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Enhanced phonon scattering due to 3d-transition metal substitution for Cu in $YBa_2Cu_3O_{7-\delta}$

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Abstract

The characteristic enhancement below T_c in the thermal conductivity κ of high-T_c oxides, $YBa_2Cu_3O_{6.92}$ (90 K phase) and $YBa_2Cu_3O_{6.7}$ (60 K phase), is promptly quenched by a small amount of 3d-transition metal (Fe, Co, Ni) substitution for Cu. The quench of the κ enhancement can be understood as being due to the enhanced phonon scattering below T_c by residual unpaired electrons. The existence of a considerable amount of the residual electrons is consistent with the d-wave symmetry of the superconducting energy gap under strong electron scattering. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal conductivity; Oxide superconductors; Cu site substitution; Magnetic impurity

The thermal conductivity κ of high-T_c cuprates (HTSC) has been widely investigated because κ can be measured below the superconducting transition temperature T_c and can provide important information concerning the superconductivity of HTSC. $YBa_2Cu_3O_{7-\delta}$ is one of the representative HTSC systems and show two typical transition temperatures at $T_c \approx 90$ K (90 K-YBCO: $\delta \approx 0.08$) and $T_c \approx 60$ K (60 K-YBCO: $\delta \approx 0.3$) depending on the oxygen deficiency δ. T_c of conventional superconductors is drastically reduced by addition of magnetic impurities. In this paper, the effect of 3d-transition metal impurities M (M = Fe, Co, Ni) substituted for Cu is investigated for both 90 K- and 60 K-YBCO and is compared with that of non-magnetic Zn substitution. The main interest is placed on the impurity effect on the thermal transport in the YBCO system.

$YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$ polycrystals were prepared by a standard solid state reaction method. The raw materials were powders of Y_2O_3, $BaCO_3$, CuO and transition metal oxides (NiO, CoO or Fe_2O_3). They were calcined at 910°C for 24 h in air, pulverized, pressed into pellets, sintered at 955°C for 30 h in flowing oxygen and then slowly cooled to the room temperature in about 24 h. Thus prepared samples correspond to the 90 K-YBCO(M_x) samples. The 60 K-YBCO(M_x) samples were obtained by quenching 90 K-YBCO(M_x) into liquid nitrogen from 600°C. The oxygen deficiency δ of 60 K-YBCO was estimated to be ~ 0.3 from the c-axis lattice parameter and from relative weight loss after quenching process. The thermal conductivity was measured by a standard continuous heat

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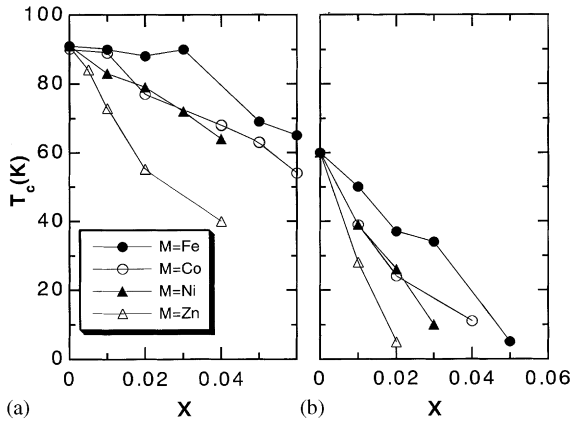

Fig. 1. T_c as a function of impurity concentration x for (a) 90 K-YBCO(M_x) and for (b) 60 K-YBCO(M_x).

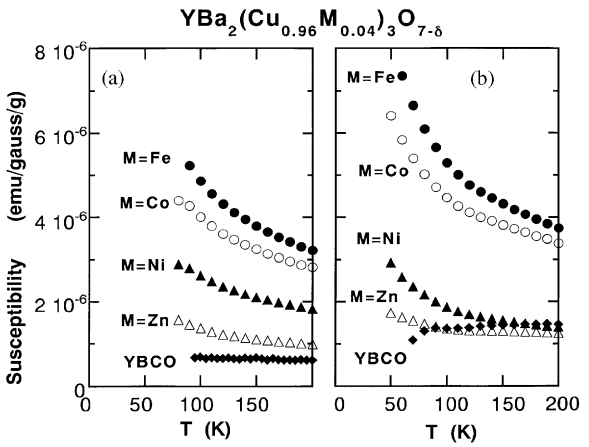

Fig. 2. Magnetic susceptibility as a function of temperature for (a) 90 K-YBCO($M_{0.04}$) and for (b) 60 K-YBCO($M_{0.04}$).

flow method [1]. The magnetic susceptibility χ was measured by a commercial SQUID magnetometer.

Fig. 1a and b show the superconducting transition temperature T_c as a function of Fe, Co, Ni and Zn impurity concentration x for 90 K-YBCO(M_x) and 60 K-YBCO(M_x), respectively. In Fig. 1a and b, we notice that the T_c depression for increasing x is the most steep for the nonmagnetic Zn impurities and is the most gradual for Fe impurities. Fig. 2a and b show the temperature dependence of the magnetic susceptibility χ of 90 K-YBCO($M_{0.04}$) and 60 K-YBCO($M_{0.04}$). In Fig. 2a and b, Fe impurities

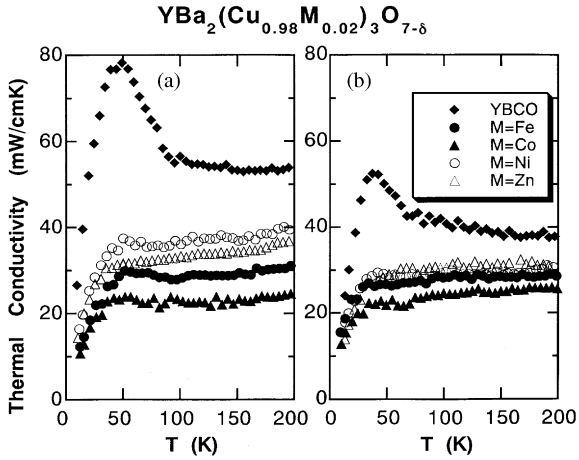

Fig. 3. (a) The thermal conductivity κ of 90 K-YBCO($M_{0.02}$) and (b) κ of 60 K-YBCO($M_{0.02}$).

are the most magnetic followed by Co and Ni in this order. In contrast, T_c depression is stronger in rather the reverse order, i.e., the more weakly magnetic ions damages the superconductivity more seriously. The results in Figs. 1 and 2 seem to indicate that the magnetic scattering for conduction electrons [2] is not the main origin of the T_c depression in both 90 K-YBCO(M_x) and 60 K-YBCO(M_x).

Fig. 3a and b show the temperature dependence of the thermal conductivity κ of 90 K-YBCO($M_{0.02}$) and 60 K-YBCO($M_{0.02}$). κ of 90 K- and 60 K-YBCO [3] is also presented for comparison. The thermal conductivities of both 90 K-YBCO and 60 K-YBCO show the characteristic enhancement below T_c, taking the maximum around $T_{max} \sim T_c/2$. In the present YBCO polycrystals, the upper limit of the electron thermal conductivity κ_e is under strong ceiling by relatively large electrical resistivity and κ_e is estimated to hardly contribute to the κ enhancement [4,5]. Then similarly to conventional alloy superconductors [6], the κ enhancement is considered to come from the reduced phonon scattering into the Cooper pairs. We analyze the phonon thermal conductivity on the basis of the following formula [7]:

$$\kappa_{ph} = \frac{3dn_0R\langle v_s^2\rangle}{2\pi M}\left(\frac{T}{\Theta_D}\right)^3 \int_0^{2\pi} d\phi \int_0^{\Theta_D/T} \times \frac{x^4 e^x}{(e^x-1)^2}\,\tau_{ph}(x)\,dx, \quad (1)$$

where x is the reduced phonon frequency, $n_0(=13-\delta)$ the number of atoms composing $YBa_2Cu_3O_{7-\delta}$, R the gas constant, d the mass density and M the molar weight. The total phonon scattering rate $1/\tau_{ph}$ is assumed to be given by the sum of scattering rates by various centers [7],

$$\tau_{ph}^{-1} = \tau_b^{-1} + sT^2x^2 + pT^4x^4 + ETxg(x,y) + E'Tx + UT^3x^2\exp\left(-\frac{\Theta_D}{bT}\right). \quad (2)$$

Here, parameters τ_b^{-1}, s, p, $Eg(x, y)$, E and U represent the phonon scattering strength due to grain boundaries, sheet-like faults, point defects, electrons, residual normal electrons and other phonons (umklapp process). The ratio of the phonon scattering by electrons $g(x, y) = \tau_{phn}^e/\tau_{phs}^e$ in the normal state to in the superconducting state was first given by BRT [8,9]. We assumed the d-wave superconducting energy gap, $\Delta = \Delta_0 \cos 2\phi$ [10]. The electron thermal conductivities κ_e was subtracted from observed κ by use of the Wiedemann–Franz law for $T > T_c$ and by use of Kadanoff's formula for $T < T_c$ [11]. κ_e is always much smaller than κ_{ph}. Examples of the fitting curves for κ_{ph} are shown in Fig. 4 for 90 K-YBCO($M_{0.02}$). Table 1 summarizes the used fitting parameters. The most impressive result is the absence of the κ enhancement below T_c caused by the impurities. As can be seen from parameter values in Table 1, we attributed the disappearance of the enhancement to the phonon scattering by residual electrons (E' term) which do not condense into Cooper pairs even at 0 K. Miyake calculated T_c/T_{c0} versus N_{res}/N_0 relation (T_c/T_{c0} is the transition temperature in the presence of impurity scattering normalized by the pure sample transition temperature T_{c0} and N_{res}/N_0 is the fraction of the residual electron density at 0 K) [12]. The calculation pointed out very large N_{res}/N_0 in the case of the d-wave energy gap and in the limit of strong (unitarity limit) electron scattering by impurities. The results of our analyses of κ_{ph} are semi-quantitatively consistent with the theoretical prediction of Miyake in the case of strong scattering. As for Zn impurities, however, a considerable reduction of the phonon–electron scattering must be postulated to explain the stronger reduction effect of Zn for the thermal conduction in the YBCO system.

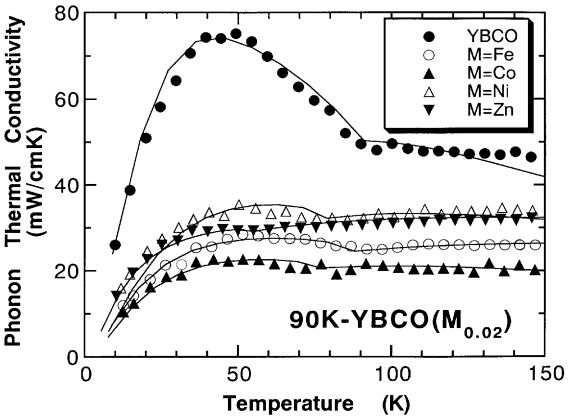

Fig. 4. Examples of the fitting curves based on the Eqs. (1) and (2) for 90 K-YBCO($M_{0.02}$).

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Table 1
Summary of the parameters used and determined in the fitting processes in pure 90 K-YBCO and 90 K-YBCO($M_{0.02}$) (M = Fe, Co, Ni, Zn) samples

Sample	T_c(K)	τ_b^{-1} (s^{-1})	s($K^{-2}s^{-1}$)	p($K^{-4}s^{-1}$)	E ($K^{-1}s^{-1}$)	E' ($K^{-1}s^{-1}$)	U($K^{-3}s^{-1}$)
YBCO	91	4.6×10^8	3.1×10^6	2.7×10^2	1.0×10^9	0	4.3×10^3
M = Fe	88	7.8×10^8	4.0×10^6	2.6×10^3	6.6×10^8	1.8×10^8	6.5×10^2
M = Co	77	4.5×10^8	3.8×10^5	3.3×10^3	5.2×10^8	3.5×10^8	3.2×10^3
M = Ni	79	4.2×10^8	3.3×10^5	1.5×10^3	1.4×10^8	4.7×10^8	2.9×10^3
M = Zn	55	2.9×10^8	4.8×10^5	5.2×10^3	5.3×10^7	1.1×10^8	3.2×10^2

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