

Thermal conductivity of impurity-doped high- T_c superconductors

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The thermal conductivity $K(T)$ of polycrystalline $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_7$ with $M = \text{Zn}$ and Al ($0 \leq x \leq 0.1$) and $\text{Y}_{1-y}\text{R}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $R = \text{Pr}$ and Gd ($0 \leq y \leq 1.0$) has been measured for temperatures $1.2 \leq T \leq 200$ K. In the pure material, $K(T)$ decreases slightly with decreasing temperature above T_c and below T_c there is a strong enhancement of $K(T)$ reaching a maximum at ~ 50 K followed by a sharp decrease. At temperatures below 10 K a T^2 dependence is evident similar to behavior reported for amorphous systems with glasslike phonon scattering on the tunneling states. Doping with Zn or Pr rapidly depresses T_c and also depresses the maximum in $K(T)$ even at concentrations that remain superconducting. This effect is observable to a lesser degree for the Al and Gd dopants. Comparisons between the $K(T)$ behavior for impurities that do not depress T_c with those that diversely alter the superconducting properties are presented together with an analysis of the data using the Tewordt-Wölkhausen (TW) theory.

I. INTRODUCTION

Thermal conductivity has been extensively studied in high- T_c superconductors due to its advantage in probing the scattering processes of phonons and electrons in both normal and superconducting states. In addition, it can also provide invaluable information on the superconducting energy gap, excitation spectrum and lifetimes, and electron-phonon coupling parameters which are still being vigorously pursued by theorists and experimentalists in these materials.

There have been many reports¹ of thermal conductivity measurements in high- T_c superconductors, however, these studies have almost exclusively concentrated on pure polycrystalline and single-crystal samples with very few studies reporting on doped compounds. A common feature of $K(T)$ for the high- T_c superconductors, e.g., $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$, is a rapid rise with increasing T below T_c , reaching a maximum at approximately $T_c/2$ followed by a decrease and a sharp break in $K(T)$ at $T = T_c$.¹ In sintered samples, this maximum is approximately 20% higher than the value of $K(T)$ at T_c , and in single crystals the maximum may approach 100%. There have been several explanations proposed for this anomaly. For example, if the total thermal conductivity in the normal state is dominated by phonon conduction, and the phonons are significantly limited by electron-phonon scattering, then for $T < T_c$, Cooper pairs form and the number of electrons available to scatter phonons falls rapidly, resulting in an increase in the mean free path of the phonons and an enhancement in $K(T)$. Such behavior has been seen in conventional superconductors, e.g., (Pb,Bi) alloys.² The electrical transport properties of these high- T_c layer oxide superconductors are extremely anisotropic and this anisotropy is also apparent in $K(T)$. Hagen, Wang, and Ong³ measured both the in-plane and out-of-plane $K(T)$ from 10 to 330 K in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals. They found that

K_c [out-of-plane $K(T)$] is four to five times smaller and apparently does not have a maximum for $T < T_c$. However, K_{ab} [in-plane $K(T)$] does have a pronounced maximum. Using the measured electrical resistivity and the Wiedemann-Franz (WF) law, the in-plane electronic contribution K_{ab}^e was estimated to be approximately 55% of the total K_{ab} above T_c . However, the K_{ab} of oxygen deficient, insulating $\text{YBa}_2\text{Cu}_3\text{O}_6$ crystals shows a large phonon contribution, approximately the same magnitude as K_{ab} in superconducting crystals. These results have led to a model where strong in-plane electron-phonon scattering in the normal state combined with an increase in the phonon lifetime due to a decrease in the quasiparticle scattering accounts for the strong enhancement of $K(T)$ below T_c for superconducting samples. It is also suggested that the electron-phonon coupling strengths are extremely anisotropic. Alternate models have been proposed. Recently, Yu *et al.*⁴ measured the in-plane thermal conductivities in single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_7$ and attributed the rapid rise in $K(T)$ with decreasing T in the superconducting state to an electron (hole) contribution from the Cu-O plane, which increases rapidly below T_c due to the strongly suppressed quasiparticle scattering and concomitant increase of the quasiparticle, i.e., electron (hole), mean free path.

These explanations serve to illustrate the controversial nature of $K(T)$ and the potential of it providing insight into the quasiparticle spectrum and lifetimes for these systems if a more definitive understanding of the T dependence of $K(T)$ is established. The controversial nature of $K(T)$ and its potential to provide indirect observations of quasiparticle parameters has driven our interest in extending these measurements to studies of impurity effects on the thermal conductivity. Such studies could lead to a greater insight into the relative contributions to $K(T)$ and possibly indirect measurements of the quasiparticle spectrum within the superconducting state.

In this paper, we present the results of thermal conduc-

tivity $K(T)$ measurements in selectively doped polycrystalline $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_7$ with $M=\text{Zn}$ and Al ($0 \leq x \leq 0.1$) and $\text{Y}_{1-y}\text{R}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $R=\text{Pr}$ and Gd ($0 \leq y \leq 1.0$) for temperatures $1.2 \leq T \leq 200$ K along with comparisons and a theoretical analysis of the data using the Tewordt-Wölkhausen (TW) theory.⁵

II. EXPERIMENT

Polycrystalline samples of composition $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_7$ with $M=\text{Zn}$ and Al ($0 \leq x \leq 0.1$) and $\text{Y}_{1-y}\text{R}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $R=\text{Pr}$ and Gd ($0 \leq y \leq 1.0$) were prepared using standard solid-state reaction techniques.^{6,7} The final specimens were checked by x-ray diffraction for phase purity and preferred orientation. In addition, electrical transport and low-field magnetization was measured to better characterize the samples. These measurements have indicated that all samples used in this study were single phase with less than 2% impurities and had T_c vs x and y was consistent with previous studies.^{6,7} In addition, x-ray and scanning electron microscopy (SEM) studies have indicated that there was no preferred orientation in any of the sintered samples. Samples with a typical size of $1 \times 2 \times 10$ mm³ were cut from pellets or directly made with a bar press. At several concentrations, numerous samples with different sample densities were prepared and measured to better define the impact of voids and particle size on $K(T)$. These studies at different densities have indicated that the results to be presented within this paper are not an artifact of the ceramic nature of the samples, and provide some valuable insight to the intrinsic response of these very interesting systems.

The thermal conductivity was measured using a conventional four-probe heat-pulse method.¹ A heater (metal film or resistor) was attached to one end of the sample while the other end was firmly epoxied (or soldered) to a variable temperature heat sink. The temperature gradient across the sample was measured using a differential chromel-constantan thermocouple for $25 \leq T \leq 250$ K and a pair of calibrated carbon thermometers for $T < 25$ K. The temperature difference ΔT during the measurements was typically between 0.3 and 1.0 K depending on the temperature of the sample.

III. RESULTS AND DISCUSSION

In Fig. 1(a), we present $K(T)$ for two fully oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_7$ polycrystalline samples with densities of 4.85 and 5.31 g/cm³. Ceramic samples typically have densities less than the theoretical value (~ 6.4 g/cm³) due to voids which may act as scattering centers for phonons and modify the measured $K(T)$. Our results clearly show that the magnitudes of $K(T)$ varies with density, however, the general features of $K(T)$, i.e., the rapid increase of $K(T)$ at T_c and the peak at $T \sim T_c/2$, are quite similar. These common features can be more clearly observed by plotting the normalized thermal conductivity, $K(T)/K(180 \text{ K})$, vs T as shown in Fig. 1(b). The $K(T)/K(180 \text{ K})$ curves of different densities nearly overlap each other, indicating that the intrinsic temperature

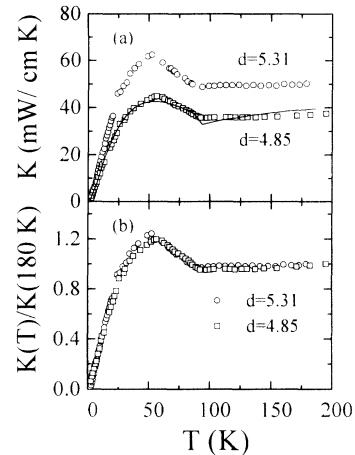


FIG. 1. $K(T)$ vs T of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with $d=5.31$ and 4.85 g/cm³. (a) The solid line is the theoretical fitting obtained from the TW theory. (b) The normalized thermal conductivity, $K(T)/K(180 \text{ K})$, vs T .

dependence of $K(T)$ is given by the normalized $K(T)/K(180 \text{ K})$ and this quantity is relatively insensitive to void density.

In the temperature range 100–180 K, $K(T)$ is essentially temperature independent. At $T \approx T_c$, a sudden increase in thermal conductivity with decreasing T reaching a peak at $T \sim 50$ K is evident, with $K(T)$ falling off at lower temperatures. These features are similar to those reported by other groups.¹ We assume a conventional additive thermal conductivity arising from charge carriers, i.e., electrons (holes), and phonons, i.e., $K(T) = K_e(T) + K_p(T)$. The charge carrier contribution to the $K(T)$ can be roughly estimated using the WF law in conjunction with the measured electrical resistivity, i.e., $K_e = L_0 T / \rho$, where $L_0 = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ is the Lorentz number and ρ is the electrical resistivity. We find that $K_e/K \leq 0.2$ for both densities at $T = 100$ K. Even though such an estimate is crude and could be slightly in error, we take the position as most previous researchers have done that the dominant contribution to $K(T)$ is due to phonon conduction. This position is consistent with other studies reported on $K(T)$, however, as indicated earlier, it is not the only interpretation. Our analysis assuming that $K(T)$ is dominated by phonon conduction is consistent with $K(T)$ measurements of oxygen deficient, insulating samples (to be discussed) and a comparison to results for the superconducting samples.

Within these assumptions, the sharp increase in $K(T)$ just below T_c can be attributed to the formation of Cooper pairs. These pairs do not scatter phonons, thus the mean free path of phonons will increase and K_p is enhanced. As the temperature is lowered, however, the population of phonons is reduced and contributions such as point defects and boundary scattering become increasingly important, thus causing a fall off in $K(T)$.

A fit to the data shown in Fig. 1(a) below 10 K gives a T^2 behavior that has also been observed in polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Ref. 8) and single crystals $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{HoBa}_2\text{Cu}_3\text{O}_7$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.^{9–11} However, devia-

tions from a T^2 dependence for $K(T)$ has been reported for $T < 2$ K in some polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_7$ $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ samples.^{1,8} The numerous reports of a T^2 dependence for $K(T)$ as $T \rightarrow 0$ for numerous high- T_c superconductors would suggest that this behavior of $K(T)$ may be a common feature to all high- T_c superconductors. It is known that glassy materials shown an unusual T^2 dependence in their thermal conductivity at low temperatures.^{12,13} This behavior has been attributed to the resonant scattering of phonon on two-level tunneling states which result from the tunneling of certain atoms or groups of atoms within a double-well potential.^{14,15} The same behavior of $K(T)$ in high- T_c superconductors may indicate a similar mechanism is present.

It is known that in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, T_c decreases with decreasing oxygen content eventually going to zero at $\delta=0.4$ where an orthorhombic-to-tetragonal structural transition occurs. This structure change with the concomitant change of the phonon spectrum¹⁶ combined with a reduction of free charge carriers obviously impacts the behavior of $K(T)$. In Fig. 2, we present $K(T)$ vs T for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ for $\delta \approx 1$ and 0. The maximum in $K(T)$ below T_c disappears in the deoxygenated nonsuperconducting sample as would be expected due to the reduction of free carriers and the absence of Cooper pairs. The magnitude also decreases consistent with our previous estimate of the charged carrier contribution to $K(T)$. Since the phonon spectrum and phonon relaxation may change due to the changes in structure, this comparison may be fortuitous.

In order to extract electron-phonon coupling strengths and estimates of other parameters from $K(T)$, we assume that it is dominated by phonon conduction and we fit our experimental $K(T)$ data on the fully oxygenated compound using a TW theory,⁵

$$K_p(t) = At^3 \int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2} [1 + at^4 x^4 + \beta t^2 x^2 + \gamma t x g(x, y)]^{-1}, \quad (1)$$

where A , α , β , and γ represent different phonon-scattering processes; boundary, point defects, sheetlike faults, and electrons, respectively. Here we assume that

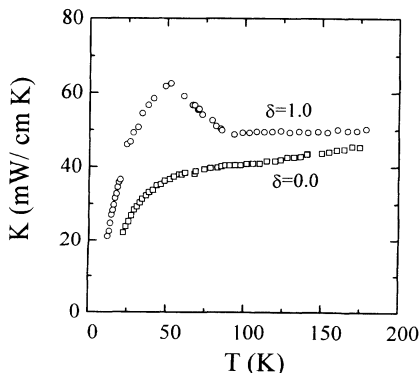


FIG. 2. $K(T)$ vs T for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ with $\delta \approx 1$ ($T_c = 93$ K) and $\delta \approx 0$.

the electron conduction is a featureless, smooth function of T and only impacts our analysis through a slight altering of the fitted parameters.

A fit to $K(T)$ using TW theory, i.e., Eq. (1), is shown in Fig. 1(a). From this fit, we obtain $A=3.5$, $\alpha=80.8$, $\beta=43.9$, and $\gamma=54.1$. Using the formula of Ref. 5, i.e.,

$$A = (4\pi/3)^{1/3} (2\pi)^{-1} (k_B^2 \theta_D / \hbar a^2) (T_c / \theta_D)^3 L_b, \quad (2)$$

$$\gamma \simeq (\pi/2) (k_B T_c / \bar{t}) (L_b / a) \lambda_{1a}, \quad (3)$$

where a is the lattice constant, θ_D is the Debye temperature, L_b is the mean free path for boundary scattering of phonons, \bar{t} is the effective hopping matrix element for a two-dimensional tight-binding band of electrons, and λ_{1a} is the coupling strength between electrons and longitudinal-acoustic phonons, we estimate the value of L_b to be $\approx 20 \mu\text{m}$ from Eq. (2) and λ_{1a} to be ≈ 0.04 from Eq. (3). In this estimation, we have used $\theta_D = 360$ K, $a = 4 \text{ \AA}$, and $\bar{t} = 5000$ K. The value of L_b is consistent with the measured particle size determined from SEM measurements. The value of λ_{1a} is consistent with the 0.03–0.08 reported by Peacor *et al.*¹⁷ on single crystals.

For selective doping by impurities that alter the superconductivity, the interesting features seen in $K(T)$ and associated with superconductivity are dramatically modified. In Fig. 3(a), we present the normalized thermal conductivity, $K(T)/K(180 \text{ K})$, vs T for $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $y=0.0, 0.1, 0.2$, and 0.4 . The anomaly in $K(T)$ at $T \sim T_c/2$ is suppressed with increasing Pr concentration. The compound with $y=0.1$ shows a small maximum in $K(T)$ below T_c ; however, no clear enhancement can be observed for $y=0.2$ and 0.4 which are still superconducting with $T_c \approx 70$ and 45 K, respectively.

Similar features in $K(T)$ also appear in Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$, as illustrated in Fig. 3(b). Zn has almost the same radius as Cu (0.75 and 0.73 \AA , respectively) and the same ionic valence (+2); however, Zn has a filled $3d$ ¹⁰ shell, and it is nonmagnetic. The rapid depression of T_c

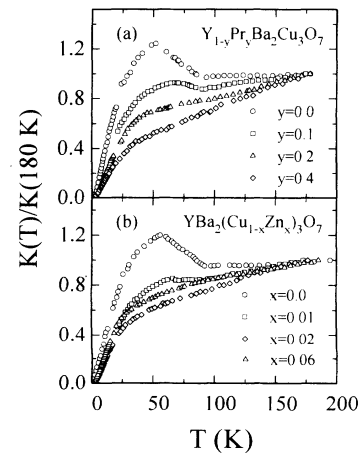


FIG. 3. $K(T)/K(180 \text{ K})$ vs T ; (a) for $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $y=0.0, 0.1, 0.2$, and 0.4 . (b) for $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ with $x=0.0, 0.01, 0.02$, and 0.06 .

with the substitution of Zn for Cu has been attributed to a localization of the Cu^{2+} d holes. This interpretation is supported by measurements of the electron-spin-resonance absorption and indirectly by transport, heat-capacity, and magnetization studies.⁷ There is a small enhancement of $K(T)$ below T_c for 1% Zn dopant, however, no clear maximum below T_c can be observed for 2% (or higher) Zn content which is still superconducting with a $T_c \approx 72$ K. Further substitution of Cu with Zn does not dramatically affect the features of $K(T)$. Although the mechanisms causing strong depression of T_c with Zn and Pr doping remain controversial and are probably different (one due to hybridization effects between Pr $4f$ electrons and conduction bands and the other due to the Cu^{2+} d holes localization), the impurity effects on $K(T)$ for both Zn and Pr doping are quite similar. Even though the details of the pair-breaking or pair-weakening mechanisms may be different, the manifestation on fundamental properties, e.g., quasiparticle excitation spectrum and/or lifetimes, appears to be similar leading to the suggestion that there may be a common mechanism causing the strong depression of the enhancement of $K(T)$ below T_c .

In order to more thoroughly explore the effect of impurities on the behavior of $K(T)$ and determine that the observed change in $K(T)$ for Zn and Pr doping is not due to a simple impurity-scattering mechanism and does not reflect a global change of the excitation spectra, we have also measured $K(T)$ of other samples in which the dopants are known to have little effect on T_c . It is well known that the transition temperature and magnetic ordering of Cu spins in Cu-O planes are essentially unchanged by substituting other rare-earth elements (except Ce, Tb, and Pr) into the Y sites in $\text{YBa}_2\text{Cu}_3\text{O}_7$. These rare-earth elements are believed to have a negligible exchange interaction between the carriers in the adjacent Cu-O planes which are intimately associated with the superconductivity and the $4f$ electrons, a high transition temperature (~ 92 K) is thus maintained. A comparison of T_c vs doping concentration for Pr and Gd-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ is shown in Fig. 4(a). The lack of sensitivity of T_c to rare-earth doping may imply these rare-earth elements do not alter other superconducting parameters, e.g., the energy gap or Cooper pair formation. We could thus expect that the substitution of Y by Gd would not dramatically affect the behavior of $K(T)$ below T_c . This is indeed the case as shown in Fig. 5(a). Even with 70% Gd substitution, $K(T)$ still sustains a clear and sharp maximum around $T_c/2$. This result is in contrast to that obtained for Pr-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ and would indicate that the strong suppression of the maximum below T_c in $K(T)$ with Pr doping must be associated with a change of other parameters, e.g., the energy gap and/or the electron-phonon coupling strength, than simply changes in the impurity scattering of the phonons.

Comparing $K(T)$ for Al- and Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$, similar statements can be made relative to Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$. Unlike Zn, which seems to prefer to substitute on the Cu-O₂ plane Cu sites,^{18,19} Al is believed to go to the Cu-O chain sites¹⁸ and causes only a slight depres-

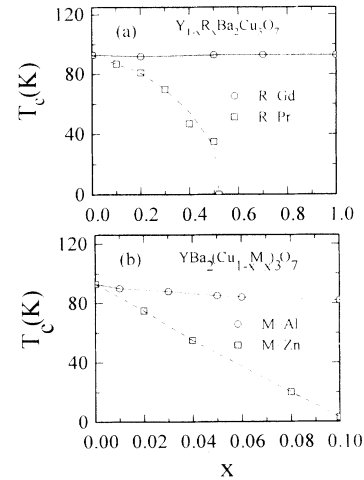


FIG. 4. T_c vs doping concentration for selective dopants; (a) for $\text{Y}_{1-x}\text{R}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ with $R = \text{Pr}$ and Gd . (b) for $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_7$ with $M = \text{Zn}$ and Al .

sion of T_c as seen in Fig. 4(b). We could therefore expect that the behavior of $K(T)$ for the Al-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ would be similar to that of Gd dopants, i.e., giving less suppression of $K(T)$ below T_c . In Fig. 5(b), we present $K(T)/K(180 \text{ K})$ vs T for 2 and 10% Al-doped compounds. The obvious maximum at $T_c/2$ can still be observed even in the 10% Al-doped sample.

A comparison of the changes in $K(T)$ for Pr- (Zn) and Gd- (Al) doped high- T_c superconductors suggests that the dramatic modification of $K(T)$ for those impurities that depress T_c can not be simply related to changes in phonon-impurity scattering. Using the same fitting parameters for Eq. (1) as for a fully oxygenated sample, we note that if T_c is scaled from 93 to 70 to 50 K, the corresponding theoretical curves of $K(T)$ vs T/T_c fall on a universal curve (Fig. 6). This indicates that if we introduce impurity dopants that just shift T_c and other con-

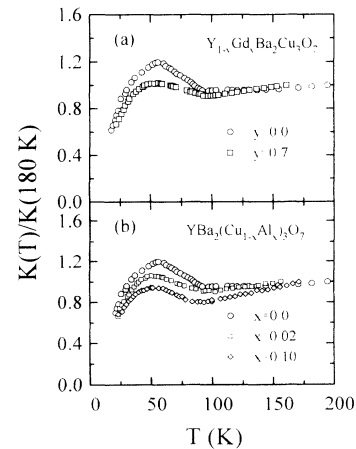


FIG. 5. $K(T)/K(180 \text{ K})$ vs T ; (a) for $\text{Y}_{1-y}\text{Gd}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $y = 0.0$ and 0.7 . (b) for $\text{YBa}_2(\text{Cu}_{1-x}\text{Al}_x)_3\text{O}_7$ with $x = 0.0, 0.02,$ and 0.1 .

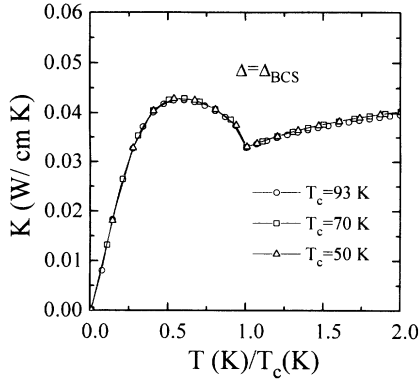


FIG. 6. $K(T)$ vs $T(K)/T_c(K)$ for three scaling curves with $T_c = 93, 70,$ and 50 K.

comitantly superconducting properties, e.g., gap, consistent with BCS theory, and the dopants do not strongly alter the relative contributions, then the maximum of $K(T)$ below T_c should retain the same height as that of the pure sample and only shift in position. Thermal conductivity results on Pr- or Zn-doped specimens contrast strongly with the modeled $K(T)$ assuming a “law of corresponding states” as shown in Fig. 6. Thus the changes in $K(T)$ for Pr- and Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ must strongly alter the relative contributions and/or modify the simple BCS scaling between T_c and gap function. Certainly, if the electron-phonon interaction is significantly reduced due to small addition of impurities, the sensitivity of $K(T)$ to the formation of a gap within the superconducting state would be diminished. Thus, if the electron-phonon interaction is “turned off,” then within the TW theory the phonons do not “see” the gap. This is demonstrated in Fig. 7 where a reduction of the electron-phonon interaction leads to a rapid depression in the $K(T)$ peak below T_c . In Fig. 7(a), we present a theoretical fit to a 1% Zn substitution, and in Fig. 7(b) a fit to

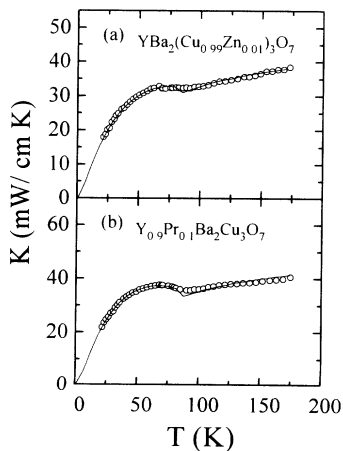


FIG. 7. $K(T)$ vs T ; (a) for $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ with $x = 0.01$. (b) for $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $y = 0.1$. Circles represent the experimental data and the continuous line indicates the fit from the TW theory.

10% Pr dopant. Clearly, the TW theory can provide reasonable fits to our results if λ is reduced, however, this appears to be an unsatisfactory explanation of the data because small levels of Zn and Pr would require substantial changes in the electron-phonon coupling. A further reduction in λ would be required to explain the $K(T)$ data for higher Zn and Pr doping.

A plausible explanation for the rapid suppression of the $K(T)$ peak for dopants that diversely effect the pairing, i.e., Pr and Zn, is a rapid suppression of the quasiparticle gap with the reduction in T_c as predicted by Nagao *et al.*²⁰ A manageable way of simulating the rapid suppression of the gap or a smearing of the gap function with Zn or Pr doping is to use the TW theory with a reduced gap to T_c ratio, i.e., a reduction in $\chi = \Delta(0)/\Delta(0)_{\text{BCS}}$. Shown in Fig. 8, the decrease of χ can also reduce the enhancement of $K(T)$ below T_c . In this figure, we employ the same fitting parameters obtained from the pure sample with $\chi = 1.0$ and vary χ from 0.3 to 1.1. Obviously, the enhancement below T_c at $\chi = 0.3$, and this feature is quite similar to that observed in 20% Pr or 2% Zn substitution. One can therefore reduce χ instead of λ to achieve a good fit for the $K(T)$ of Pr- or Zn-doped compounds. The decrease of $\chi[\Delta(0)/\Delta_{\text{BCS}}(0)]$ implies a more rapid depression of the energy gap that reflected by the reduced $T_c(x)$. This suggestion is consistent with heat-capacity measurements in doped $\text{YBa}_2\text{Cu}_3\text{O}_7$, e.g., Roth *et al.*²¹ found that the specific jump ΔC at T_c decreases very quickly with increasing Zn content. With 5% Zn substitution, ΔC was completely suppressed. This strongly suggests that Zn-doped samples exhibit a tendency to gapless superconductivity. Phillips *et al.*²² measured the specific jump ΔC at T_c on $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$, finding that ΔC decreases rapidly with increasing Pr concentration and with no clear ΔC at T_c to be observed at $y = 0.2$. $\Delta C/T_c$ (~ 8 mJ/mol K²) of the 10% Pr dopant was only $\sim 10\%$ that of the pure sample. As mentioned earlier, Nagao *et al.*²⁰ have theoretically examined the effects of a nonmagnetic impurity on the energy gap of high-temperature superconductors using a spin-density-wave model.²³ The re-

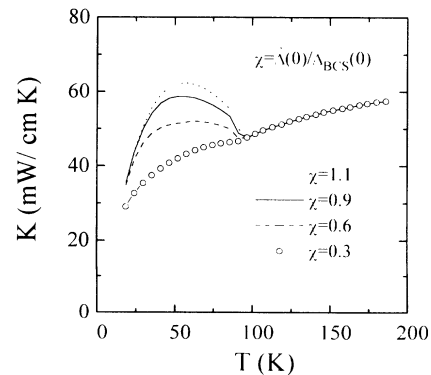


FIG. 8. The theoretical curves of $K(T)$ vs T for $\text{YBa}_2\text{Cu}_3\text{O}_7$ with different χ values: 0.3, 0.6, 0.9, and 1.1. The enhancement of $K(T)$ below T_c decreases with reducing χ values.

sults show that the impurity atoms suppress the superconducting energy gap Δ_{sc} below that predicted using a BCS model. More direct evidence of the gapless behavior in nonmagnetic impurity-doped high- T_c superconductors was provided by Akimenko *et al.*²⁴ They have used point-contact spectroscopy to directly probe the energy gap of $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$, and observed a two-gap structure, Δ_{\min} and Δ_{\max} . Both Δ_{\min} and Δ_{\max} decrease with increasing Zn content with Δ_{\min} being suppressed much faster than Δ_{\max} .

The above theoretical and experimental results support suggestion that the rapid decrease of $K(T)$ below T_c of Pr- or Zn-doped compounds originates from the suppression of the superconducting energy gap. This rapid depression of the gap as compared to that seen in conventional, low- T_c system may be related to the extremely short coherence length for the high- T_c systems as compared to low- T_c systems. These impurities coupled with the short coherence length may lead to a broadening of the electronic states on both sides of the energy gap resulting in a decrease of the gap and enhancement of $K(T)$ below T_c . We therefore suggest that the decrease in superconducting gap causes the suppression of the enhancement of $K(T)$ below T_c in Pr and Zn substitution. More experimental and theoretical work is necessary to clarify this conclusion, particularly on doped single crystals.

Shown in Fig. 9(a) is the $\ln[K(T)/K(180\text{ K})]$ vs $\ln[T(K)]$ of $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $y=0.0, 0.2,$ and 0.4 for $1.8 \leq T \leq 10$ K. The linear dependence of $\ln[K(T)/K(180\text{ K})]$ vs $\ln[T(K)]$ suggest a power-law relationship, i.e., $K(T) \propto T^n$. From the linear fit, we obtain $n \approx 1.99$ for $y=0.0$, 1.88 for $y=0.2$, and 1.81 for $y=0.4$. Thus, for $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$, the measured $K(T)$ roughly follows $K(T) \propto T^n$ with $n \approx 1.9 \pm 0.1$. A slight change in n with Pr dopants may be from the small increase of sheetlike fault scattering upon Pr doping. This approximate T^2 temperature dependence of $K(T)$ as $T \rightarrow 0$ for both pure and Pr-doped samples is consistent

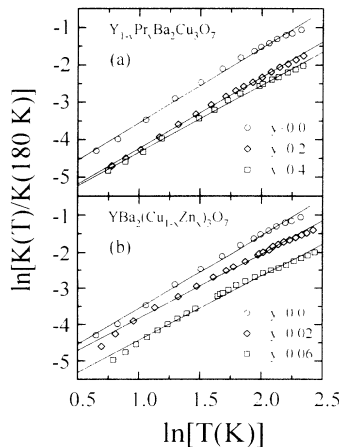


FIG. 9. $\ln[K(T)/K(180\text{ K})]$ vs $\ln[T(K)]$ at $1.8 \leq T \leq 10$ K; (a) for $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $y=0.0, 0.2,$ and 0.4 . (b) for $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ with $x=0.0, 0.02,$ and 0.06 . All fitting slopes follow approximately 1.9 ± 0.1 .

with previous results for pure $\text{YBa}_2\text{Cu}_3\text{O}_7$ and, as suggested previously, that two-level tunneling scattering may play an important role in this low-temperature range. The fact that the value of n is not strongly affected by the Pr dopants is consistent with the phonon density results from inelastic neutron-scattering measurements.²⁵ This data shows that even with 50% Pr substitution, no remarkable shift in peak positions in the generalized phonon density of $\text{YBa}_2\text{Cu}_3\text{O}_7$ can be detected. In Fig. 9(b), we also present the $\ln[K(T)/K(180\text{ K})]$ vs $\ln(T)$ for several Zn concentrations. The $K(T)$ follows a similar temperature dependence as that of Pr doping, namely $K(T) \propto T^{1.9 \pm 0.1}$. This lack of sensitivity in the power-law dependence of $K(T)$ agrees with a similar lack of sensitivity of the phonon spectrums obtained from neutron-scattering measurements due to Zn doping, i.e., the generalized phonon density of states are essentially unchanged with Zn dopants.²⁶

In Fig. 10(a), we present the $K(T)/K(180\text{ K})$ vs T for $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ ($y=0.0, 0.2,$ and 0.4) and Fig. 10(b) for $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ ($x=0.0, 0.02,$ and 0.06) at temperatures $1.8 \leq T \leq 18$ K. Clearly, $K(T)/K(180\text{ K})$ decreases with increasing Pr or Zn concentrations. This behavior appears to be consistent with expected behavior assuming it is limited by a two-level tunneling mechanism, namely $K(T) \propto T^2/D$ where D is the tunneling density of states. The decrease of $K(T)$ with increasing Pr or Zn concentrations implies D should increase with increasing dopant. If such glass behavior is responsible for the $K(T) \propto T^2$, as observed, than $C = \gamma T$ with $\gamma \propto D$ and increasing with increasing doping. The low temperature C/T vs T measurements^{6,7} show that for both dopants, γ increases with increasing doping concentrations leading to a rise in the density of states. These results are consistent with the above argument, however, the details associated with this model are not clear.

In summary, we have performed measurements of the thermal conductivity of pure and doped compounds. Both Pr and Zn dopants suppress the enhancement of

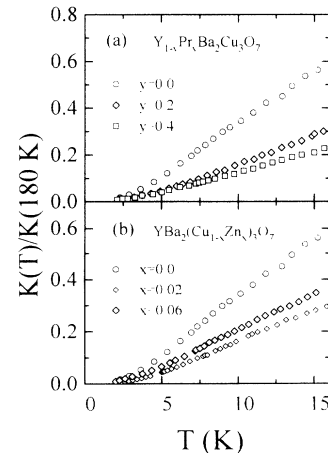


FIG. 10. $K(T)/K(180\text{ K})$ vs T at $1.8 \leq T \leq 10$ K; (a) for $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_7$ with $y=0.0, 0.2,$ and 0.4 . (b) for $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ with $x=0.0, 0.02,$ and 0.06 .

$K(T)$ below T_c dramatically and this can be ascribed to the reduction of superconducting energy gap. Contrary to Pr and Zn dopants, Gd and Al doping do not significantly affect the enhancement of $K(T)$ below T_c . The superconducting energy gap and electron-phonon coupling strength are essentially sustained in these materials.

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