Thermal conductivity of partially substituted $YBa_2Cu_3O_{7-\delta}$

R. K. Williams, P. M. Martin, and J. O. Scarbrough
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6116
(Received 24 August 1998; revised manuscript received 29 October 1998)

Partially substituted $YBa_2Cu_3O_{7-\delta}$ (Y123) samples are produced by replacing part of the Y with appropriate rare-earth elements and/or part of the Ba with Sr. Partial substitution has little effect on the normal-state resistivity or superconducting transition temperature, but should reduce the phonon part of the thermal conductivity, λ_p. Ambient temperature measurements on several polycrystalline samples show a thermal conductivity, λ, reduction relative to Y123. The effect persists to lower temperatures and data for Y123 and $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$ show that the λ peak at $T_c/2$ is also affected. [S0163-1829(99)03918-1]

INTRODUCTION

Several studies[1–3] have shown that the thermal conductivity λ of $YBa_2Cu_3O_{7-\delta}$ (Y123) does not undergo a sudden change at the superconducting transition temperature T_c, and reaches a maximum at roughly $T_c/2$. The two explanations that have been proposed for this behavior are (a) enhancement of the phonon conductivity due to the disappearance of phonon scattering by the unpaired electrons and (b) electronic energy transport at temperatures well below T_c. At present the electronic-transport mechanism that is based on *d*-wave superconductivity[4–8] appears to be more generally accepted.

In a recently published study[9] of the thermal conductivity of $YBa_2Cu_4O_8$ (Y124) we suggested that both electrons and phonons make significant contributions to the λ of superconducting Y124 and Y123. For Y123, it seemed that the relative roles of phonons and electrons might be experimentally identified by making λ measurements on partially substituted Y123. The purpose of this paper is to report λ measurements on several Y123 materials in which Sr replaces some of the Ba and Dy or Yb replaces some of the Y. In particular, the measurements on $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$ show that interesting low-temperature effects can be produced by partial substitution.

SAMPLE PREPARATION AND PROPERTIES

The polycrystalline Y123 and partially substituted Y123 samples were prepared by mixing and grinding the oxides, firing in oxygen at 950 °C, regrinding to form a sinterable powder that was then pressed into pellets and sintered at 950 °C. Phase purity, as determined by x-ray diffraction was generally greater than 99% and carbon contents as low as 80 ppm were obtained. Examination by scanning electron microscopy–energy dispersive x-ray analysis showed that, at least to the scale of 1 μm, the samples were solid solutions. Density and room-temperature resistivity values for the samples are shown in Tables I and II. Resistivity data obtained before and after the λ measurements were obtained show that the samples degraded in the vacuum environment. Resistivity-temperature data obtained after the low-temperature λ measurements are shown in Fig. 1. These results showed zero resistance T_c values of 89 and 87.2 K for Y123 and $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$. Descriptions of the two thermal conductivity measurement devices that were employed have been presented previously.[9,10]

EXPERIMENTAL RESULTS

Ambient temperature λ data for five partially substituted Y123 samples are shown in Fig. 2. Data for three Y123 samples[11] are included for comparison. Barium carbonate was used to prepare these samples and carbon contents were typically 800–1500 ppm. The best sample[2] contained a slight excess of Ba, 2.005. Excess Ba lowers the resistivity of Y123. Lower-temperature data for Y123 and $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$ are shown in Fig. 3. Data from the cut-bar λ apparatus are included in Fig. 3. The results for two measurements on samples from different batches of partially substituted Y123 differ by 4%.

DISCUSSION

The data presented in Fig. 2 show that partial substitution reduces both the magnitude and temperature dependence of the λ. The resistivities of these samples varied from 638 to $1100\times10^{-8}\ \Omega$ m, but the λ data do not show much correlation with resistivity. This indicates that the phonon λ component λ_p dominates. Using the Sommerfeld-Lorenz number L_o to make a correction for the electronic component λ_e, yields estimates of λ_p for Y123 and the partially substituted samples.

At 295 K, the average λ_p value for Y123 is 2.73

TABLE I. Characteristics of cut-bar thermal conductivity samples.

Nominal Composition	Density (% Theoretical)	Room Temperature Resistivity[a] ($10^{-8}\ \Omega$ m)
$Y_{0.5}Yb_{0.5}Ba_{1.4}Sr_{0.6}Cu_3O_{7-\delta}$	89.8	1077
$Y_{0.5}Yb_{0.5}Ba_{1.4}Sr_{0.6}Cu_3O_{7-\delta}$	90.1	1101
$Y_{0.2}Dy_{0.8}Ba_{1.4}Sr_{0.6}Cu_3O_{7-\delta}$	87.9	638
$DyBa_{1.4}Sr_{0.6}Cu_3O_{7-\delta}$	85.7	695
$Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$	97.5	883

[a]Corrected for porosity.

TABLE II. Characteristics of samples used for low-temperature measurements.

Sample Composition	T_c[a] (K)	Room Temperature[b] Electrical Resistivity (10^{-8} Ω m) Initial[c]	Final[c]	Density (% Theoretical)	Room Temperature Absolute Secbeck Coefficient[d] (μV K^{-1})
$YBa_2Cu_3O_{7-\delta}$	88.8	871	3407	95.9	2.38
$Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$	87.2	1082	1792	96.0	−0.20

[a]Measured resistively after the λ data had been generated.
[b]Corrected to theoretical density.
[c]Values measured before and after the thermal conductivity data were taken.
[d]Measured after the λ data had been generated.

$W\,m^{-1}\,K^{-1}$ (±3%). This agreement shows that the variation in λ values for the three samples is probably due to differences in the electronic component. Calculation of λ_p for the sample prepared from BaO yields a value at least 10% greater than the average value for the three carbonate process samples. For the partially substituted samples the λ_p values are 10–30 % lower. Presumably this reduction is associated with phonon-point defect scattering but it should be noted that the reduction does not correlate very well with composition. The largest λ_p reduction was observed for $DyBa_{1.4}Sr_{0.6}Cu_3O_{7-\delta}$.

The lower-temperature λ data are shown in Fig. 3. The λ values for Y123 reach a maximum at $0.3T_c$ and the maximum has usually been observed at about $0.5T_c$.[2,3] Also, our maximum λ value is about twice as large as the earlier results. Our apparatus was tested by making measurements on a NIST[9] standard, so there is not much reason to doubt their validity. One explanation for this difference is that we had a better (lower carbon) sample than those available to earlier investigators. Previous studies on both metallic elements and insulating compounds have shown that the λ maximum can increase and shift to lower temperatures as the defect concentration is reduced. Our results on Y124 (Ref. 9) also seem to show this behavior.

The Yb for Y partial substitution reduces the maximum λ by ~50% and the maximum value occurs at $\sim 0.5T_c$. One explanation for this reduction is that point-defect scattering persists to low temperatures, which requires a low characteristic temperature. An analysis[9] of the λ data for Y123 suggests that this may be the case. The λ_p estimates shown in Fig. 4 also suggest a low characteristic temperature and strong point-defect scattering. These λ_p estimates were obtained by correcting for electronic transport by using the resistivity data shown in Fig. 1 with L_o. For $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$ the result is that λ_p is reduced relative to Y123 and the temperature dependence becomes weaker. Callaway's model[12] predicts this kind of behavior. Extrapolating this two-component description of the normal-state data down to ~50 K yields λ values that agree with the experimental data. The λ_e estimates fall slowly as the temperature is lowered and they were graphically extrapolated to ~50 K. The λ_p extrapolations were based on Fig. 4.

At lower temperatures the λ data for both samples vary as T^n, where $n \sim 0.4$. This has also been reported by Cohn *et al.*[3] and is similar to the T dependence found for $YBa_2Cu_4O_8$.[9] This behavior may be due to the presence of unpaired charge carriers that can transport energy and scatter phonons.[9]

The results that have been presented suggest that the Y123 λ peak has a phonon component. To test this further requires additional data on other Y-Yb compositions, and also data for partially substituted Y123 containing a lighter rare earth such as Nd. Phonon-point defect-scattering theory predicts the composition and mass-difference dependence of the λ_p, and assuming that λ_e remains unaffected would allow an experimental separation of λ_e and λ_p. Another approach might be to change λ_e without changing λ_p. Unsubstituted Nd123 is not a line compound[13] and Nd^{+3} ions on

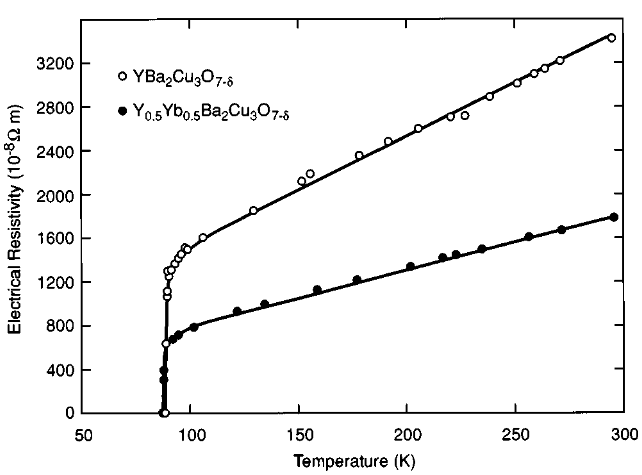

FIG. 1. Electrical resistivity data for Y123 and YYb123. Four probe dc measurements were obtained after the thermal-conductivity data had been obtained.

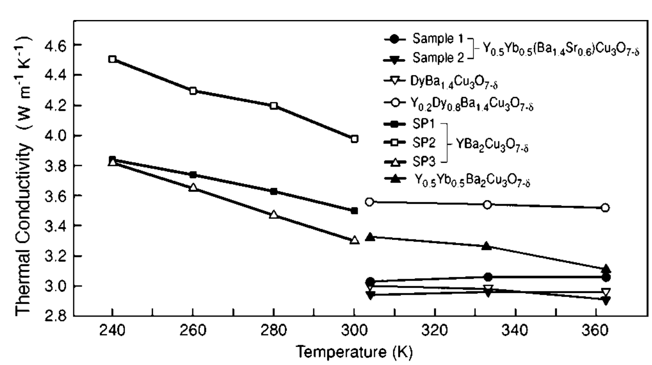

FIG. 2. Ambient temperature thermal-conductivity data for five partially substituted Y123 samples. The data for three Y123 samples are from Ref. 11.

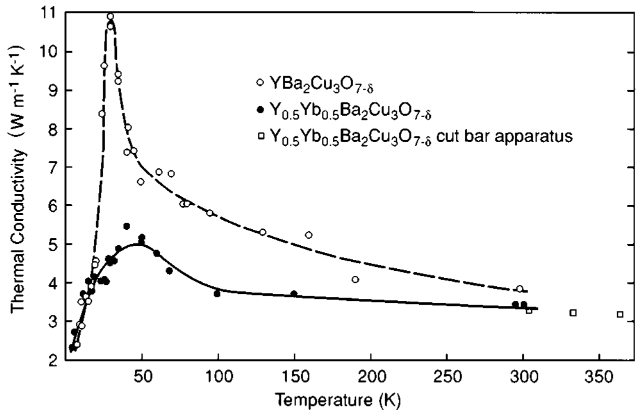

FIG. 3. Thermal-conductivity data for polycrystalline Y123 and $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$. The lower-temperature measurements were made in a guarded longitudinal heat-flow apparatus (Ref. 9) and data obtained in an ambient temperature cut-bar apparatus are included to demonstrate accuracy and batch-to-batch variability.

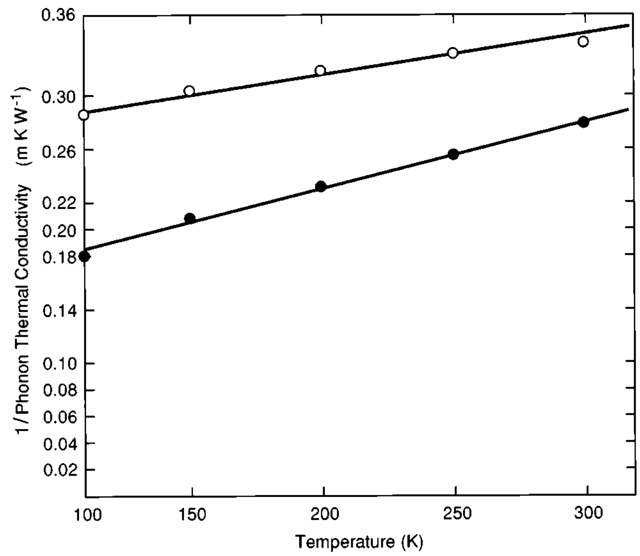

FIG. 4. Estimated phonon thermal-resistivity curves for Y123 and $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-\delta}$. The Sommerfeld-Lorenz number and the data shown in Fig. 1 were used to correct for electronic transport.

the Ba^{2+} sites constitute charge perturbations that should scatter unpaired electrons.

ACKNOWLEDGMENTS

This research was sponsored in part by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, and by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory. Funding was provided under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

[1] A. Jezowski, K. Rogacki, R. Horyn, and J. Klamut, Physica C **153-155**, 1347 (1988).
[2] S. J. Hagen, Z. Z. Wang, and N. P. Ong, Phys. Rev. B **40**, 9389 (1989).
[3] J. L. Cohn, S. A. Wolf, T. A. Vanderah, V. Selvamanickam, and K. Salama, Physica C **192**, 435 (1992).
[4] Y. Pogorelov, M. A. Arranz, R. Villar, and S. Vieira, Phys. Rev. B **51**, 15 474 (1995).
[5] K. Krishana, J. M. Harris, and N. P. Ong, Phys. Rev. Lett. **75**, 3529 (1995).
[6] T. Wolkhausen, Physica C **234**, 57 (1994).
[7] M. Houssa and M. Ausloos, Physica C **257**, 321 (1996).
[8] L. Tewordt and T. Wolkhausen, Solid State Commun. **70**, 839 (1989).
[9] R. K. Williams, J. O. Scarbrough, J. M. Schmitz, and J. R. Thompson, Phys. Rev. B **57**, 10 923 (1998).
[10] R. K. Williams, R. K. Nanstad, R. S. Graves, and R. G. Berggren, J. Nucl. Mater. **115**, 211 (1983).
[11] D. W. Yarbrough, R. K. Williams, and D. R. Shockley, in *Thermal Conductivity 22*, edited by T. W. Tong (Technomic, Lancaster, 1994), p. 554.
[12] J. Callaway, Phys. Rev. **122**, 787 (1961).
[13] T. B. Lindemer, E. D. Specht, P. M. Martin, and M. L. Flitcroft, Physica C **255**, 65 (1995).