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Thermal conductivity and diffusivity of $Nd_{2-X}Ce_XCuO_4$

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Abstract

The thermal conductivity $\kappa(T)$, thermal diffusivity $\alpha(T)$ and electrical resistivity $\rho(T)$ of sintered $Nd_{2-X}Ce_XCuO_4$ ($0 \leqslant X \leqslant 0.2$) were measured for 'annealed' materials. $\rho(T)$ decreased with increasing Ce concentration and only the sample of $X = 0.2$ showed metallic behavior. The thermal conductivity showed maximum near $X = 0.15$, at which the superconductivity occurred. Taking account of the phonon–phonon interaction, $\kappa(T)$ was analyzed based on the Tewordt and Wölkhausen (TW) theory. The phonon scattering by electrons was confirmed to be very small up to $X = 0.15$ and it became discernible only for $X = 0.2$.

1. Introduction

$Nd_{2-X}Ce_XCuO_4$ (NCCO) belongs to the T'-phase structure with Cu–O squares in which the electron-doped superconductivity can be realized for $0.15 \leqslant X \leqslant 0.18$. This structure makes a contrast with that of the T-phase with Cu–O octahedrons such as a hole-doped $La_{2-X}Sr_XCuO_4$ (LSCO). The thermal conductivity of NCCO was reported for sintered materials [1,2] and single crystals [3,4]. Larger $\kappa(T)$ values and the maximum of $\kappa(T)$ near 30 K are characteristics of NCCO in comparison to LSCO. In this paper, we report the thermal conductivity $\kappa(T)$ and diffusivity $\alpha(T)$ of the sintered $Nd_{2-X}Ce_XCuO_4$ ($0 \leqslant X \leqslant 0.2$) whose electrical properties were controlled by heat treatments in Ar. The phonon scattering mechanisms were analyzed based on the Tewordt and Wölkhausen (TW) theory [5]. It was found that the phonon scattering by carriers was ineffective up to $X = 0.15$ in this system and the measured $\kappa(T)$ can be reproduced by varying the boundary and point defect scattering under a unified phonon-phonon scattering strength.

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2. Experimental

$Nd_{2-X}Ce_XCuO_4$ ($0 \leqslant X \leqslant 0.2$) samples were prepared from stoichiometric mixtures of Nd_2O_3, CeO_2 and CuO raw powders. The mixtures were calcined twice at 900°C for 21 h in air. They were pressed into pellets and sintered at 1100°C for 18 h in air. These samples are named 'as-sintered' samples. Subsequently, they were heat-treated at 910°C for 18 h in flowing Ar gas and were named 'annealed' samples. The X-ray diffraction analyses showed that all samples exhibited the single T'-phase. The density of each sample was higher than 93% of the ideal density. $\kappa(T)$ and $\alpha(T)$ were measured from 10 to 150 K under an identical experimental setup with a fully automated measuring system [6]. $\kappa(T)$ was measured by a steady-state heat flow method and $\alpha(T)$ was measured by an arbitrary heating method which was one of non-steady state methods.

3. Results and discussion

The annealing process in Ar is expected to create the electron carriers, and at the same time, introduce the scattering centers due to oxygen deficiency in the

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samples. The Ce substitution for Nd site also creates the electron carriers and may also act as scattering centers. Thus, $\rho(T)$ and $\kappa(T)$ of the samples are to be changed by the carrier doping and the scattering effects. The temperature dependence of the electrical resistivity of 'annealed' samples is shown in Fig. 1. $\rho(T)$ decreased with increase in Ce concentration and only the sample of $X = 0.2$ showed metallic behavior. $\rho(T)$ decreased by annealing process except for $X = 0.15$. The annealing sample of $X = 0.15$ showed the superconducting transition at $T_c = 20$ K.

The temperature dependence of the thermal conductivity of 'annealed' samples is shown in Fig. 2. $\kappa(T)$ increased with increase in temperature and exhibited a maximum near 30 K; it then gradually decreased with further increase in temperature. The maximum κ value increased with increase in Ce concentration up to $X = 0.15$; it then decreased for the sample of $X = 0.2$. $\kappa(T)$ for the samples of $0 \leqslant X \leqslant 0.1$ decreased by annealing in Ar. Since the electronic contribution for κ, which is estimated by the Wiedemann–Franz law, is very small for all samples, the measured $\kappa(T)$ is nearly the phonon thermal conductivity and can be analyzed using the following TW formulation [5]:

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

where d is the mass density, n (= 7) the number of atoms per mole, M the molar weight of the sample, R the gas constant, v (= 5000 m/s) the sound velocity, Θ_D (= 450 K) the Debye temperature and x ($= \hbar\omega/k_BT$) is the reduced phonon frequency. The phonon relaxation time τ_{ph} is assumed to obey Matthiessen's rule:

$$\tau_{ph}^{-1} = \tau_b^{-1} + \tau_p^{-1} + \tau_U^{-1} + \tau_e^{-1}$$
$$= \tau_b^{-1} + pT^4x^4 + Ux\exp(-\Theta_D/aT) + ETx. \quad (2)$$

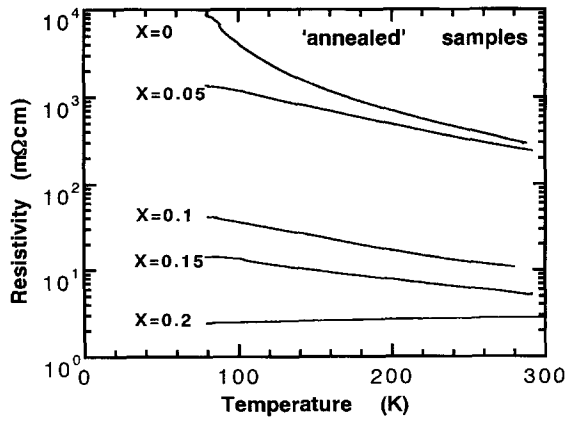

Fig. 1. Temperature dependence of electrical resistivity of 'annealed' samples with various Ce concentrations.

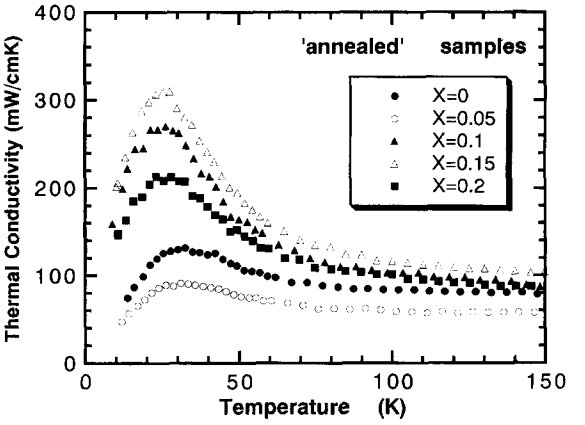

Fig. 2.Temperature dependence of thermal conductivity of 'annealed' samples with various Ce concentrations.

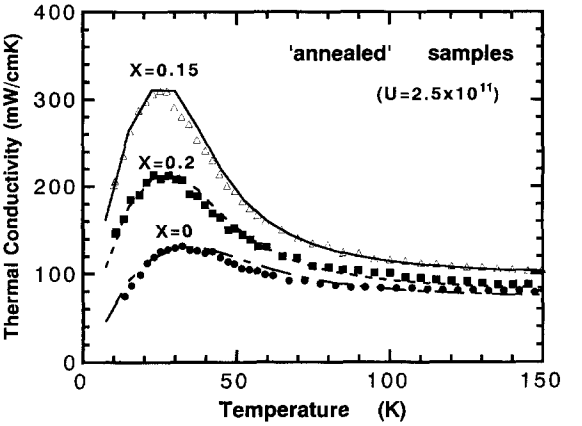

Fig. 3. The measured (symbols) and calculated (lines) thermal conductivity data of 'annealed' samples of $X = 0$, 0.15 and 0.2.

Here, τ_b is the phonon relaxation time due to grain boundaries and p, U and E refer to the strength of the phonon scattering by point defects, other phonons and charge carriers, respectively. a is a constant which varies the effectie Umklapp cutoff temperature. We tried several models for the phonon–phonon interaction term τ_U^{-1}. The function $Ux\exp(-\Theta_D/aT)$ ($a = 1.8$), which is a standard form at relatively low temperatures [7], was found to result in the best fit for all samples under common U and a values.

The measured and calculated $\kappa(T)$ data of 'annealed' samples ($X = 0$, 0.15 and 0.2) are shown in Fig. 3. For the samples of $0 \leqslant X \leqslant 0.15$ in which electron carriers are very few, the calculated $\kappa(T)$ can fully reproduce the measured $\kappa(T)$ without the parameter E. On the other hand, for the sample of $X = 0.2$ with increased electron

Table 1
Summary of fitting parameters analyzed by TW theory under a unified U ($= 2.5 \times 10^{11}$ (s^{-1})) value

Sample	τ_B^{-1} (s^{-1})	p ($K^{-4}s^{-1}$)	E ($K^{-1}s^{-1}$)
$X = 0$ (S)	6.5×10^8	1949	0
$X = 0$ (A)	6.5×10^8	2470	0
$X = 0.05$ (S)	5.2×10^8	2617	0
$X = 0.05$ (A)	5.2×10^8	4711	0
$X = 0.1$ (S)	1.0×10^8	1675	0
$X = 0.1$ (A)	1.0×10^8	1780	0
$X = 0.15$ (S)	9.4×10^7	1790	0
$X = 0.15$ (A)	9.4×10^7	1555	0
$X = 0.2$ (S)	9.4×10^7	2544	4.7×10^6
$X = 0.2$ (A)	9.4×10^7	2167	4.7×10^6

Note: S and A show the 'as-sintered' and 'annealed', respectively.

carriers, the best fit $\kappa(T)$ was possible by introducing also the parameter E, the scattering due to carriers. The values of the fitting parameters determined in this study are summarized in Table 1. The crystal grain size in the samples increases with increase in Ce concentration up to $X = 0.1$, and then saturates for $X = 0.15$ and 0.2 (from the scanning electron microscope (SEM) observation). Ce concentration dependence of τ_b^{-1} is consistent with the SEM observation.

Finally, the temperature dependence of the thermal diffusivity of the 'annealed' samples ($X = 0$ and 0.15) is shown in Fig. 4. $\alpha(T)$ increases gradually with decrease in temperature. $\alpha(T)$ for the sample of $X = 0.15$ was larger than that for $X = 0$ at low temperatures. This reflects the decrease of the number of phonon scattering centers at $X = 0.15$ and may be correlated with the appearance of superconductivity.

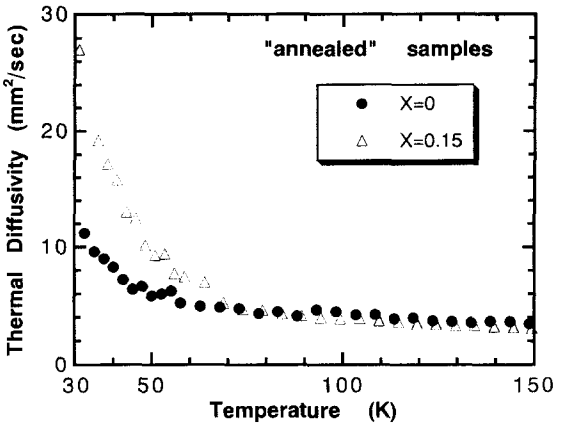

Fig. 4. Temperature dependence of the thermal diffusivity of the 'annealed' samples of $X = 0$ and 0.15.

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