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Electron–phonon interaction in $Gd_{1-x}Ca_xBaSrCu_3O_{7-\delta}$ superconductors

T.V. Chong[a,c], S. Kambe[a,*], H. Kawaji[b], T. Atake[b], O. Ishii[a]

[a] Yamagata University, Graduate School of Science and Engineering, Human Sensing Program, 4-3-16 Johnan, Yonezawa City, Yamagata 992-8510, Japan
[b] Tokyo Institute of Technology, Materials and Structures Laboratory, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan
[c] INTI International University, Faculty of Applied Science, Persiaran Perdana BBN, Putra Nilai, 71800 Nilai, Negeri Sembilan, Malaysia

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ABSTRACT

Polycrystalline $Gd_{1-x}Ca_xBaSrCu_3O_{7-\delta}$ samples ($0 \le x \le 0.1$) were prepared via solid-state reaction. The superconducting critical temperature T_c and lattice parameter decrease with doping content. Temperature dependence of the specific heat of all samples was measured with the thermal relaxation technique using a Physical Property Measurement System from about 2 K to 150 K. The calculated Debye temperature Θ_D at 10 K is found to be inversely proportional to T_c. Subsequently, the electron–phonon coupling constant was estimated based on standard BCS theory (λ_{BCS}) in the weak coupling limit and two-dimensional Van Hove scenario (λ_{VH}). The calculated values of λ_{VH} in this study (around 0.04) are close to the experimental data as reported by other researchers on Bi-based and YBCO samples. Hence, the two-dimensional Van Hove scenario seems to be a viable candidate for the mechanism of superconductivity if electron–phonon coupling plays a role in superconductivity of these materials.

1. Introduction

It is well known that the electronic state of high-T_c superconductors (HTSCs) dramatically changes with carrier concentration. Substitution of Gd^{3+} ion by Ca^{2+} ion with lower valence is one of the methods for increasing the hole concentration in this system. Previous studies on YBCO system imply that the reduction of charge at Y site due to the Ca substitution is partially balanced by oxygen loss [1–3] as a result hole concentration little exceeds that of non-substituted compound [4]. Decrease of the oxygen content by Ca doping decreases the value of lattice parameters and the distance between CuO_2 planes as well. This enhances the antiferromagnetic correlation between Cu-spins in the planes along the *c*-axis and destroys the superconductivity.

Besides, the electron–phonon coupling strongly influences the electronic properties of the HTSC materials. Various experimental results point towards the important role of phonons in the mechanism of cuprate high temperature superconductors ([5,6] and references therein). In two dimensions, electrons in a periodic potential show a logarithmic density of states, named a Van Hove singularity. The Van Hove singularity is based on the assumption that, in HTSC, the Fermi level lies close to such a singularity. This hypothesis has been confirmed by many experiments, in particular by angular resolved photoemission spectroscopy in different compounds.

Specific heat measurements, for example, are a reliable technique to investigate the elastic properties of these HTSC especially at low temperatures. The Debye temperature derived from specific heat measurements may explain the importance of the phonons and their interaction with T_c as well in order to explore the possible mechanism of HTSC materials.

In this study, polycrystalline $Gd_{1-x}Ca_xBaSrCu_3O_{7-\delta}$ samples ($0 \le x \le 0.1$) were prepared via solid-state reaction. Four point probes were used for resistance versus temperature measurement. Results show decrease in T_c with increase of doping content (x). This variation is assumed to be irrelevant to the different of phases or impurity effects since X-ray patterns show all samples are in tetragonal phase.

Specific heat measurements from about 2 K to 150 K of all samples were carried out using the thermal relaxation technique in a Physical Property Measurement System (PPMS). Results reveal an obvious specific heat jump around the critical temperature for the $GdBaSrCu_3O_{7-\delta}$ sample reflecting the bulk nature superconductivity in this HTSC material. This specific heat jump is shifted to lower temperature upon decreasing T_c. Subsequently, the Debye temperature Θ_D at 10 K was calculated and used to estimate the electron–phonon coupling constant based on standard BCS theory (λ_{BCS}) in the weak coupling limit and a two-dimensional Van Hove scenario (λ_{VH}). Details of this research will be discussed in this communication.

* Corresponding author. Tel.: +81 238 26 3287; fax: +81 238 26 3177.
E-mail addresses: kambe@yz.yamagata-u.ac.jp, beshiro@mac.com (S. Kambe).

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Table 1
Lattice parameter, oxygen content, Cu valence, critical temperature ($T_{c\,onset}$ and $T_{c\,zero}$), Debye temperature (Θ_D) measured at 10 K, electron–phonon coupling constant with BCS theory (λ_{BCS}) and two-dimensional van Hove scenario (λ_{VH}) of $Gd_{1-x}Ca_xBaSrCu_3O_{7-\delta}$ samples.

Doped content, x	Lattice parameter		Oxygen content	Cu valence	$T_{c\,onset}$ (K)	$T_{c\,zero}$ (K)	Θ_D (K)	λ_{BCS}	λ_{VH}
	a (Å) = b (Å)	c (Å)							
0	3.854 ± 0.004	11.571 ± 0.007	6.9371	2.2914	83 ± 1	70 ± 1	297.5 ± 0.5	0.637	0.044
0.01	3.841 ± 0.003	11.536 ± 0.006	6.9198	2.2832	77 ± 1	64 ± 1	301.4 ± 0.2	0.598	0.042
0.04	3.840 ± 0.003	11.530 ± 0.005	6.9138	2.2892	77 ± 1	65 ± 1	303.8 ± 0.2	0.601	0.043
0.07	3.842 ± 0.003	11.540 ± 0.006	6.8804	2.2769	57 ± 1	50 ± 1	305.9 ± 0.5	0.517	0.038
0.1	3.851 ± 0.003	11.569 ± 0.007	6.8754	2.2836	52 ± 1	34 ± 1	300.6 ± 0.2	0.434	0.033

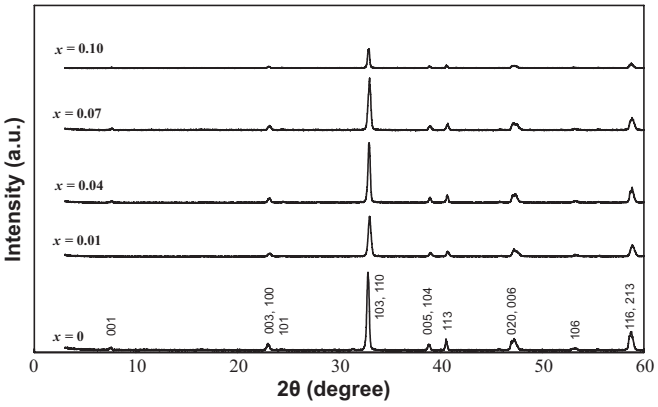

Fig. 1. X-ray powder diffraction patterns of $Gd_{1-x}Ca_xBaSrCu_3O_{7-\delta}$ samples (x = 0, 0.01, 0.04, 0.07 and 0.10).

2. Experimental

Polycrystalline $Gd_{1-x}Ca_xBaSrCu_3O_{7-\delta}$ (x = 0, 0.01, 0.04, 0.07 and 0.1) samples were prepared by mixing stoichiometric amounts of high purity (≥99.99%) Gd_2O_3, $CaCO_3$, $BaCO_3$, $SrCO_3$ and CuO powders. The mixed powders were calcined in air at around 950 °C for 48 h with several intermittent grindings and naturally cooled in furnace. The powders were then pressed into pellets. The pellets were sintered at 950 °C for another 24 h and naturally cooled in furnace. The samples were then annealed in flowing of O_2 gas at 950 °C for more than 10 h to increase the oxygen content. After that, the samples were cooled at 80 °C/h until 600 °C and then furnace cooled to room temperature.

Temperature dependence of the dc electrical resistance was carried out using a four-point probe technique with indium as contacts between sample and the probes. Oxygen content and Cu valence of the samples were determined by an iodometric titration method.

The crystallographic phase of these samples was examined by X-ray powder diffraction with Cu K_α radiation using a RINT 2000 Wilder-angle goniometer. Scanning electron microscope (SEM) micrographs were recorded using a JSM-6330F scanning electron microscope to determine the variation of morphology (if any) among all samples.

Subsequently, samples were cut into cube shape of approximately 2 mm in edge length for the specific heat measurement, which was performed from around 2 K to 150 K using a PPMS at zero magnetic field.

3. Results and discussion

Powder X-ray diffraction patterns (Fig. 1) show all samples are single phase with tetragonal structure (space group $P4/mmm$) since all peaks could be identified. The calculated lattice parameters are shown in Table 1. Results show that lattice parameters ($a = b$, c) are decreased by Ca doping. However, notable correlation of lattice parameters with doping content is not observed. Scanning electron micrographs (SEMs) of the internal section of the $Gd_{0.93}Ca_{0.07}BaSrCu_3O_{7-\delta}$ sample (one of the samples' micrograph in which taken as example here) is shown in Fig. 2. The micrograph shows the existence of voids and pores indicating the degree of porosity of the sample. However, there is no significant variation in microstructure among all samples as observed by SEM.

Besides, oxygen content determined by iodometric titration method shows that such doping would decrease the oxygen content of these samples and this is similar as YBCO samples as reported by other researchers [1,2]. However, Cu valence remains close to 2.29 even after doped by Ca. This is contrary with YBCO samples in which Ca substitution increases the average Cu valence [7].

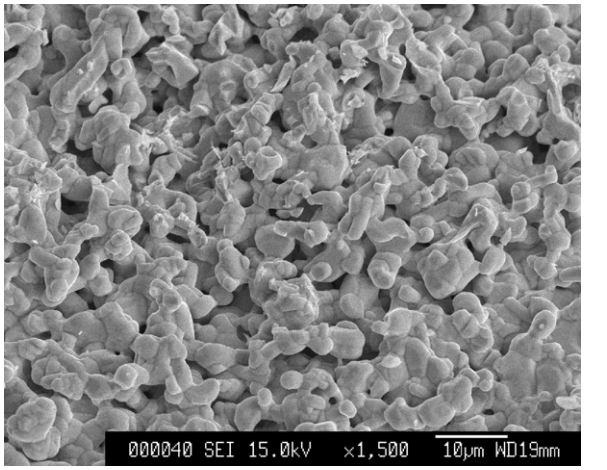

Fig. 2. Scanning electron micrograph of $Gd_{0.93}Ca_{0.07}BaSrCu_3O_{7-\delta}$ sample.

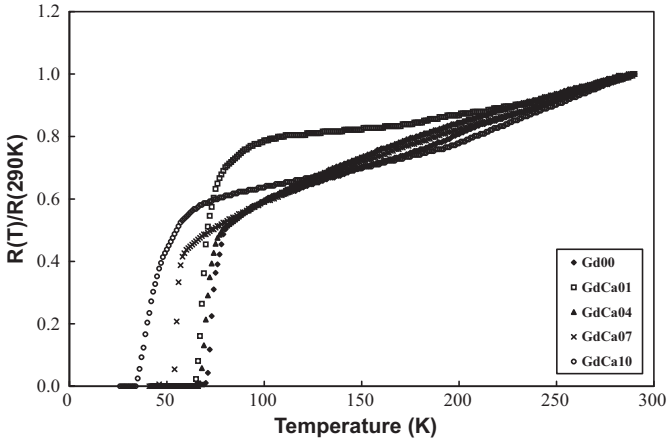

Fig. 3. Normalized electrical resistance versus temperature of $GdBaSrCu_3O_{7-\delta}$ (Gd00), $Gd_{0.99}Ca_{0.01}BaSrCu_3O_{7-\delta}$ (GdCa01), $Gd_{0.96}Ca_{0.04}BaSrCu_3O_{7-\delta}$ (GdCa04), $Gd_{0.93}Ca_{0.07}BaSrCu_3O_{7-\delta}$ (GdCa07) and $Gd_{0.90}Ca_{0.10}BaSrCu_3O_{7-\delta}$ (GdCa10).

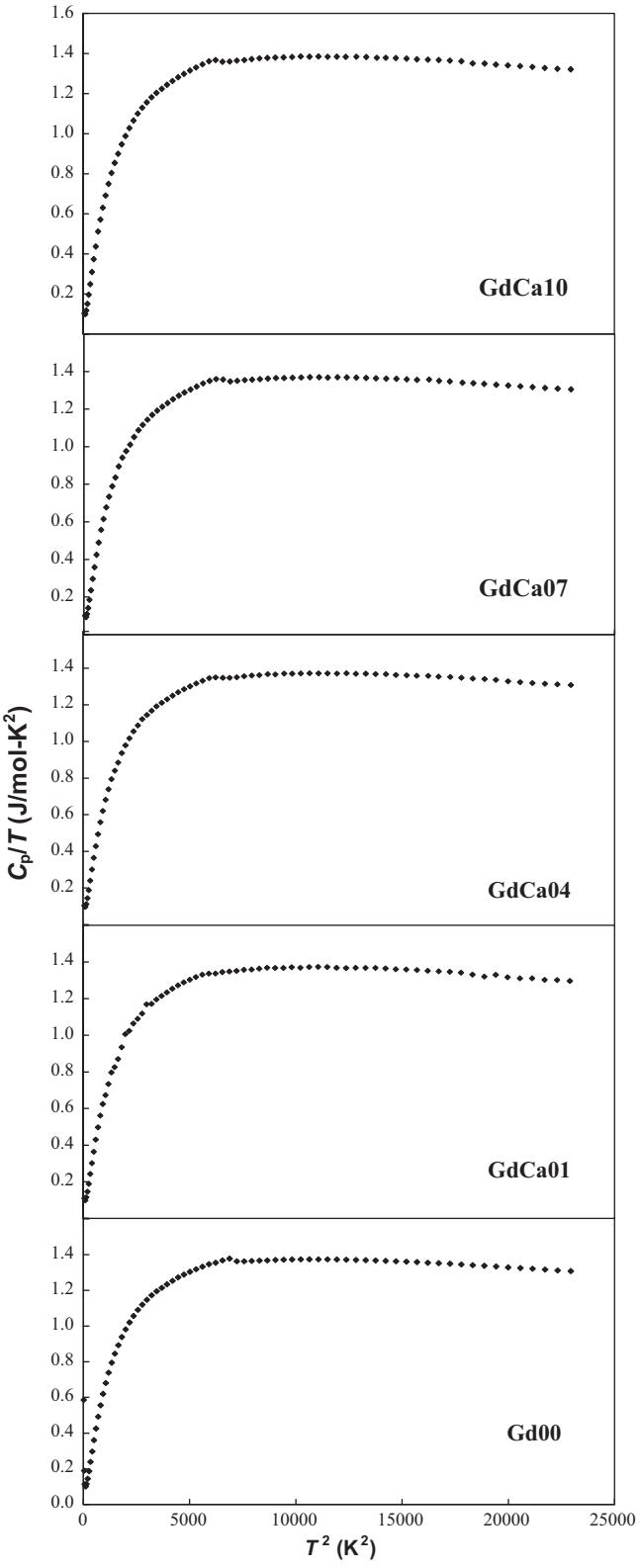

Fig. 4. Temperature dependence (on T^2 scale) of specific heat (C_p/T) for $GdBaSrCu_3O_{7-\delta}$ (Gd00), $Gd_{0.99}Ca_{0.01}BaSrCu_3O_{7-\delta}$ (GdCa01), $Gd_{0.96}Ca_{0.04}BaSrCu_3O_{7-\delta}$ (GdCa04), $Gd_{0.93}Ca_{0.07}BaSrCu_3O_{7-\delta}$ (GdCa07) and $Gd_{0.90}Ca_{0.10}BaSrCu_3O_{7-\delta}$ (GdCa10).

The temperature dependence of electrical resistance measurements of $Gd_{1-x}Ca_xBaSrCu_3O_{7-\delta}$ samples with $x = 0$, 0.01, 0.04, 0.07 and 0.10 exhibit metallic normal state behaviour and superconducting transition temperature, $T_{c\,onset}$(onset critical temperature) of 83 K, 77 K, 77 K, 57 K and 52 K, respectively and $T_{c\,zero}$ (zero critical temperature) of 70 K, 64 K, 65 K, 50 K and 34 K, respectively (Fig. 3).

Discussion on the effects of Ca substitution on the physical and superconducting properties in $GdBaSrCu_3O_{7-\delta}$ samples has been reported before [8].

The results of specific heat measurements are shown in Fig. 4. Measurements were taken from around 2 K to 150 K, but it was difficult to obtain $C_p(T)$ at temperatures below 6 K because of a Schottky-like anomaly caused by the splitting of the Gd^{3+} ions ground state due to crystal field effects, and such an anomaly is usually observed in most of the high temperature superconductors [9,10].

Further investigation is necessary to define in detail the reason of the differences in the temperature dependences of T_c and heat capacity anomaly of $x = 0.01$ sample compared with the other samples. Generally, it probably because of the small amount of Ca doped (1%) is very hard to produce a very fine and homogeneous sample. It is shown by the result of temperature dependences of T_c measurement, in which the $x = 0.01$ sample behaves like a semi-metallic sample.

The specific heat jump observed around T_c of these samples clearly shows the second order phase transition. This specific heat jump is related to the difference between the electronic contribution to the specific heat in the normal and the superconducting state, which confirms the bulk nature of HTSC in the samples. Such specific heat jump shifts to lower temperature as the decrease in T_c.

The Debye temperature Θ_D determined from C_p at 10 K for each sample was calculated according to the Debye model by the following equation, and the results are shown in Table 1.

$$\frac{C_p}{T} = n\frac{12\pi^4 R}{5\Theta_D^3}T^2$$

where n is the number of atoms per molecule and R is the gas constant (8.315 J/mol-K). However, the calculated Θ_D is strongly dependent on temperature, and it is similar to the case of YBCO reported by Junod et al. [11]. At low temperatures $T < \Theta_D/10$, results show that $C_p(T) \approx \beta T3$ and hence, it is considered that lattice vibrations or phonons play a major role in the specific heat of these superconductors. Besides, calculations show that Θ_D is inversely proportional to T_c and it may be some interactions between Θ_D and T_c that may provide important information on the mechanism of superconductivity. However, further investigation is necessary to determine the relationship between Debye temperature, critical temperature, and hole carriers as well.

From the calculated Debye temperature, the electron–phonon coupling constant, λ can be calculated by using BCS theory in the weak coupling limit as $T_c = 1.13\Theta_D e^{-1/\lambda}$. On the other hand, as an extension of BCS theory in two-dimensional system, the electron–phonon coupling constant can be calculated in the two-dimensional Van Hove scenario as follows:

$$T_c = 2.72T_F e^{-1/\sqrt{\lambda}}$$

where $T_F = E_F/k$ (E_F is the Fermi energy) and T_F is $10\Theta_D$ for high-T_c material in the weak coupling limit [12].

Debye temperature, electron–phonon coupling constant, λ calculated using the BCS theory (λ_{BCS}) and in the two-dimensional Van Hove scenario (λ_{VH}) are given in Table 1. The calculated electron–phonon coupling constant from the Van Hove scenario (λ_{VH}) is much lower than λ_{BCS}, which varies from 0.033 to 0.044. These values are similar to those reported on the same material doped by Zn measured by ultrasonic velocity [13]. Moreover, these values are close to the values found in $YBa_2Cu_3O_{7-\delta}$ and Bi-based samples (λ around 0.04) from Raman scattering data [14–16]. Since

the calculated λ_{VH} in this study seems to agree well with other experimental data, it should be relevant to superconductivity in the cuprates. Hence, the Van Hove scenario seems to be a possible option to explain the mechanism superconductivity in HTSC materials.

4. Conclusions

The effects of Ca substitution in $GdBaSrCu_3O_{7-\delta}$ samples on their physical and thermodynamic properties through specific heat measurement is investigated. The critical temperature decreases with increasing Ca doping content. The Debye temperature Θ_D (derived from specific heat measurements) calculated near 10 K is found to be inversely proportional to the T_c in these superconducting materials. Moreover, results show that the calculated λ_{VH} is much lower than λ_{BCS} and close to other experimental values of λ in Bi-based and YBCO samples; hence, we suggest that the two-dimensional Van Hove scenario is a viable candidate for the mechanism of superconductivity in the HTSC materials.

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