Enhanced Phonon Scattering below T_c Caused by Zn and Ni Substitution in La_{1.85}Sr_{0.15}CuO₄

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The thermal conductivity κ has been measured for $La_{2,X}Sr_XCuO_4$ and $La_{1,85}Sr_{0.15}Cu_{0.98}M_{0.02}O_4$ (M; Zn, Ni). The characteristic enhancement in κ below T_c was confirmed for $La_{1.85}Sr_{0.15}CuO_4$. The phonon scattering mechanisms were analyzed in detail and the electron-phonon coupling constant λ was estimated to be ~0.05. The κ enhancement becomes indetectable on Zn or Ni substitution for Cu, which indicated survival of the phonon scattering by charge carriers down to lower temperatures as a result of reduced T_c .

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1. INTRODUCTION

The thermal conductivity κ of several high T_c cuprates, typically YBa₂Cu₃O₇^{1,3}, shows a characteristic enhancement below the superconducting transition temperature T_c . In contrast, La_{2.x}M_xCuO₄ with T-type structure does not clearly show the corresponding enhancement.⁴ In this paper, we present observation of the κ enhancement in La_{1.85}Sr_{0.15}CuO₄ and its rapid quenching by a small amount substitution of Cu by Zn and Ni. The origin of the κ enhancement is discussed and the phonon scattering mechanisms are analyzed in detail.

2. EXPERIMENTAL

La_{2-x}Sr_xCuO₄ and La_{1.85}Sr_{0.15}Cu_{0.98}M_{0.02}O₄ (M; Zn, Ni) samples were prepared by a solid state reaction method. The density of the samples was higher than 90% of the ideal one. The κ measurement was made between 10K and 150K by a continuous heat flow method and the thermal diffusivity α was measured by an arbitrary heating method simultaneously with κ .⁵

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3. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the electrical resistivity $\rho(T)$ of La_{2-X}Sr_XCuO₄ (LSCO) for X=0.10, 0.15 and 0.20. The ρ values decrease with increasing Sr concentration X. The superconducting transition temperature T_c (= T_c^{end}) is 31K, 38K and 33K for X=0.10, 0.15 and 0.20, respectively. Figure 2 shows the phonon thermal conductivity κ_{ph} as a function of temperature T. κ_{ph} of LSCO (X=0.15) shows an enhancement below T_c and takes a weak maximum at $T\sim$ 30K. For LSCO (X=0.20), a trace of the κ enhancement below T_c is discernible.

The heat conduction in metals is due to both the electrons (κ_e) and the phonons (κ_{ph}). We assume that the normal state electronic component κ_{en} follows the Wiedemann-Franz law, while that of the superconducting state κ_{es} follows the theory by Kadanoff and Martin⁶ with the d-wave energy gap $\Delta = 1.5 \Delta_{BCS} \cos 2\phi$.³ We also assume a T^3 dependence of $\rho(T)$ below T_c .³ κ_e is always much smaller than total κ because of a large residual resistivity $\rho(0)$ ($\geq 0.25m\Omega cm$) as estimated by the extrapolation to T=0K.

The phonon thermal conductivity κ_{ph} (= κ - κ_e) is given by

$$\kappa_{\rm ph} = \frac{3dn_0 R < v_s^2 >}{2\pi M} \left(\frac{T}{\Theta_{\rm D}}\right)^3 \int_0^{2\pi} d\phi \int_0^{6\pi} \frac{x^4 e^x}{(e^x - 1)^2} \tau_{\rm ph}(x) dx \quad , \tag{1}$$

where $n_0(=7)$ is the number of atoms composing the 214 compounds, R the gas constant $v_s (\sim 3700 \text{ m/s})^7$ the average sound velocity and x is the reduced phonon frequency. Assuming a kind of Matthiesen's rule for the scattering rates, the



Fig. 1. The temperature dependence of the electrical resistivity $\rho(T)$ of La_{2-x}Sr_xCuO₄ (X=0.10, 0.15, 0.20).

Fig. 2. κ_{ph} vs *T* of La_{2-X}Sr_XCuO₄. The dashed line represents the estimated electronic component κ_{o} for X=0.15.

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phonon relaxation time τ_{ph} is given by

$$\tau_{pk}^{-1} = \tau_{b}^{-1} + \tau_{p}^{-1} + \tau_{s}^{-1} + \tau_{s}^{-1} + \tau_{k}^{-1}$$

= $\tau_{b}^{-1} + PT^{4}x^{4} + ST^{2}x^{2} + ETxg(x,y) + KTx \tanh\left(\frac{x}{2}\right).$ (2)

Here, τ_b is the phonon relaxation time due to grain boundaries and *P*, *S* and *E* refer to the strength of the phonon scattering by point defects, sheet-like faults and conduction electrons, respectively.⁸ *KTX*tanh(*X*/2) stands for the scattering due to two-level like tunneling states,⁹ which was suggested to be operative in this system.^{4,10} We assumed that the dynamical phonon scattering of apical oxygens is an important origin of the *K* term, which comes from the phase instability between LTO and HTT(or LTT) phases. The function, $g(x,y) = \tau_{en}/\tau_{es}$, gives the ratio of the phonon scattering by electrons in the normal and the superconducting states, which depends on the energy gap through the parameter $y = \Delta(T)/k_BT$.¹¹

In order to analyze the phonon scattering on the basis of the eqs. (1) and (2), we need the value of the Debye temperature Θ_D . The specific heat C was estimated from the relation $C = \kappa/\alpha$ and an average value of $\Theta_D = 350$ K was found to be appropriate for all the samples. The data of the $\alpha(T)$ measurement are presented in Fig. 3. $\tau_b = l_b/v_s$ was determined from the average grain size of each sample observed by a SEM. The results of the fitting for κ_{ph} are given by the solid lines in Fig. 2. The determined parameters are summarized in Table I. The calculated κ_{ph} can reproduce the measured κ_{ph} data satisfactorily.

In Table I, the electron-phonon coupling parameter λ is estimated from the relation, $\lambda = 2a < t > E \pi v_{,}^{12} a = 4$ Å being the lattice parameter and < t > = 5000K, the

Table I. Used and determined parameters in the fitting for κ_{ph} of the La_{2-X}Sr_XCuO₄ (X=0.10, 0.15, 0.20) and La_{1.85}Sr_{0.15}Cu_{0.98}M_{0.02}O₄ (M; Zn, Ni) samples.

	X=0.10	X=0.15	X=0.20	X=0.15	X=0.15
				M=Zn	M=Ni
$\tau_{b}^{-1}(s^{-1})$	1.7×10^{8}	3.5×10 ⁸	3.5×10 ⁸	3.4×10 ⁸	3.5×10 ⁸
$l_{\rm b}(\mu m)$	15.7	7.8	7.7	7.9	7.7
$S(K^{2}s)$	2.7×10^{6}	3.0×10^{6}	1.0×10^{7}	2.8×10^{6}	2.8×10^{6}
$P(\mathbf{K}^{4}\mathbf{s}^{1})$	7.6×10^{3}	8.1×10^{3}	5.9×10^{3}	6.0×10^{3}	5.4×10^{3}
$E(\mathbf{K}^{1}\mathbf{s}^{1})$	1.9×10^{7}	1.4×10^{8}	7.6×10^{7}	1.4×10^{8} *	$1.4 \times 10^{8} *$
$K(\mathbf{K}^{1}\mathbf{s}^{1})$	3.3×10 ⁸	3.8×10 ⁸	5.2×10^{8}	8.9×10 ⁸	9.9×10 ⁸
λ	0.01	0.05	0.03	(0.05)	(0.05)
<i>T</i> _c (K)	31	38	33	16	19
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* E value for X=0.15(M=Zn) and X=0.15(M=Ni) is assumed to be the same as that of the non-doped $La_{2,X}Sr_{X}CuO_{4}$.



Fig. 3. Thermal diffusivity $\alpha(T)$ of La_{2-X}Sr_X-CuO₄. The right hand ordinate provides a rough measure for the phonon mean free path l_{ob} .

Fig. 4. ρ vs *T* for La_{1.85}Sr_{0.15}Cu_{0.98}-M_{0.02}O₄ (M; Zn, Ni).

effective matrix element for the electron hopping in the CuO₂ plane. The obtained λ value is 0.05 for La_{1.85}Sr_{0.15}CuO₄. The origin of the pretty clear enhancement of κ for this compound is explained as to come from κ_{ph} similarly to that of the sintered YBa₂Cu₃O_{7- δ} system (λ ~0.4 and ~0.15 for 90K- and 60K-phase YBa₂Cu₃O_{7- δ}).

Figure 4 shows $\rho(T)$ of La_{1.85}Sr_{0.15}Cu_{0.98}M_{0.02}O₄ (M; Zn, Ni) and Fig. 5(a) shows $\kappa_{ph}(T)$ of the same samples. By substituting Zn (non-magnetic) or Ni (magnetic) for Cu by only 2%, T_c is drastically depressed. The depression effect is somewhat more conspicuous for Zn (T_c =16K) than Ni (T_c =19K). In Fig. 5(a), the behaviors of $\kappa_{ph}(T)$ for LSCO (2% Zn) and LSCO (2% Ni) are quite similar and almost indistinguishable. In comparison to $\kappa_{ph}(T)$ of non-substituted La_{1.85}Sr_{0.15}CuO₄, $\kappa_{ph}(T)$ of



Fig. 5 (a) κ_{ph} vs T for La_{1.85}Sr_{0.15}Cu_{0.98}M_{0.02}O₄ (M; Zn, Ni). (b) The fitting results for the samples. The origin of the y axis is shifted by 10mW/cmK for each sample.

Zn and Ni substituted LSCO is larger for $T \ge 35$ K, which is, however, strongly surpressed below T < 35K. The results of the fitting and the determined parameters are presented by solid lines in Fig. 5(b) and in Table I, respectively. These fittings suggest that the phonon-electron scattering term (ETxg(x, y) in eq.(2)) remains effective down to lower temperatures in the Zn and Ni substituted LSCO samples owing to the depression of T_c .

4. SUMMARY

The thermal conductivity $\kappa(T)$ of sintered La_{2-x}Sr_xCuO₄ (X=0.10, 0.15, 0.20) and La_{1.85}Sr_{0.15}Cu_{0.98}M_{0.02}O₄ (M; Zn, Ni) has been measured and the phonon scattering mechanisms in these compounds have been analyzed.

(1) La_{1.85}Sr_{0.15}CuO₄ showed the κ enhancement below T_c . The enhancement is attributable to the phonon component κ_{ph} , and the electron-phonon coupling parameter was determined to be $\lambda \sim 0.05$ from the size of the enhancement.

(2) The large residual electrical resistivity $\rho(0)$ excluded the electronic origin for the κ enhancement in the present sintered samples.

(3) By substituting Zn or Ni for Cu by 2%, the enhancement in κ_{ph} became indetectable. κ_{ph} of Zn or Ni substituted LSCO was more strongly depressed than that of the non-substituted mother compound below T<35K. This is because the phonon scattering by electrons still survives down to lower temperatures owing to the reduced transition temperature T_c caused by the substitution.

(4) The effect of the non-magnetic Zn substitution and that of magnetic Ni substitution on the thermal conductivity are very similar.

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