonon thermal resistivity W_{pp} vs. T/Θ. Curves show W_{pp} as given by τ^{-1} = 1: DT^3x^2, 2: DT^4x^2, 3 & 4: $DT^3x^2\exp(-\Theta/\alpha T)$, with α = 2.2 (curve 3) and 5 (curve 4).

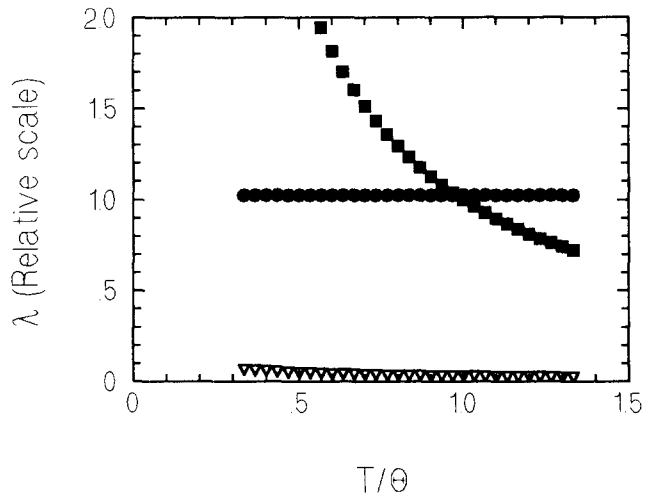

Figure 5. Calculated thermal conductivity λ vs. T/Θ.
● - defect scattering only, ■ - phonon scattering only, ▽ - both mechanisms acting.

usually give $\alpha \approx 2.2$ [9].

To illustrate this, we define an effective thermal resistivity W_{pi} (i = b,d,e, or p) as $W_{pi} = (\lambda_{pi})^{-1}$, where λ_{pi} is calculated from Eq. (1) using only one single term in Eq. (2) for τ. Thus, W_{pp} corresponds to the thermal resistivity that would be observed if phonons were *only* scattered by other phonons, such that, for example, $\tau^{-1} = \tau_{pp}^{-1} = DT^3x^2$. In figure 4, we show calculated values for W_{pp} vs. T/Θ using four different expressions for τ_{pp}: The "classical" [13] term $\tau_{pp}^{-1} = DT^3x^2$, the modified term [1,8,11,12] DT^4x^2, and two terms $DT^3x^2\exp(-\Theta/\alpha T)$, one with α = 2.2 as often found experimentally [9], and one with α = 5 which gives $W_{pp} \propto T$ to a very good approximation at all T. Calculated data are shown for $0 \le T \le 2\Theta$ and normalised such that W_{pp}=1 at T=Θ. Experimentally it is observed that $W_{pp} \propto T$ at high T and decreases exponentially towards zero at low T, as Umklapp processes freeze out [9]; of course, only the two terms containing an exponential strictly show this behaviour. Figure 4 also suggests that the reason for the very good fit to experimental data near T_c (0.2 - 0.25Θ) observed by Uher and others for $\tau^{-1} = DT^4x^4$ is that this term is very similar in magnitude to the experimentally found [9] exponential term with $\alpha \approx 2.2$ discussed above.

For the electrical resistivity ρ it is usually assumed that we can add components due to different scattering mechanisms, such that $\rho = \rho_{ep} + \rho_0$ (Matthiessen's rule). This is not generally true for the thermal resistivity $W = \lambda^{-1}$, as is easily shown by calculating λ from Eq. (1). Figure 5 shows calculated data for λ_{pd} and λ_{pp} (as defined above) as functions of T/Θ, both normalized to 1 at T=Θ. In this particular case we used an exponential term with α = 5 in λ_{pp}; similar results were found using other parameters. If both phonon and defect scattering acted simultaneously and Matthiessen's rule were valid, the total λ would be 0.5 at T=Θ. Carrying out the calculation using the same values for constants B and D as before, we find instead λ = 0.035, hardly distinguishable from zero on the scale of the figure. In the corresponding case with electron-phonon and defect scattering we find an even smaller λ = 0.009. This is *not* a simple scaling effect: In the particular cases studied, the total W can be very well approximated by the functions $W_{tot} = W_{pe} + 109W_{pd}^{0.66}$ and $W_{tot} = W_{pp} + 27.7W_{pd}^{0.53}$, respectively. Adding defect scattering thus also changes the slope of W vs. T. If phonon-phonon and phonon-electron scattering act together, on the other hand, we find Matthiessen's rule to be approximately valid (to within about 10%). The presence of even small amounts of impurities or defects can thus have very large non-linear effects on the total λ and depress its value much more than naïvely expected. It is thus not possible to write the total thermal resistivity $W = W_{pd} + W_{pe} + W_{pp}$ when strong defect scattering is present, and the recent analysis of λ in 1-2-3 by Yu et al. [14] along these lines is thus doubtful.

3.2 Analysis of data for 1-2-4

We have fitted Eq. (1) to the preliminary normal-state data shown in figure 2 for 1-2-4, after subtracting $\lambda_e = L_0T/\rho$. We postpone the analysis of the range near and below T_c to a later publication [2] and concentrate

here on the range above 80 K. For the phonon-phonon scattering we used the exponential modification of the "classical" term, with α=2.2 as suggested by experiments on insulators.

Since λ decreases more rapidly with increasing T than in 1-2-3, we would expect that the ratio between the phonon-phonon and the phonon-electron scattering terms would be larger for 1-2-4. With the model discussed above, we find a best fit for Θ = 325 K, and with the parameters B = 3.0×10^{-2}, C = 2.13, and D = 6.55×10^{-3}. (Boundary scattering was not included in this model.) A direct comparison with the data for 1-2-3 from Refs. 8 and 11 is made difficult by the different models used. A simple way to do this, however, is to calculate the phonon thermal resistivity W_p using the above parameters, but putting each separately equal to zero to see the effect of removing each scattering mechanism. This was done by Peacor et al. [13] for single crystal 1-2-3, with results shown in their figure 3. Carrying out the same type of analysis, we find that the phonon thermal resistivities of 1-2-4 and 1-2-3 are limited by the same mechanisms. Both are completely dominated by point defect scattering at all temperatures. Near 200 K, phonon-phonon scattering and phonon-electron scattering contribute equally to the total thermal resistivity in both material; as expected, phonon-phonon scattering gives a larger contribution to W_p near 300 K.

Further measurements are being carried out in the range close below T_c. The very small enhancement of λ observed in this range is most likely caused simply by the approach to the boundary scattering regime, but further data are needed in order to verify this.

References

1 C. Uher, J. Supercond., **3** (1991) 337.
2 B.M. Andersson et al. (to be published).
3 J. Niska et al., J. Mater. Sci. Lett., **9** (1990) 770.
4 B.M. Andersson et al., Physica C, **170** (1990) 521.
5 A.J. Ångström, Ann. Phys. Chem., **64** (1861) 513.
6 P. Jacobsson and B. Sundqvist, J. Phys. Chem. Solids **49** (1988) 441.
7 A. Junod et al., Physica C, **168** (1990) 47.
8 J.L. Cohn et al., Phys. Rev. B, **45** (1992) 511.
9 R. Berman, Thermal Conduction in Solids, Clarendon, Oxford, 1976.
10 L. Tewordt and Th. Wölkhausen, Solid State Commun., **70** (1989) 839.
11 S.D. Peacor et al., Phys. Rev. B, **44** (1991) 9508; J.L. Cohn et al., Physica C, **192** (1992) 435.
12 S.D. Peacor et al., Phys. Rev. B, **43** (1991) 8721.
13 S. Pettersson, Phys. Rev. B, **43** (1991) 9238; P.G. Klemens, Solid State Physics, **7** (1958) 1.
14 R.C. Yu et al., Phys. Rev. Lett., **69** (1992) 1431.