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Effect of annealing on thermal and electrical transport in $Nd_{1.85}Ce_{0.15}CuO_4$

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A quenching process followed by annealing in Ar atmosphere was confirmed to stabilize superconductivity in sintered $Nd_{1.85}Ce_{0.15}CuO_4$ crystals. The electrical resistivity and the thermal conductivity were examined at each stage of the heat treatments. The phonon scattering mechanisms are analyzed in a systematic way.

Key words: high T_c cuprates, stabilization of superconductivity, phonon scattering, electron scattering.

1. Introduction

$Nd_{2-x}Ce_xCuO_4$ (NCCO) with T'-phase crystal structure belongs to a rather peculiar class of high T_c cuprates because the doped charge carriers are of electron type in contrast to hole type carriers in the majority of cuprates [1, 2]. Superconductivity is realized for a small range of Ce concentration $0.15 \le x \le 0.18$ in NCCO only if these crystals are properly annealed in deoxidizing atmosphere. We previously studied the Ce concentration dependence of the thermal conductivity of NCCO for 'anneal' specimen [3], where furnace-cooled sintered ('as-sinter') samples were heat-treated in Ar at 910 °C. These 'anneal' samples, however, did not stably show superconductivity even for $x = 0.15$. We have found that addition of quenching process reliably realize superconductivity in $Nd_{1.85}Ce_{0.15}CuO_4$. In this paper, we try to fix the best heat-treatment conditions for superconductivity in sintered $Nd_{1.85}Ce_{0.15}CuO_4$ crystals. The electrical resistivity and the thermal conductivity were measured for typical samples in order to get the information on the origin of superconductivity in this system.

2. Experimental procedure

$Nd_{2-x}Ce_xCuO_4$ 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 hours in air. The calcined mixtures were pressed into pellets and sintered at 1100 °C for 18 hours in air and then furnace-cooled ('as-sinter' sample). One group of 'as-sinter' samples were annealed in flowing Ar gas for 18 hours at 910 °C ('anneal' sample). Another group of 'as-sinter' samples were again kept 1100 °C in air for 2 hours and quenched into liquid N_2 ('quench'

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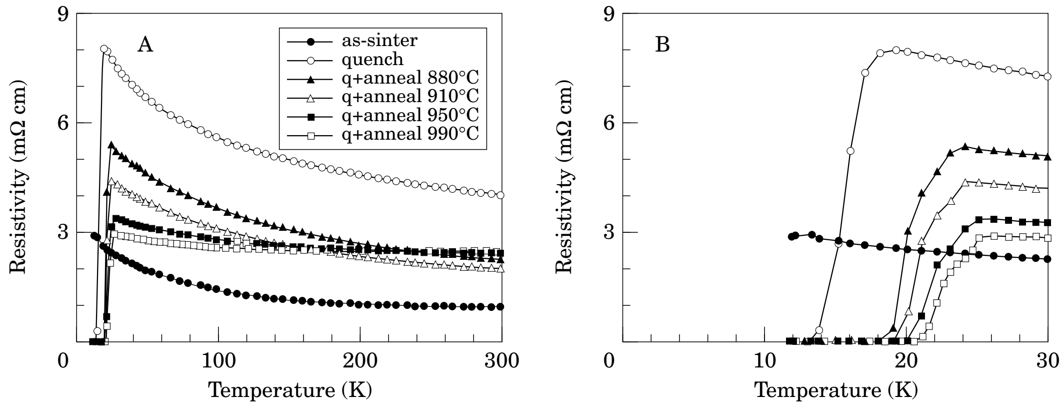

Fig. 1. A, The electrical resistivity $\rho(T)$ as a function of temperature T for $Nd_{1.85}Ce_{0.15}CuO_4$ samples subjected to several heat treatments. B, ρ versus T near T_c in an extended scale.

sample). The 'quench' samples, of which superconductivity had already been confirmed, were annealed for 18 hours in flowing Ar gas at various temperatures and then furnace cooled ('q + anneal' sample). The x-ray diffraction analyses confirmed that all samples belonged to the single T'-phase. The densities of the present sintered materials which were measured by Archimedian method were higher than 93% of the ideal density. The size of the grains were observed by a scanning electron microscope. The thermal conductivity $\kappa(T)$ was measured by a steady state heat flow method between 15 K and 150 K. A Gifford-McMahon (GM) cycle helium refrigerator was used as a cryostat and the measurement was made fully automatically [4]. The electrical resistance was measured by a usual four-terminal method.

3. Experimental results

In this study on sintered $Nd_{1.85}Ce_{0.15}CuO_4$ crystals, the superconductive transition was not observed above 10 K for samples in 'as-sinter' state nor 'anneal' state at annealing temperature $T_A = 910\,^\circ$C. The transition first appeared in 'quench' state at relatively low $T_c^{end} \approx 13$ K, where T_c^{end} means the zero resistivity transition point. By annealing the 'quench' sample in Ar, T_c^{end} was found to systematically increase with increasing annealing temperature T_A up to 990 °C. The T_c enhancement almost saturated around $T_A \approx 970\,^\circ$C. Fig. 1A shows the electrical resistivity $\rho(T)$ of 'as-sinter', 'quench' and the typical 'q + anneal' $Nd_{1.85}Ce_{0.15}CuO_4$ as a function of temperature T. Fig. 1B shows $\rho(T)$ versus T near T_c in an extended scale. The annealing process resulted in also the reduction of $\rho(T)$ relative to 'quench' sample. It is to be noticed, however, that the absolute values of $\rho(T)$ of 'as-sinter' sample are the smallest among all of the studied $Nd_{1.85}Ce_{0.15}CuO_4$ samples. The overall temperature dependence of every $Nd_{1.85}Ce_{0.15}CuO_4$ sample was semiconductive, i.e. $\rho(T)$ increased with decreasing temperature. Figure 2 shows the transition temperatures T_c^{end}, T_c^{mid}, T_c^{onset} and the resistivity ratio $\rho(30\text{ K})/\rho(300\text{ K})$ as a function of T_A, T_c^{end} and T_c^{mid} increased with increasing T_A up to 970 °C while T_c^{onset} remained relatively constant.

Figure 3 shows the temperature dependence of the thermal conductivity $\kappa(T)$ of 'as-sinter', 'quench' and typical 'q + anneal' $Nd_{1.85}Ce_{0.15}CuO_4$ samples. $\kappa(T)$ increased with increasing temperature and exhibited a maximum around 25 K. It then gradually decreased with further increase of temperatures. The peak is considered to come from phonon–phonon Umklapp processes and the behavior of $\kappa(T)$ is consistent with that of other reports on $Nd_{2-x}Ce_xCuO_4$ [5–7]. $\kappa(T)$ of 'as-sinter' sample was reduced by the quenching process.

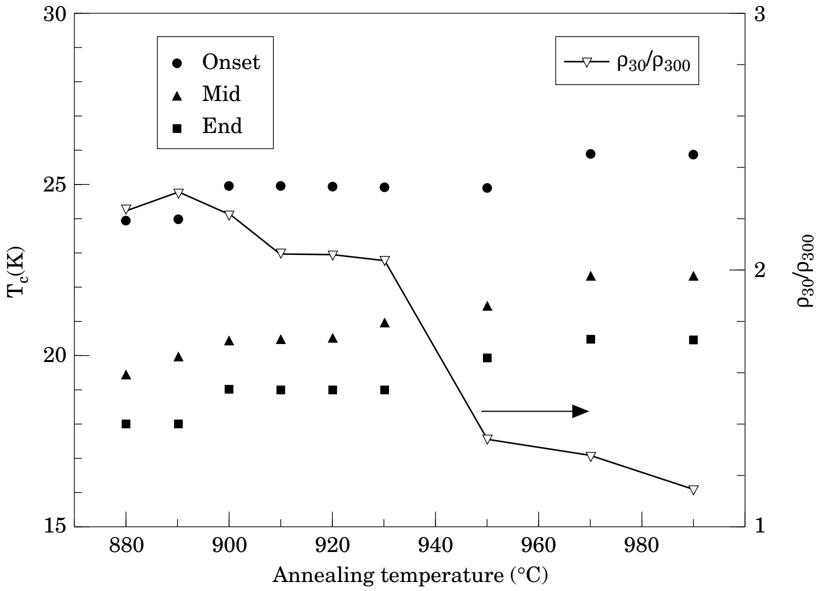

Fig. 2. Transition temperature T_c and ratio of resistivity ($\bigtriangledown$) at 30 K to at 300 K as a function of annealing temperature T_A.

The Ar annealing process on 'quench' sample enhanced κ, resulting in higher κ values of 'q + anneal' samples above those of 'as-sinter' sample.

4. Discussion

Accompanied with the appearance of superconductivity, the electrical resistivity of 'quench' sample increased in comparison with 'as-sinter' one. This means the increase of carrier scattering centers such as oxygen vacancies through the quenching process. On the other hand, the introduction of oxygen vacancies should increase the electron density of NCCO. The observed enhance of $\rho(T)$ means that the increase of electron scattering resultantly overwhelm that of electron density. Here we notice two important points for the appearance of superconductivity in this system: (i) introduction of oxygen vacancy, (ii) enhancement of electron scattering.

Accompanied with the reduction of $\rho(T)$, the superconducting transition temperature T_c is enhanced through the annealing process in Ar followed by slow cooling down of the sample temperature. One reasonable explanation for this enhancement of T_c may be attributed to the reduction of the effect of localization caused by the reduction of scattering centers. It is to be noticed, however, that $\rho(T)$ of 'q + anneal' sample with the highest T_c is still larger than that of 'as-sinter' one. This fact seems to suggest another key point that a certain unidentified scattering mechanism besides due to crystalline defects may be at work in superconducting NCCO.

In order to elucidate how the above mentioned key points are reflected in the thermal transport, we analyze our results of the thermal conductivity $\kappa(T)$ based on the relaxation time approximation. Since the Wiedemann–Franz law indicates that the electronic contribution κ_e is very small ($\sim$ 1% of the total κ at 100 K), we assume that the thermal conduction is entirely due to phonons in this system. Then $\kappa(T)$ is

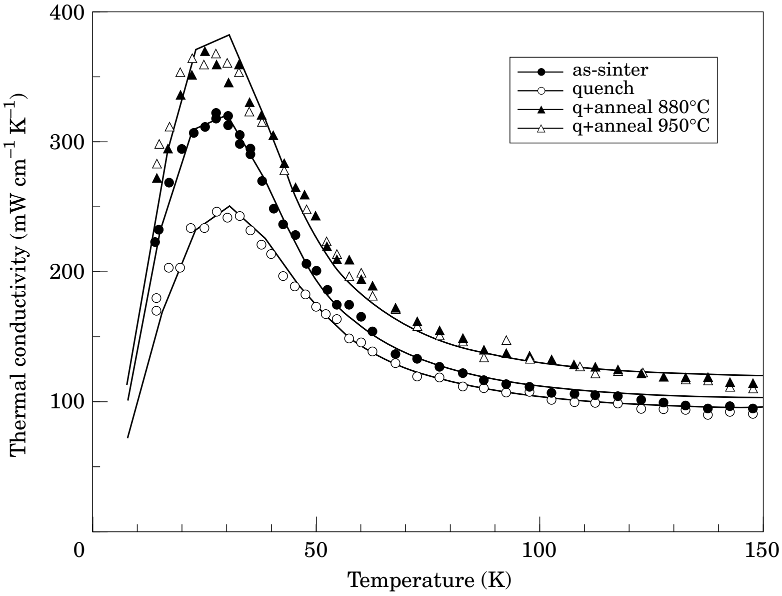

Fig. 3. The thermal conductivity $\kappa(T)$ as a function of T for $Nd_{1.85}Ce_{0.15}CuO_4$ at typical stages of heat treatment. The lines represent the calculated fitting curves for respective samples.

expressed as [8, 9]

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

where d is the mass density, $n(=7)$ the numbers of atoms in the formula, M the molar weight, R the gas constant, $v(=5200\ {\rm m\ s^{-1}})$ the measured sound velocity, $\Theta_{\rm D}(=450\ {\rm K})$ the Debye temperature and x is the reduced phonon frequency. The phonon relaxation time $\tau_{\rm ph}$ is assumed to follow Matthiessen's rule,

$$\tau_{\rm ph}^{-1} = \tau_{\rm b}^{-1} + \tau_{\rm p}^{-1} + \tau_{\rm U}^{-1} + \tau_{\rm e}^{-1} = l_{\rm b}/v + PT^4x^4 + Ux\exp(-\Theta_{\rm D}/aT) + ETx. \tag{2}$$

Here $\tau_{\rm b}$ is the scattering time due to grain boundaries, $l_{\rm b}$ the mean value of grain size of the sample and P, U and E refer to the strength of phonon scattering by point defects ($\tau_{\rm p}^{-1}$), other phonons ($\tau_{\rm U}^{-1}$) and charge carriers ($\tau_{\rm e}^{-1}$), respectively. The function $Ux\exp(-\Theta_{\rm D}/aT)$, which is a standard form for Umklapp processes [10] at relatively low temperatures, was found to result in the best fit for all the samples under common U and a $(=1.8)$ values.

The calculated curves for $\kappa(T)$ based on eqns (1) and (2) are also presented in Fig. 3. The parameter values used and determined in the fitting process are summarized in Table 1. In Table 1 we notice that the reduction in κ of 'quench' sample is caused by both the appearance of scattering by carriers (E term) and the enhancement of scattering by point defects (P term) presumably due to increase of oxygen vacancies. The enhancement in κ of 'q + anneal' samples originates from the reduction of scattering by point defects in addition to the 'disappearance' of phonon scattering by carriers.

A peculiar and puzzling point in the $\kappa_{\rm ph}$ analyses given above is the appearance of phonon scattering due to charge carriers in superconducting 'quench' sample. The appearance of E term was observed not only for the present sintered NCCO but also for a single crystal specimen. Figure 4 presents the detailed fitting curves for the present 'quench' sample as well as our fitting curves for in-plane $\kappa(T)$ of a heat-treated superconductive single crystal of NCCO ($x = 0.145$) due to Ogasawara *et al.* [7]. It is clearly demonstrated in the figure that

Table 1: Fitting parameters determined by $\kappa(T)$ analyses for various treated samples.

	'as-sinter'	'quench'	'q + anneal' (880 °C)	'q + anneal' (950 °C)	single crystal [7] as-grown	single crystal [7] annealed
$\tau_b^{-1}(s^{-1})$	3.6×10^8	3.6×10^8	3.6×10^8	3.6×10^8	1.4×10^8	1.4×10^8
$l_b(\mu m)$	15	15	15	15	36	36
$U(s^{-1})$	6.9×10^{11}	6.9×10^{11}	6.9×10^{11}	6.9×10^{11}	7.6×10^{11}	7.6×10^{11}
$P(K^{-4}\ s^{-1})$	577	650	433	433	695	708
$E(K^{-1}\ s^{-1})$	0	1.1×10^7	0	0	0	1.8×10^7
T_c (K)	—	13	18	20	—	18

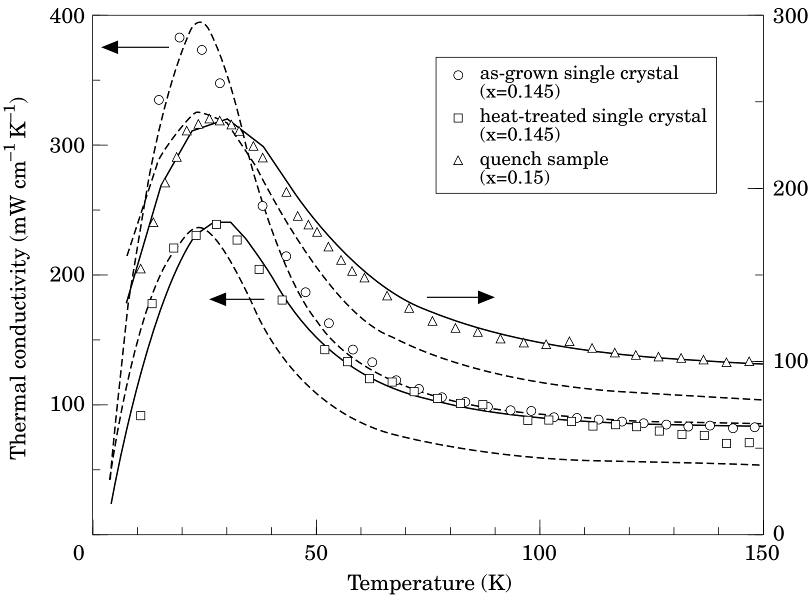

Fig. 4. Fitting curves of $\kappa(T)$ for 'quench' sample (△), for an as-grown non-superconductive $Nd_{1.85}Ce_{0.15}CuO_4$ single crystal (○) and for a heat-treated superconductive single crystal (□). Dotted lines without ETx term cannot reproduce the $\kappa(T)$ data of heat-treated superconductive $Nd_{1.85}Ce_{0.15}CuO_4$ crystals.

E term linear in frequency x is necessary for both samples to get a reasonable fitting. The more puzzling result is, however, the 'disappearance' of E term in 'q + anneal' samples. As for 'q + anneal' samples, it is noteworthy that $\kappa(T)$ values are larger in these samples than those of 'as-sinter' one and the point defect scattering is weaker from the viewpoint of the thermal transport. In contrast, $\rho(T)$ of 'as-sinter' sample is smaller than the best superconductive 'q + anneal' sample suggesting weaker electron scattering in 'as-sinter' sample. It seems probable that a certain electron scattering mechanism other than crystalline defect scattering may be operative in superconducting NCCO samples.

5. Summary

Superconductivity is stabilized by adding the quenching process to sintered $Nd_{1.85}Ce_{0.15}CuO_4$ crystals.

Introduction of oxygen vacancies seems to play a key role for the stabilization of superconductivity and, possibly, for the destabilization of the antiferromagnetic order.

Annealing process in Ar atmosphere on quenched ('quench') samples reduces phonon scattering by point defects. This is consistent with the observed reduction of the electrical resistivity $\rho(T)$ of annealed $Nd_{1.85}Ce_{0.15}CuO_4$ after the quenching process. The enhancement of T_c in these 'q + anneal' samples is consistent with the reduction of the competing effect of electron localization.

From the analyses of the thermal conductivity $\kappa(T)$, the point defect density is smaller in superconductive 'q + anneal' sample than non-superconductive as-sintered ('as-sinter') sample, while $\rho(T)$ values of 'q + anneal' samples are larger than those of 'as-sinter' one. Some additional scattering mechanism such as due to anti-paramagnons may be operative in superconducting samples.

A characteristic scattering mechanism proportional to linear in phonon frequency ω has been confirmed in 'quench' sample but it has disappeared through the annealing process. The origin of this scattering mechanism is not clear at present stage but it seems to have some important connection with superconductivity.

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