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Influence of Cu site impurities on the thermal conductivity of $YBa_2Cu_3O_{7-\delta}$

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Abstract

The effect of Zn substitution at in-plane Cu sites in 90 K and 60 K phase $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ sintered materials ($0 < x < 0.04$) was investigated from the viewpoint of thermal conduction. The characteristic enhancement of the thermal conductivity κ just below T_c in pure YBCO was rapidly suppressed in both phases by the Zn substitution. Based on the phonon heat conduction model, the disappearance of the κ enhancement is attributed to the depressed phonon–electron scattering caused by the Zn substitution.

1. Introduction

In the $YBa_2Cu_3O_{7-\delta}$ (YBCO) system, two stable superconducting phases are known to exist, the 90 K and the 60 K phase. Impurity Zn atom substitution at Cu sites increases the electrical resistivity ρ in the normal state and results in the reduction of the transition temperature, T_c. The rapid reduction of T_c has been attributed to a localization of Cu^{2+} d-holes. [1] The thermal conductivity κ is a valuable probe for the scattering processes of phonons in both normal and superconducting states. A characteristic feature of thermal conductivity $\kappa(T)$ in YBCO is a rapid rise just below T_c and the existence of a maximum at about $T_c/2$ [2]. In this report, we investigate the effect of Zn impurity on the thermal conductivity $\kappa(T)$ for both the 90 K and 60 K phase YBCO samples. The experimental results are systematically analyzed on the basis of the phonon heat conduction model.

2. Experimental procedure

90 K phase $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ ($0 < x < 0.04$) samples were prepared from stoichiometric mixtures of Y_2O_3, $BaCO_3$, CuO and ZnO raw powders. The mixtures were calcined at 910°C for 24 h in air. They were pulverized, pressed into pellets and then sintered at 955°C for 30 h in flowing oxygen. 60 K phase samples were fabricated by a quenching process from 600°C down to liquid nitrogen temperature. The oxygen deficiency δ of the 90 K phase and 60 K phase samples was estimated to be $\delta \approx 0.1$ and ≈ 0.3, respectively [3]. The density of these samples was about 90% and independent of the oxygen deficiency and the Zn concentration. The thermal conductivity measurement was made by a continuous

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heat flow method between 10 and 150 K using an automated measuring apparatus with Au(0.07 at.%Fe)–chromel thermocouples as thermometers [4].

3. Experimental results

Fig. 1 shows the temperature dependence of the electrical resistivity ρ of 90 K and 60 K phase $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ samples. The metallic behavior of $\rho(T)$ was preserved for all 90 K phase samples, though ρ increased with increasing Zn concentration x. $\rho(T)$ of the 60 K phase samples showed a bump just above T_c and the height of the bump increased with increasing x. The inset in Fig. 1 shows the Zn concentration dependence of T_c of these samples. T_c decreased linearly with increasing Zn concentration x and the T_c depression rate for x $(\Delta T_c/\Delta x)$ was almost the same for 90 K and 60 K phase samples.

Fig. 2 shows the thermal conductivity κ as a function of temperature T for the 90 K and 60 K phase $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ samples. For 90 K phase samples, the characteristic enhancement was suppressed quite rapidly by the Zn substitution. The enhancement was barely discernible even for the specimen with $x = 0.005$, which showed a sharp superconducting transition at $T_c = 85$ K. The $\kappa(T)$ values decreased with increasing x in the normal state. The κ enhancement was also observed in the 60 K phase YBCO below $T_c(= 58$ K) but it was less obvious than that of the 90 K phase YBCO. The κ enhancement of the 60 K phase $YBa_2Cu_3O_{7-\delta}$ is, however, far clearer than that of the 90 K phase $YBa_2(Cu_{0.98}Zn_{0.02})_3O_{7-\delta}$, in spite of almost the same T_c values of both samples. In the 60 K phase the enhancement was completely suppressed by the Zn substitution, even for the specimen with $x = 0.005$ ($T_c = 40$ K).

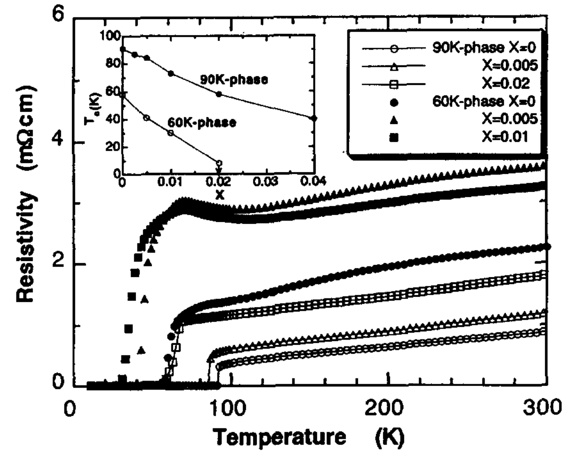

Fig. 1. The temperature dependence of the electrical resistivity ρ of the 90 K and 60 K phase $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ sintered samples. The inset shows the Zn concentration dependence of T_c of these samples.

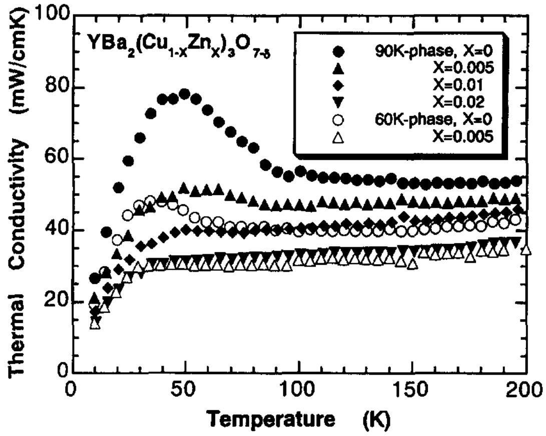

Fig. 2. The temperature dependence of the thermal conductivity κ of the 90 K phase and 60 K phase $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ samples with various Zn concentrations.

4. Discussion

The heat transport in conductors is due to both electrons (κ_e) and phonons (κ_{ph}). In the normal state the electron contribution κ_{en} can be estimated by using the Wiedemann–Franz law. In the superconducting state, we assume that κ_{es} follows the theory proposed by Kadanoff and Martin [5], which predicts the reduction of κ_e below T_c because of the formation of Cooper pairs. Taking account of the phonon scattering by various crystal defects and electrons, the phonon contribution is given by Tewordt and Wölkhausen [6] in the following way:

$$\kappa_{ph} = \frac{3dnRT^3v^2}{M\Theta_D^3}\int_0^{\Theta_D/T}\frac{x^4e^x}{(e^x-1)^2}\tau_{ph}\,dx, \qquad (1)$$

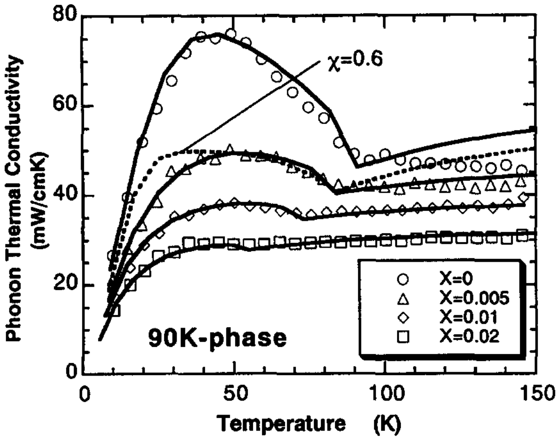

Fig. 3. The fitting of κ_{ph} by the TW-BRT theory for the 90 K phase samples with various Zn concentrations. The solid lines are the calculated curves using parameter values in Table 1 ($\chi = \Delta(0)k/\Delta(0)_{BCS} = 1$). The dotted line for the $x = 0.005$ sample presents the fitting in which $\chi = 0.6$ is used as the reduced gap.

where d is the mass density, M the mass of 1 mole, $n(= 13)$ the number of atoms composing YBCO compounds, R the gas constant, Θ_D the Debye temperature, v the average phonon velocity and x the reduced phonon frequency. The phonon relaxation time τ_{ph} is given by

$$\frac{1}{\tau_{ph}} = \tau_b^{-1} + sT^2x^2 + pT^4x^4 + ETxg(x, y). \tag{2}$$

Here, τ_b is the phonon relaxation time due to grain boundaries and s, p and E refer to the strength of the phonon scattering by sheet-like faults, point defects and electrons, respectively. The function $g(x, y) = \tau_{phn}/\tau_{phs}$ stands for the ratio of the phonon–electron relaxation time in the normal and superconducting states, which depends on the energy gap through the parameter $y = \Delta(T)/k_BT$ as given by Bardeen, Rickayzen and Tewordt [7].

Fig. 3 shows fitting curves of the phonon thermal conductivity $\kappa_{ph}(= \kappa - \kappa_e)$ for the 90 K phase samples. The parameters used and determined in the fitting process are summarized in Table 1. As can be seen, the theoretical curves reproduced the measured $\kappa_{ph}(T)$ quite satisfactorily. The electron–phonon coupling parameter $\lambda(= 2a\langle t\rangle E/\pi v$, where a and $\langle t\rangle$ are the lattice spacing and the effective hopping matrix element of electrons, respectively [6]) suddenly decreases by addition of Zn impurity. The strength of the phonon scattering by point defects, p, increases with increasing x because of the alloying effects, but the increase is somewhat moderate. The rapid suppression of the $\kappa(T)$ peak for Zn substitution might also be explained by a suppression of the superconducting gap, $\chi = \Delta(0)/\Delta(0)_{BCS}$, because then the phonon scattering by electrons survives at lower temperatures [8]. An example of the fitting for a reduced energy gap ($\chi = 0.6$) is shown in Fig. 3 for the 90 K phase sample with $x = 0.005$. However, the fitting curve did not reproduce the measured $\kappa_{ph}(T)$ in the low-temperature region. Thus, the disappearance of the κ enhancement is mainly attributed to the depressed phonon–electron coupling strength λ. As can be seen in Fig. 1, ρ increases by addition of Zn. As Pippard pointed out [9], the electron–phonon interaction is diminished by shorter

Table 1
Characteristic parameters of the 90 K phase and 60 K phase $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$

Sample	90 K phase $x = 0$	90 K phase $x = 0.005$		90 K phase $x = 0.02$	60 K phase $x = 0$
χ	1	1	0.6	1	1
T_c (K)	91	85		57	58
Θ_D (K)	430	430		430	380
d (g/cm^3)	5.68	5.47		5.73	5.53
τ_b^{-1} (s^{-1})	3.0×10^8	3.1×10^8	2.9×10^8	3.2×10^8	3.2×10^8
p (K^{-4} s^{-1})	456	1507	439	4497	1402
s (K^{-2} s^{-1})	2.7×10^6	2.7×10^6	2.8×10^6	2.9×10^6	4.5×10^6
E (K^{-1} s^{-1})	6.9×10^8	1.3×10^8	7.1×10^8	2.9×10^7	3.3×10^8
λ	0.26	0.05	0.27	0.01	0.13

electron mean free paths. The rapid depression of λ might be related to the d-hole localization caused by Zn impurities [1].

The electron–phonon coupling parameter λ of the 60 K phase $YBa_2Cu_3O_{7-\delta}$ sample is larger than that of the 90 K phase $YBa_2(Cu_{0.98}Zn_{0.02})_3O_{7-\delta}$ sample with almost the same T_c (see Table 1). This indicates that the small amount of Zn substitution at in-plane Cu sites more directly and seriously suppresses the superconductivity than the oxygen reduction from the CuO chains, making the anomaly of the phonon thermal transport below T_c disappear.

A central point in the recent dispute on the enhancement of $\kappa(T)$ is concerned with its origin; phonons or electrical carriers. In this paper, we consistently assumed the phonon origin model, and the disappearance of the κ peak caused by the Zn substitution was attributed to the depression of electron–phonon interaction. If the electrical carrier is responsible for the κ enhancement, a very small amount of Zn impurity should dramatically enhance the quasi-particle scattering rate below T_c. Experiments to determine the quasi-particle scattering rate in a Zn-doped crystal are highly desirable.

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