$YBa_2Cu_3O_{7-\delta}$ films: Calculation of the thermal conductivity and phonon mean-free path

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We estimate the phonon mean-free path (mfp) in $YBa_2Cu_3O_{7-\delta}$ by performing a theoretical fitting procedure on bulk single-crystal data. This analysis indicates that the mfps of the phonons that are most responsible for the transport of heat are much longer than would be predicted from kinetic theory. These values are incorporated into a recently proposed treatment of the size effect to provide an estimate of the thermal conductivity of $YBa_2Cu_3O_{7-\delta}$ films.

I. INTRODUCTION

High T_c thin films have shown considerable promise in a variety of technological applications.[1] In a number of these, such as liquid-nitrogen bolometers and thin-film microbridges,[2] it is advantageous to know the thermal conductivity of the film. This quantity is difficult to measure directly, as standard steady-state techniques are rendered ineffective by the fact that the film substrate acts as a thermal short. In the absence of such measurements, it is of use to make the best possible theoretical predictions of this quantity to serve as a guide to engineers seeking to exploit these promising materials. In this article, we seek to provide such an estimate by extending our previous work[3] on bulk single crystals of $YBa_2Cu_3O_{7-\delta}$ to incorporate the effects of boundary scattering in the thin film geometry. We also perform the analysis on a *c*-axis aligned granular sample.

II. THE MODEL

We employ a frequency dependent model (described in detail in Ref. 3) for the phonon thermal conductivity that is based on a model proposed by Tewordt and Wölkhausen.[4] According to this model, the phonon thermal conductivity $\kappa_p(T)$ is given by[3]

$$\kappa_p(T)=\frac{k_B}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} dx \frac{x^4 e^x}{(e^x-1)^2}\tau(T,x), \qquad (1)$$

where

$$\tau(T,x)^{-1}=B+D_p T^4 x^4+D_{sf}T^2x^2+ETxg(x,y)+UT^4x^2. \qquad (2)$$

In this expression, $\tau(T,x)$ represents the total phonon scattering time and the equation for $\kappa_p(T)$ is an integration over phonon modes. The parameter x is the reduced phonon frequency, $\hbar\omega/k_BT$, and the terms in the expression for $\tau(T,x)$ represent the individual scattering contributions from boundaries, point defects, sheet-like faults, electrons, and other phonons, respectively. The electron term contains the function $g(x,y)$. This function is equal to the ratio of phonon-electron scattering times in the normal and superconducting states, and was calculated within the Bardeen–Cooper–Schrieffer (BCS) framework in a classic paper by Bardeen, Rickayzen, and Tewordt.[5] In our previous work,[3] we included an integration over the polar angle with respect to the *c* axis of the crystal to account for anisotropy in the electron-phonon scattering term[6] but this addition does not affect the qualitative results and is omitted in this discussion. We also note that the above treatment makes use of the Debye approximation for the distribution of phonon modes and ignores possible interdependence of the various scattering mechanisms.

We add to the above expression for the phonon term an electronic contribution to the thermal conductivity. We employ the results of Geilikman, Dushenat, and Chechetkin[7] in which they tabulate $\kappa_{ep}^s/\kappa_{ep}^n$, the ratio of the electronic thermal conductivity in the superconducting and normal states, for the case in which the dominant electron scatterers are phonons. We have also examined the case in which the electronic term is defect dominated and this form can also be made to fit the data with a modest change in the fitting parameters. This form, however, does not fall away as rapidly below T_c and does not provide as good a description of the data as the phonon-dominated form. Except in the region near T_c, this choice is not crucial, in that both forms become overwhelmed by the phonon term at low temperatures. The electronic contribution κ_e we employ is then

$$\kappa_e=\begin{cases} K, & T>T_c \\ K\dfrac{\kappa_{ep}^s}{\kappa_{ep}^n}, & T<T_c \end{cases} \qquad (3)$$

where K is a constant representing $\sim 30\%$ of the total thermal conductivity at T_c.[3]

A fit to our data for a $YBa_2Cu_3O_{7-\delta}$ single crystal is shown by the solid curve in Fig. 1(a) and it can be seen that the model describes the data remarkably well. (This fit actually employs a modification of the boundary scattering term that will be discussed fully below.) A primary conclusion resulting from this analysis is that point defects constitute the major source of scattering, a feature that we shall see has significant consequences for the phonon mean-free path.

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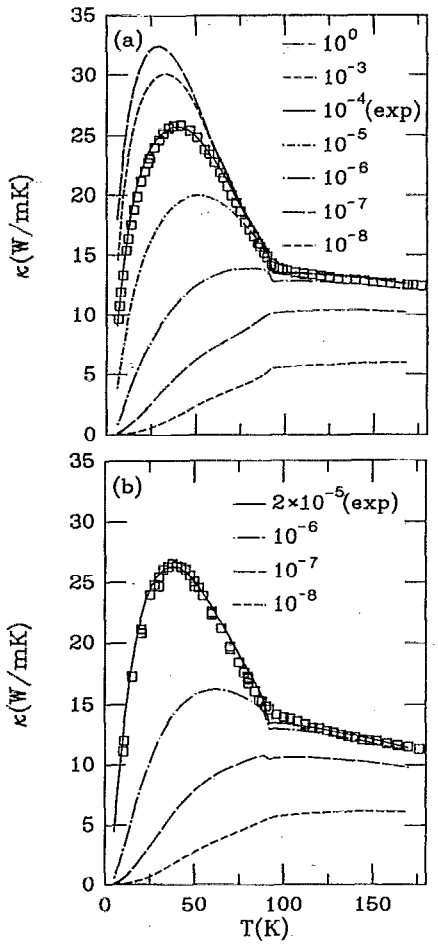

FIG. 1. (a) Data for $\kappa(T)$ of a single crystal of $YBa_2Cu_3O_{7-\delta}$ (□). Solid line represents the best fit when the actual width of the crystal is inserted in the model. Other curves are predictions for samples of various other widths (indicated in meters). (b) Corresponding results for a grain-oriented sample.

III. MEAN-FREE PATH OF THERMAL PHONONS

By evaluating the integrand of Eq. (1), we are able to obtain an estimate of which phonon wavelengths are most important in the transfer of heat in these materials. We find that the thermal conductivity at low temperatures is dominated by long-wavelength phonons and that phonon-boundary scattering is significant up to $T\sim75$ K. This result is surprising when examined in the context of the kinetic equation for the thermal conductivity, $\kappa=\frac{1}{3}cvl$, where c is the phonon specific heat, and l is the phonon mfp. This expression would suggest that, for 10 K$<T<T_c$, the mfp is within 0.005 μm$<l<$1.5 μm, orders of magnitude less than the smallest dimension of the crystal. However, because point defects are the major source of scattering and because the frequency dependence of the mfp for scatterers of this type is very strong, $l^{-1}\sim\omega^4$, phonons of high frequency are disproportionately affected, leaving a large part of the heat conduction to long wavelength phonons. This is a key point; *in samples where point defect scattering plays a major role, the value for l which is obtained from kinetic theory can be wrong by several orders of magnitude.* This phenomena was demonstrated clearly in a study of irradiated silicon by Savvides and Goldsmid.[8] They found that samples that had previously shown no thickness dependence in their thermal conductivity developed such a dependence after the introduction of point defects by irradiation. This indicated that phonons whose mfps were long enough to be influenced by the boundaries of the sample were playing a significant role in the thermal conduction, even though the predictions of kinetic theory would suggest otherwise. The kinetic expression would, in fact, predict a *shorter* mfp after irradiation since the overall thermal conductivity has decreased.

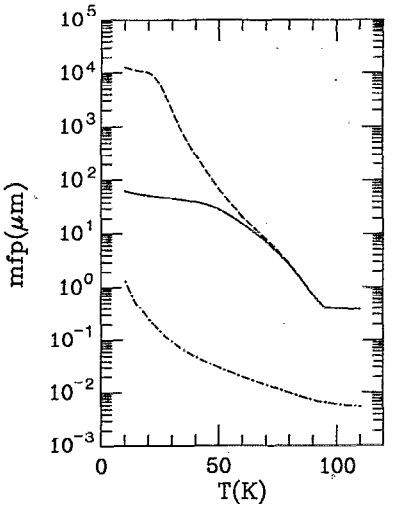

FIG. 2. Mean-free path of the phonons that contribute most strongly to the heat transport in the single-crystal sample. Solid curve indicates estimate for our sample (width 80 μm), dashed curve shows prediction for a 1 m (bulk) sample. These values are the effective mfps in the in-plane direction in the presence of boundary scattering. Dot-dash curve shows kinetic theory result using experimental values of κ.

The mfps of the phonons that we believe are contributing most significantly to the heat conduction in our single-crystal sample are shown in Fig. 2. These values are those that correspond to the maximum in the integrand function of Eq. (1) when it is plotted versus x. (We assume a sound velocity v of 5000 m/s.) Also shown are the results for a hypothetical sample of width 1 m (see below). The values that one derives from the kinetic theory expression are shown in the inset for comparison. These are obtained from our experimental data and the specific heat data of Shaviv *et al.*[9]

One can readily observe that the frequency dependent treatment is in serious disagreement with kinetic theory. The simple reason for this is that the kinetic formalism yields only an "average" mfp for the phonon distribution. It does not give any information about the extent to which the phonons that correspond to this average value actually participate in the conduction of heat. In our case, these particular phonons are largely scattered out.

IV. CALCULATION OF THE SIZE EFFECT IN THIN FILMS

Given that phonons of long wavelength and mfp appear to play a greater role in the transport than one might

TABLE I. Coefficients of Eqs. (1)–(5) used to fit the experimental data for the two samples under study.

Sample	Single crystal	Grain oriented
K ($W\,m^{-1}\,K^{-1}$)	4.4	3.2
Width (μm)	80	20
D_p ($K^{-4}s^{-1}$)	363	188
D_{sf} ($K^{-2}s^{-1}$)	2.74×10^5	2.6×10^5
E ($K^{-1}s^{-1}$)	1.2×10^8	1.55×10^8
U ($K^{-4}s^{-1}$)	87	165
χ	1.8	1.63

expect, it is clear that the size effect in the thermal conductivity of thin films will also be stronger than expected. To obtain an estimate of this effect, we modify our approach somewhat and utilize the equations for the size effect developed in Ref. 2. In this work, the authors show that the thermal transport in the *ab* plane of an epitaxial thin film can be obtained from measurements along this direction in bulk materials by modifying the bulk value of the phonon mfp according to a simple geometrical argument. They show that for a film of thickness d, the effective mfp in the film, l_{eff}, can be related to the bulk value, l according to the expression

$$\frac{l_{\text{eff}}}{l}=1-\frac{2}{3\pi\delta}\quad \delta>1, \tag{4}$$

$$\frac{l_{\text{eff}}}{l}=1-\frac{2(1-Z^3)}{3\pi\delta}+\frac{2\delta}{\pi}\ln\frac{1+\delta+Z}{1+\delta-Z}-\frac{2}{\pi}\arccos\delta\quad \delta\leqslant 1, \tag{5}$$

where $\delta=d/l$ and $Z=(1-\delta^2)^{1/2}$. In Eqs. (1) and (2), the boundary scattering term is treated by simply adding a constant to the inverse scattering time $\tau(T,x)^{-1}$. To make our analysis compatible with the method of Flik and Tien, this boundary term is omitted and rather, the overall frequency dependent mfp, $l=v\tau(T,x)$, was modified according to Eqs. (4) and (5) and the modified mfp, l_{eff}, is what is inserted into the integrand. Estimates of the thermal conductivity for various film thicknesses are then obtained by changing d. These results are shown in Fig. 1. It should be noted that the size effect has some impact on the electronic contribution κ_e as well, though to a much lesser degree than the phonon term. This was demonstrated in an extension of the work of Ref. 2 by Goodson and Flik.[10] Though this effect is relatively small, we attempted to include it to a first-order approximation by assuming a constant value for the bulk electron mfp of 200 Å (Ref. 10) and modifying it according to Eqs. (4) and (5) for the various film thicknesses, in a manner analogous to the phonon part. The above method makes use of several assumptions that should be mentioned. We assume an isotropic bulk mfp, diffuse scattering at the film boundaries, and negligible phonon transmission to the substrate. A discussion of the validity of these assumptions is given in Ref. 10.

The fit to our single-crystal data, [shown by the solid line in Fig. 1(a)], determines the scattering coefficients used in all the predicted curves. These coefficients are given in Table I. The parameter χ is the gap scaling factor, $\Delta/\Delta_{\text{BCS}}$.[3] The values of χ used in these fits correspond to $2\Delta/k_BT_c=5.6$–7.3. We note that the sample data could not be treated as true "bulk" measurements in our analysis. Our sample was relatively thin, ~0.1 mm, and we observed in our calculations that boundary scattering had a noticeable effect when treated according to Eq. (4). To give a sense of the "true" bulk behavior, we include a curve for a sample with a hypothetical width of 1 m and the difference between this curve and that corresponding to our actual measurement is obvious. Even this sample shows some evidence of boundary scattering at low temperatures, however, as can be seen from the mfp results shown in Fig. 2.

Also included, for comparison, are the results for one of the grain-oriented YBCO samples studied by Cohn *et al.*[11] This sample is a *c*-axis aligned aggregation of plate-like crystallites that measure approximately 20 μm in the *c* direction and many times that in the *a* and *b* directions. Because of the small size of these crystallites as compared to the single-crystal sample, the grain-oriented sample will be subject to greater resistance from grain boundaries. The fact that the overall thermal conductivity is similar to the single-crystal sample indicates that the resistance from other defects must be correspondingly weaker. This is reflected in the parameters used in the fit [see Table I and Fig. 1(b)].[12] In analogy with the single crystal, we have extrapolated what the thermal conductivity of a material with this defect structure would be for various film thicknesses according to Eqs. (4) and (5). Despite the different defect parameters used, the results are quite similar to those for the single-crystal material.

V. DISCUSSION AND CONCLUSIONS

We observe that, at a sample width of 100 nm, the peak that is characteristic of the thermal conductivity of high T_c materials has been essentially obliterated for both materials. This indicates that even at temperatures as high as T_c, the phonon mfp is boundary limited for very thin films and therefore does not experience the usual enhancement due to charge-carrier condensation.[13] One can observe that at the 1 μm thickness, the peak is somewhat more in evidence in the grain-oriented material. As can be seen from the values of the fitting parameters used for this sample, point defects do not dominate to quite the same extent as in the single crystal and therefore the impact of the reduced sample thickness is not as great, for the reasons discussed above.

We wish to point out that, though we have studied two samples with quite disparate preparation techniques and defect structures, they do not encompass the entire range of possible sample microstructures. The value of the thermal conductivity of a given film will be dependent upon the particular defect structure of that material. The convergence of our results for small thicknesses, however, leads us to believe that our predictions for this regime will be fairly general. There is still a need for definitive experiments where crystals of varying widths but identical defect structures could be compared to observe the effect of sample size on the thermal conductivity.

We conclude that the mfp of the phonons that are responsible for the heat transport in $YBa_2Cu_3O_{7-\delta}$ is substantially larger than is predicted by kinetic theory due to the importance of point defect scattering in these materials. This enhancement leads to a surprisingly large size effect in the thermal conductivity of thin films.

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