Thermal conductivity and superconductivity in $EuBa_2Cu_3O_{7-x}$

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(Received 23 February 1988)

We have measured the thermal conductivity κ from 2 to 200 K in the superconducting ceramic $EuBa_2Cu_3O_{7-x}$ observing an anomaly at the superconducting transition temperature T_c. Using general arguments and approximations, and supposing that the electrical resistivity is due to electron-phonon interaction, we separate quantitatively the different contributions to κ. The "observed" electron-limited phonon conductivity fairly follows the Bardeen-Rickayzen-Tewordt theory and a Bardeen-Cooper-Schrieffer-like energy gap with $2\Delta(0)/k_BT_c = 3.3 \pm 0.7$, in agreement with published data from other kinds of measurements.

The thermal conductivity (κ) of superconducting metals generally suffers from important anomalies at the superconducting transition: it either decreases or increases below T_c depending on the nature of the heat carriers and their interactions. Useful information for understanding the superconducting mechanism can hence be extracted.[1,2] The Bardeen-Rickayzen-Tewordt (BRT) approach,[3] which gives the ratio electronic κ_e to lattice thermal conductivity κ_{ph} between the normal and superconducting states, has been well proved for the case where κ_e is "defect" limited[1,2] or where κ_{ph} is limited by the conduction electrons.[4,5] The question is now posed if a similar approach can be applied to the high-temperature superconductors.[6] Recently, several authors[7-9] indeed reported clear changes of behavior in κ in the ceramic $YBa_2Cu_3O_{7-x}$ at $T_c = 90$ K. A qualitative and quantitative interpretation of the observed behavior can help in determining which are the main carriers at these high temperatures and the interactions that are presumably the same that yield the not yet well understood linear temperature dependence of the electrical resistivity.[10,11] On the other hand, a clear determination of the phonon-"disorder" or "defect" contribution can be useful in analyzing the low-temperature behavior, where the thermal conductivity follows a T^2 dependence that has been interpreted in terms of scattering against tunneling systems (TS) in both families of superconducting oxides.[12,13] In this work we report on measurements of the thermal conductivity of the ceramic (polycrystalline) superconductor $EuBa_2Cu_3O_{7-x}$ between 2 and 200 K. With the measured electrical resistivity, using general arguments and approximations, no free parameters and a careful study of the errors involved, we can quantitatively understand the thermal-conductivity behavior.

The high-density, $\rho_m = 6.35$ g/mm^2, sample was prepared in a two-stage procedure. A precursor material was made by thoroughly mixing stoichiometric amounts of $BaCO_3$, EuO, and CuO and firing it at 950 °C in an oxygen atmosphere. It was subsequently ground and pressed into pellets at 2500 kg/cm^2 and left overnight at 750 °C. The sample was then cooled down to 425 °C in about 8 h and kept at this temperature overnight under a slight flow of oxygen. The oven was then stopped and the sample extracted at 200 °C. The sample showed a defined metallic character and a superconducting critical temperature $T_c = 90.0$ K defined at 50% of the resistive transition with a transition width of 1 K (taken from 10% to 90% of the transition). The absolute value of the resistivity at 285 K was 560 $\mu\Omega$ cm. Scanning electron microscopy measurements indicated an average grain size > 20 μm. X-ray studies showed no evidence (within 1% resolution) of phases other than a well-defined superconducting orthorhombic phase. Magnetization measurements performed with the vibrating-reed method[14] showed a sharp magnetic transition between 85 and 90 K, and a critical field $B_{c1}(0) = 250$ G. Thermal-conductivity measurements were done using the standard technique.[13] In Fig. 1 measurements are shown as a function of temperature. The inset shows an expansion of the data around T_c. Our results show an overall agreement with thermal-conductivity data obtained for $YBa_2Cu_3O_{7-x}$ in Refs. 7–9. The absolute maximum error due to geometry uncertainty is estimated to be 50%.

At low temperatures ($T < 10$ K), κ has a T^2 dependence which has been interpreted as coming from a resonant scattering of phonons with TS which are probably related with oxygen movements or vacancies.[12,15]

To interpret quantitatively[1,2,5,6] the thermal conductivity behavior around T_c we shall assume that the thermal conductivity can be separated into its differents components. Supposing that Mathiessen's rule is valid, it can then be expressed as

$$\kappa = \kappa_e + \kappa_{ph} = [(\kappa_e^{ph})^{-1} + (\kappa_e^{d})^{-1}]^{-1} + [(\kappa_{ph}^{e})^{-1} + (\kappa_{ph}^{d})^{-1}]^{-1}, \quad (1)$$

where the subscripts "e" and "ph" refer to the electron and phonon contributions and the superscripts "e", "ph", and "d" refer to the electron, phonon, or defect-limited thermal conduction.

The electronic thermal conductivity κ_e can be calculated with the Wiedemann-Franz (WF) law taking the extrapolated residual resistivity $\rho(0) = 170$ $\mu\Omega$ cm and according to the relation

$$\kappa_e = L_0 T/\rho(0), \quad (2)$$

where $L_0 = 2.45 \times 10$ W Ω K^{-2}.

For the phonon-limited electronic thermal conduction

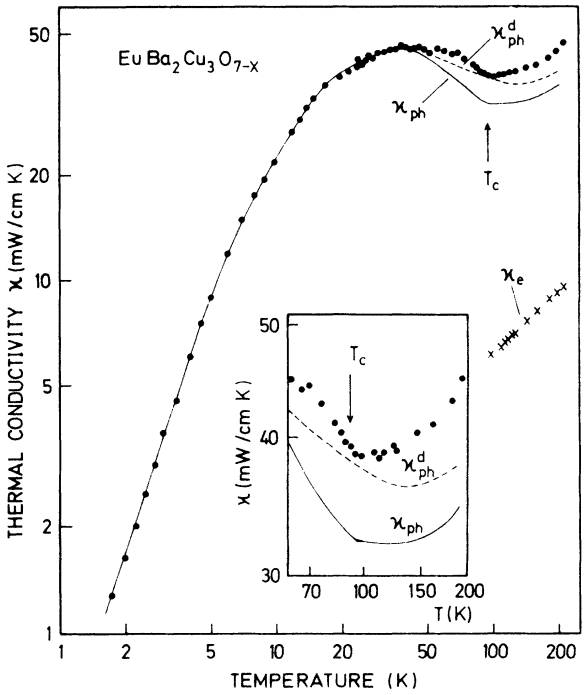

FIG. 1. Thermal conductivity data against temperature (●); × represent the electronic contribution to κ. The solid line represent the phonon thermal conduction and the broken line the "defect" (or "disorder") limited contribution. The arrows indicate $T_c = 90$ K. The inset is only an expansion around T_c. Below 10 K, κ has a T^2 dependence.

κ_e^{ph} we use the simplified model for an isotropic metal (free electron and a roughly spherical Fermi surface), neglecting contributions coming from umklapp processes and dispersion. Note that at high temperature the limit $ql_e > 1$ holds, where l_e (electron mean free path) is of the order of 40 Å at 100 K (Ref. 10) and $2\pi/q$ (phonon wavelength) is of the order of the interatomic distance. With these approximations the classical formula using the notation of Ref. 2 is[16]

$$(\kappa_e^{ph})^{-1} = \frac{A}{L_0 T}\left(\frac{T}{\theta}\right)^5 J_5\left(\frac{\theta}{T}\right) \times \left[1+\frac{3}{\pi^2}\left(\frac{k_F}{q_D}\right)^2\left(\frac{\theta}{T}\right)^2 \frac{J_7(\theta/T)}{(2\pi^2)J_5(\theta/T)}\right], \quad (3)$$

where the Debye temperature $\theta \cong 400$ K, and A is taken from the experimental resistivity slope $\alpha = A/4\theta = 1.4\ \mu\Omega$ cm/K. This is an important assumption because we suppose that the T dependence of $\rho(T)$ is due to the electron-phonon interaction. The linear T dependence has been also obtained in single crystals of $YBa_2Cu_3O_{7-x}$,[11] meaning that it is an intrinsic property of these type of compounds, and not a consequence of the sintered nature of our sample. The fact that a linear regime is obtained at $T \ll \theta$ has been explained by arguing that for a low carrier concentration, and small Fermi wave vector a new energy scale appears $T^* = 2sp_F/k_B \ll \theta$, where s is the sound velocity and p_F the Fermi momentum, which controls the passage to the linear temperature dependence.[17] The error in taking the large-angle scattering which comes from the WF law, as the prefactor in Eq. (3) gives only a second-order correction because of the small deviation from a strictly linear T dependence. For simplicity we take Eq. (3) with A obtained from the linear T dependence of the electrical resistivity.

The small-angle scattering term in Eq. (3) is proportional to the ratio $(k_F/q_D)^2$ which, for a spherical Fermi surface and one electron per atom, is equal to $(0.5)^{2/3}$. Due to probably highly anisotropic Fermi and Debye surfaces in these superconducting oxides, it is reasonable to suppose that the true ratio (k_B/q_D) would be between those computed with the experimental value of the number of electrons $n_e = 0.015$ and $n_e = 1$. Varying n_e between these values leads to a 25% change in κ_e. This error will be taken into account later. In Fig. 1 the plotted values for κ_e are calculated from Eqs. (1), (2), and (3) with $(k_F/q_D)^2 = (0.5)^{2/3}$. An independent estimation of κ_e can be also obtained using an effective Lorenz number L_{eff}, which for $T/\theta \sim 0.25$ gives $L_{\text{eff}} \cong 1.4\times10^{-8}\ \text{V}^2\text{K}^{-2}$, and Eq. (2). This estimation agrees with the values plotted in Fig. 1.

To obtain the phonon contribution κ_{ph} at $T < T_c$ we need to subtract κ_e in the superconducting state. The dependence of κ_e at $T < T_c$ can be obtained with the theoretical BRT ratio κ_{es}/κ_{en} (subscripts s and n refer to the superconducting and normal states). To simplify the calculations and due to the rather small contribution of κ_e to κ, we estimate κ_{es} taking the BRT ratio for the elastic scattering case with the effective Lorenz number. With Eq. (1) we obtain κ_{ph} in the whole T range. In a second possible method we have used the supposition that at $T \leq 45$ K no electrons contribute to κ, so then $\kappa = \kappa_{ph}$, and as we have already κ_{ph} for $T > T_c$ we made a smooth numerical interpolation between 45 and 90 K. Both approaches to calculate κ_{ph} in the whole measured T range gave the same curve within 5%.

The phonon contribution to the thermal conductivity can be expressed, according to Eq. (1), as a function of an electron- and a "defect"-limited part. To obtain κ_{ph}^d at $T > T_c$ we calculate κ_{ph}^e with the following relation:[2,16]

$$(\kappa_{ph}^e)^{-1} = \frac{A}{L_0 T}\left(\frac{\theta}{T}\right) J_5\left(\frac{\theta}{T}\right) \frac{\pi^2 n_e^2}{27[J_4(\theta/T)]^2}. \quad (4)$$

We obtain the constant A from the electrical resistivity, and $n_e \sim 0.15$.

The values of κ_{ph}^e at $T > T_c$ calculated with Eq. (4) are shown in Fig. 2. It is interesting to note that the order of magnitude of κ_{ph}^e can be understood by comparison with Cu alloys,[2,18] for example. For these alloys the "observed" κ_{ph}^e at 100 K is of the order of 120 W/m K and from our calculations we obtain for the ceramic sample $\kappa_{ph}^e(100\ \text{K}) \cong 30$ W/m K. If we take for simplicity Eq. (4) in the high-temperature limit $\kappa_{ph}^e \propto n_e^2$, the ratio of the measured κ values for the ceramic sample and for Cu is of the order of 200 and for the n_e^2 values the ratio is 2.3×10^{-2}. Then the difference in the values of κ_{ph}^e can be understood in terms of the electrical resistivity slope and the small number of electrical carriers.

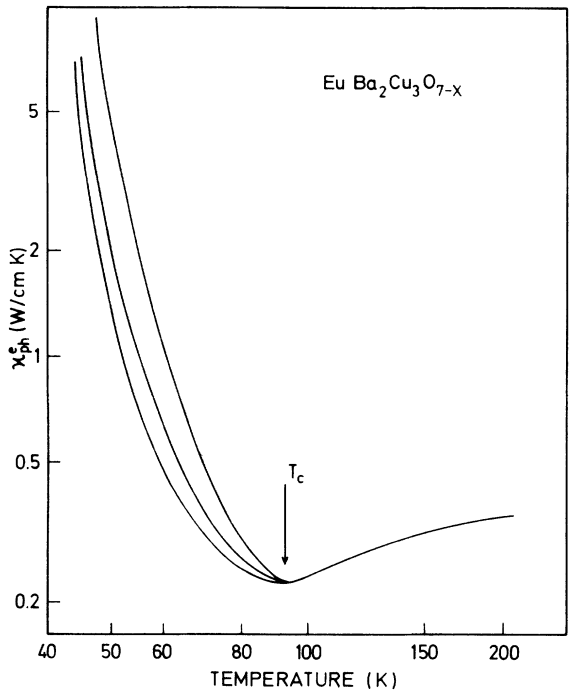

FIG. 2. Phonon thermal conductivity limited by electronic scattering against temperature. At $T > T_c$ κ^e_{ph} is calculated with Eq. (4) and no free parameters and below T_c it is obtained from Eq. (1) (for more details see text). The three curves shown below T_c correspond to shift 50% the measured κ leaving constant κ_e and κ_{ph} for $T > T_c$.

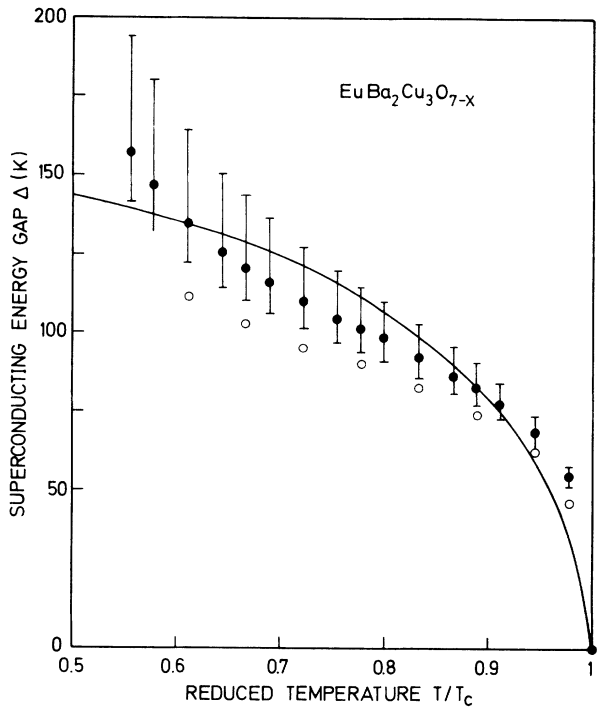

FIG. 3. Superconducting energy gap in kelvin against temperature, obtained using the BRT expression for $\kappa_{phs}/\kappa_{phn}$, the curves of Fig. 2, and the table of Ref. 4. The error bars indicate the maximum estimated error due to the used approximations or geometrical uncertainty. The points (o) are calculated using the thermal-conductivity data for Y-Ba-Cu-O taken from Ref. 7.

The phonon "defect" contribution can now be calculated with κ_{ph} and κ^e_{ph} from Eq. (4) for $T > T_c$. As it is impossible to subtract experimentally κ^e_{ph} at $T < T_c$ we perform a smooth numerical interpolation for κ^d_{ph} between 45 and 90 K. In analogy with what was done above to estimate κ_{ph} it is expected that the error involved in this interpolation with respect to the true value would be not more than 5%. Note that at $T < 45$ K $\kappa = \kappa_{ph} = \kappa^d_{ph}$. The calculated curve for κ^d_{ph} is shown in Fig. 1. It has the shape very similar to that found in amorphous materials, and is probably caused by disorder due to oxygen vacancies and/or twining.[19] Using κ_{ph} and κ^d_{pd} for $T < T_c$ and Eq. (1) we obtain κ^e_{ph} in the superconducting state; see Fig. 2. The three curves shown in this figure at $T < T_c$ are calculated taking κ_e and κ^e_{ph} $(T > T_c)$ constant and varying 50% (geometry uncertainty) the measured κ. This variation also represents the maximum estimated error due to the different errors and approximations involved in the derivation of κ^e_{ph} $(T < T_c)$.

From the curves in Fig. 2 we can compute now the corresponding superconducting energy gap as a function of temperature.[3,6] The obtained gap values are plotted in Fig. 3. The error bars correspond to the three curves for κ^e_{phs} (Fig. 2) obtained as mentioned above. For comparison we plotted in Fig. 3 the BCS gap temperature dependence with $2\Delta(0)/k_B T_c = 3.3$. We can see that there is a fair agreement between both temperature dependences. The deviations of $\Delta(T)$ observed at $T/T_c < 0.6$ are probably only an artifact coming from the used numerical method. In Fig. 3 we also show the energy-gap values obtained by the same method from the thermal conductivity measurements in $YBa_2Cu_3O_{7-x}$.[7]

Infrared reflectivity measurements[20] showed for oriented films of Y-Ba-Cu-O an energy gap $2\Delta(0) = (4.7 \pm 1.2)k_B T_c$ and for bulk polycrystalline samples $2\Delta(0) \cong 2.7 k_B T_c$. Similar values are also obtained by tunneling,[21] while specific-heat measurements[22] also seem to favor a weak-coupling behavior. Our weak-coupling value $2\Delta(0) \cong 3.3 k_B T_c$ is in fair agreement with these measurements.

Within the reservations of using the free-electron and isotropic model for the calculations of κ_e and κ^e_{ph}, the overall reasonable results would indicate that the electrical resistivity might be due to the electron-phonon interaction. This would sustain previous general considerations[10] based on the nonsaturation behavior of $\rho(T)$ that led to the conclusion that superconductivity in these new materials cannot be due to an electron-phonon interaction due to the rather small estimated coupling constant λ. Because κ^e_{ph} is inversely proportional to ρ, an independent way to estimate λ from our results is not, however, possible.

Two different mechanisms could lead also to a linear T dependence in the electrical resistivity: electron-electron scattering[23] and interactions of electron with tunneling systems (TS).[24] This last possibility is attractive since at low temperatures our thermal conductivity results, in agreement with acoustic measurements, provide evidence

for the existence of these excitations.[12,15] Rough estimations of the electronic relaxation time within the rather simplified Korringa-like model for the electron-TS interaction give the right order of magnitude of α using reasonable values for the electron-TS coupling constant.[25] Our results, however, would indicate that if this contribution exists it should be smaller than $\sim 30\%$.

We conclude that with simple and general arguments appropriate for isotropic solids it is possible to estimate the different contributions to the thermal conductivity in superconducting ceramics. The thermal conductivity anomaly at T_c in the $T_c = 90$ K superconductor ceramics can be well understood with the usual BRT expression for the phonon-electron contribution and a BCS-like energy gap with $2\Delta(0) = (3.3 \pm 0.7) k_B T_c$, in fair agreement with other experimental data performed in polycrystalline materials. Our results would indicate that the main part of the linear T dependence in the electrical resistivity comes from an electron-phonon interaction.

We are thankful to D. Arias, R. Zysler, and C. Duran for useful aid during sample characterization. Helpful discussions with B. Alascio and D. Castello are gratefully acknowledged.

[1]K. Mendelssohn and H. M. Rosenberg, in Solid State Phys. **12**, 233 (1961).

[2]See, for example, R. Berman, *Thermal Conduction in Solids,* Oxford Studies in Physics (Clarendon, Oxford, 1979).

[3]J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959).

[4]J. B. Sousa, J. Phys. C **2**, 629 (1969).

[5]P. Esquinazi and F. de la Cruz, Phys. Rev. B **27**, 3069 (1983).

[6]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986); M. K. Wu, J. R. Ashburn, C. J. Tong, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. O. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[7]A. Jezowski, J. Mucha, K. Rogacki, R. Horyn, Z. Bukowski, M. Horobiowski, J. Rafalowicz, J. Stepien-Damm, C. Sulkowski, E. Trojmar, A. J. Zaleski, and J. Klamut, Phys. Lett. A **122**, 431 (1987).

[8]D. T. Morelli, J. Heremans, and D. E. Swets, Phys. Rev. B **36**, 3917 (1987).

[9]V. Bayot, F. Delannay, C. Dewitte, J-P. Erauw, X. Gonze, J-P. Issi, A. Jonas, M. Kinany-Alaoui, M. Lambricht, J-P. Michenaud, J-P. Minet, and L. Piraux, Solid State Commun. **63**, 953 (1987).

[10]M. Gurvitch and A. T. Fiory, Phys. Rev. Lett. **59**, 1337 (1987).

[11]S. W. Tozer, A. W. Kleinsasser, T. Penney, D. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1768 (1987).

[12]M. A. Izbizky, N. Núñez Regueiro, P. Esquinazi, C. Duran, and C. Fainstein, Phys. Lett. A **129**, 71 (1988).

[13]M. Núñez Regueiro, D. Castello, M. A. Izbizky, D. Esparza, and C. D'Ovidio, Phys. Rev. B **36**, 8813 (1987).

[14]P. Esquinazi and E. H. Brandt, in *Proceedings of the Eighteenth International Conference on Low Temperature Physics, Kyoto, 1987* [J. Phys. Soc. Jpn. **26**, 1513 (1987)].

[15]P. Esquinazi, C. Duran, C. Fainstein, and M. Núñez Regueiro, Phys. Rev. B **37**, 545 (1988).

[16]A. H. Wilson, *The Theory of Metals,* 2nd ed. (Cambridge Univ. Press, London, 1953).

[17]R. Micnas, J. Ranninger, and S. Robaszkiewicz, Phys. Rev. B **36**, 4051 (1987); L. Civale and E. Martinez, *ibid.* **38**, 928 (1988).

[18]W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh, Aust. J. Phys. **10**, 454 (1957).

[19]M. Núñez Regueiro, M. A. Izbizky, and P. Esquinazi, Solid State Commun. (to be published).

[20]R. T. Collins, Z. Schlesinger, R. A. Koch, R. B. Laibowitz, T. S. Plaskett, P. Freitas, W. J. Gallagher, R. L. Sandstrom, and T. R. Dinger, Phys. Rev. Lett. **59**, 704 (1987).

[21]J. R. Kirtley, R. T. Collins, Z. Schlesinger, W. J. Gallagher, R. L. Sandstrom, T. R. Dinger, and D. A. Chance, Phys. Rev. B **35**, 8846 (1988).

[22]S. E. Inderhees, M. B. Salamon, T. A. Friedmann, and D. M. Ginsberg, Phys. Rev. B **36**, 2401 (1987); M. V. Nevitt, G. W. Crabtree, and T. E. Klippert, *ibid.* **36**, 2398 (1987).

[23]P. A. Lee and N. Read, Phys. Rev. Lett. **58**, 2691 (1987).

[24]J. L. Black, in *Glassy Metals,* edited by H. J. Güntherodt and H. Beck, Topics in Applied Physics, Vol. 46 (Springer, Berlin, 1981), p. 176.

[25]D. Castello (private communication).