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Suppression of superconductivity in the $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system

KYEONG BOCK LEE, CHOON MAHN PARK, HYUN SIK NOH, CHUL KOO KIM
Department of Physics, Yonsei University, Seoul 120-749, Korea
KYUN NAHM
Department of Physics, Yonsei University, Kangwondo 222-701, Korea

Measurements of electrical resistivity, X-ray diffraction patterns, magnetic susceptibility and thermoelectric power of the $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system have been made. The superconducting transition temperature was found to decrease monotonically with praseodymium concentration, x. From the susceptibility data, it was determined that the valence of praseodymium lies between $+3$ and $+4$. The thermoelectric power was found to increase with x, and the slopes of dS/dT were negative except for the case $x = 0$. The tendency of the thermopower to change with increasing praseodymium concentration has been qualitatively explained using the theory for strongly correlated systems.

1. Introduction

For the high T_c superconductor $Y_1Ba_2Cu_3O_{7-\delta}$, it is well known [1, 2] that replacement of yttrium by rare-earth elements does not affect its superconducting properties. However, in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, the superconducting transition temperature, T_c, decreases gradually to zero as x is increased to 0.6 and, for the non-superconducting region of $x \geq 0.6$, a negative temperature coefficient of electrical resistivity is observed [3]. For similar systems with other rare-earth elements, the suppression of superconductivity by praseodymium doping has also been found experimentally and the amount of decrease in T_c due to praseodymium substitution strongly depends on ionic radius of the elements [4]. Proper understanding of suppression of superconductivity by praseodymium doping is expected to provide a clue to the true physical mechanism of the high T_c superconductivity.

It is believed that the valence of praseodymium lies between $+3$ and $+4$ and thus praseodymium substitution reduces mobile carriers. Such results have been inferred from various experimental results, such as structural investigations [5], chemical substitution studies [6, 7], Hall effects [8], and magnetic susceptibility measurements [8–10]. These investigations suggest that the predominent holes on oxygen sites in the CuO_2 planes will be filled when trivalent yttrium is replaced by tetravalent praseodymium. Furthermore, Mössbauer spectroscopy [9] and μSR (muon-spin-relaxation) measurements [10] suggest a magnetic ordering of copper ions due to hole filling on oxygen sites. On the other hand, X-ray absorption spectroscopy [11] and optical investigations [12] indicate a fixed praseodymium valence of $+3$. Also, many investigators have reported evidence of hole localization against hole filling due to praseodymium substitution in $Y_1Ba_2Cu_3O_{7-\delta}$ [13, 14]. Therefore, it appears imperative to study in detail the role of praseodymium doping in order to determine finally the praseodymium valence and, consequently, solve the problem of the high T_c superconductivity.

In this paper, we present the results of electrical resistivity, X-ray diffraction (XRD) studies, thermoelectric power, and magnetic susceptibility of the $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system which has not been studied in detail so far and compare the results with other rare-earth element-based systems.

2. Experimental procedure

The system $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ was synthesized by standard solid-state reaction. Starting from Er_2O_3, $BaCO_3$, CuO and Pr_6O_{11} of 99.9% purity, powders were well mixed and pressed into pellets. The pellets were sintered at 950 °C for 3 days in flowing oxygen at a rate 200 $cm^3\,min^{-1}$ and then cooled to 400 °C at a speed of $-100\,°C\,h^{-1}$. At 400° C, the samples were annealed for 8 h in oxygen flowing at a rate of 500 $cm^3\,min^{-1}$.

The electrical resistivity of the samples was measured using a standard four-probe technique and XRD pattern measurements were made at room temperature using CuK_α X-rays. Thermoelectric power and d.c. magnetic susceptibility measurements were taken over the temperature range from 10–300 K. The temperature dependence of magnetic susceptibility was measured with a SQUID magnetometer. Fields of 10 G and 1.4 T were used to measure the susceptibility. From the 1.4 T susceptibility data above T_c, we derived the Curie–Weiss temperature, θ_p, and the effective magnetic moment, μ_{eff}.

3. Results and discussion

The superconducting transition temperatures from the electrical resistivity data for the series of

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$Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \leq x \leq 0.4$) are shown in Fig. 1. The non-linear depression of T_c with increasing praseodymium concentration is consistent with the explanation using a simple BCS-like, but non-phononic expression, as in a previous report [15].

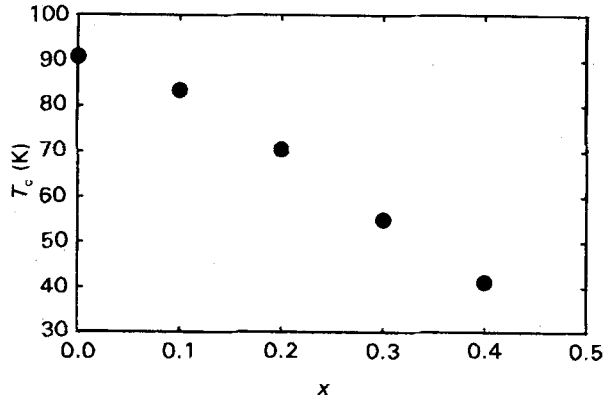

Figure 1 Superconducting transition temperature, T_c, versus praseodymium concentration, x.

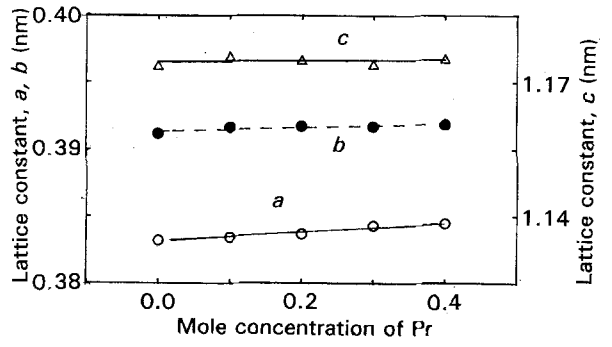

Figure 2 Lattice parameters a, b and c as a function of praseodymium concentration.

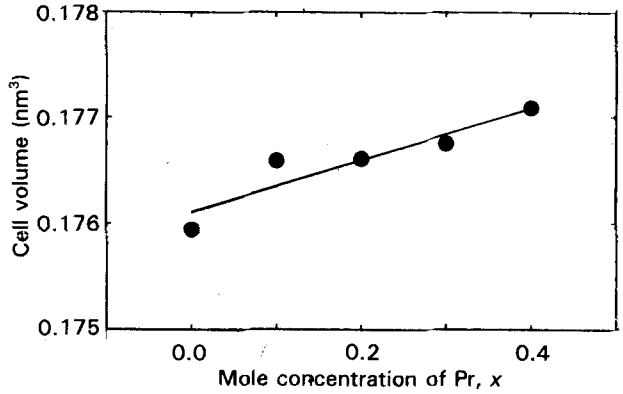

Figure 3 Unit cell volume as a function of praseodymium concentration.

The relationships between praseodymium concentration and lattice parameters and cell volume are shown in Figs 2 and 3. A tabular summary is given in Table I. $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ remains orthorhombic with almost single phase for the range of $0 \leq x \leq 0.4$. The lattice parameters a and b increase slightly with praseodymium concentration and c is almost constant. Thus the cell volume also increases with increasing concentration, x. These results are in agreement with yttrium- [5] and gadolinium- [4] based system.

Fig. 4 shows a plot of the temperature dependence of the absolute thermopower. Because the value of thermopower for the sample of $x = 0$ is very small, we believe that it has metallic property. The sample of $x = 0$ also shows a negative value of thermopower below 190 K. This contradicts the results of Bhatnager *et al.* [16] The thermopowers of $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ increase with x and, except for $x = 0$, the slopes of the curves are negative above T_c. Anderson [17] has suggested that the Hubbard model with strong correlation would at least provide a qualitative explanation for transport mechanism in $RBa_2Cu_3O_{7-\delta}$ superconductors. In the high-temperature and strong correlation limit, it is known that the thermopower is given by the modified Heikes formula [16, 18]

$$S = -\frac{k_B}{e}\ln 2 - \frac{k_B}{e}\ln\frac{1-n}{n} \quad (1)$$

where n is the number of electrons per site. In the case of $RBa_2Cu_3O_{7-\delta}$, $-e$ and n must be replaced by $+e$ and p which is the hole concentration per Cu–O plane.

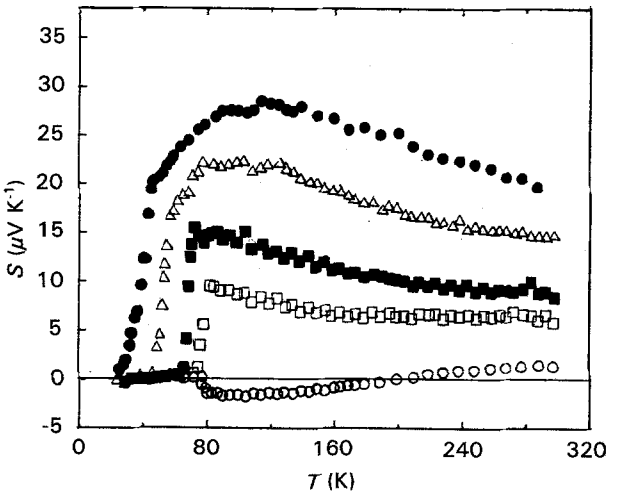

Figure 4 Thermoelectric power of $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ versus temperature (○) $x = 0$, (□) $x = 0.1$, (■) $x = 0.2$, (△) $x = 0.3$, (●) $x = 0.4$.

TABLE I T_c and lattice constants of $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

x	T_c(K)	a (nm)	b (nm)	c (nm)	V (nm³)
0.0	90.8	0.383 21 ± 0.000 16	0.391 18 ± 0.000 41	1.173 70 ± 0.000 32	0.175 94
0.1	83.5	0.383 45 ± 0.000 08	0.391 67 ± 0.000 54	1.175 81 ± 0.000 08	0.176 59
0.2	70.5	0.383 69 ± 0.000 17	0.391 74 ± 0.000 45	1.174 99 ± 0.000 36	0.176 61
0.3	55.0	0.384 32 ± 0.000 20	0.391 72 ± 0.000 53	1.174 06 ± 0.000 41	0.176 75
0.4	41.2	0.384 48 ± 0.000 14	0.391 90 ± 0.000 39	1.175 28 ± 0.000 30	0.177 09

We reported previously [18], a formula for the hole concentrations in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ as

$$p = 0.5 - 0.87x \quad (2)$$

and assume that this expression is valid also in the $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, because in deriving the above formula, no atomic nature of yttrium was included. Using Equations 1 and 2, we calculate the thermopowers due to the change in the hole concentration which are shown in Table II, where $\Delta S = S(x) - S(x = 0)$ at 300 K. We observe that the tendency of the variation of calculated thermopowers with x is similar to that of observed thermopowers, although the magnitude of observed values is smaller than the experimental data by a factor of about 6. From this tendency we infer that the $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system is properly described by the strong correlation scheme of the Hubbard Hamiltonian. However, for a quantitative comparison, we believe that the theory is much too simplified, and, other factors, such as finite correlation and temperatures and the lattice distortions, should be included. We also note that the decrease in charge carrier density and lattice distortion are spontaneously occurring effects, as was observed by structural investigations [5]. In our data, we can hardly find the broad precursor peak which Trodahl and Mawdsley claimed to have found [19] and which also indicates enhancement of the phonon mean-free path in the presence of superconducting fluctuation.

From the magnetic susceptibility measurements in low magnetic fields below T_c (Fig. 5), we observe that the diamagnetic property becomes reduced and the diamagnetic onset temperature is lowered when the praseodymium concentration is increased. The inverse susceptibility curves which are measured at $B = 1.4$ T are shown in Fig. 6. Including the temperature-independent diamagnetic contributions, the measured susceptibility above T_c can be written [20]

$$\kappa = \kappa_0 + \frac{C}{T - \theta_p} \quad (3)$$

TABLE II The variation of thermopowers, $\Delta S = S(x) - S(x = 0)$, at 300 K

x	ΔS(theory) ($\mu V K^{-1}$)	ΔS(experiment) ($\mu V K^{-1}$)
0.1	21.3	4.2
0.2	46.3	6.9
0.3	77.4	12.7
0.4	120.6	18.1

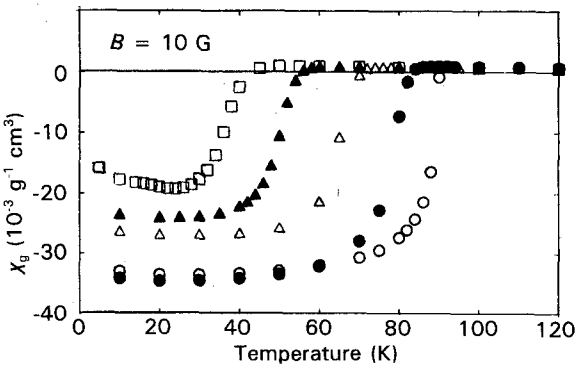

Figure 5 Field cooling data of magnetic susceptibility as a function of temperature. (○) $x = 0$, (●) $x = 0.1$, (△) $x = 0.2$, (▲) $x = 0.3$, (□) $x = 0.4$.

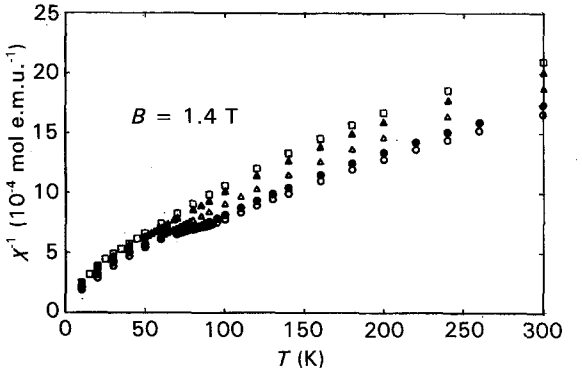

Figure 6 Inverse susceptibility measured at $B = 1.4$ T (○) $x = 0$, (●) $x = 0.1$, (△) $x = 0.2$, (▲) $x = 0.3$, (□) $x = 0.4$.

where C is the Curie constant and θ_p the paramagnetic Curie–Weiss temperature. Constants in Equation 3 are estimated by non-linear least square fitting and are shown in Table III. The temperature-independent susceptibility term, κ_0, remains almost the same in spite of increasing x, and the paramagnetic Curie–Weiss temperature, θ_p, has a weak praseodymium concentration dependence. The effective magnetic moment, μ_{eff}, is determined experimentally using the formula $(3k_BC/N)^{1/2}$, where C is the Curie constant and N the Avogadro constant. For the case of $x = 0$, the observed value of magnetic moment, 9.2 μ_B, is very close to that of free ion Er^{3+} (9.5 μ_B). The effective magnetic moment decreases as the praseodymium concentration increases and the praseodymium valence evaluated from the total moment for each x is greater than + 3.6. The average valency is + 3.67 and this value is somewhat smaller than that reported previously for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, namely + 4 [21] and + 3.87 [3]. In our study, it is assumed that praseodymium

TABLE III Parameter values obtained by fitting susceptibility data for the $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system

Pr concentration	κ_0 (10^{-4} cm^3 mol^{-1})	θ_p (K)	μ_{eff} (μ_B)	μ per Pr ion (μ_B)	Pr valence
0.0	2.636	− 13.30	9.20		
0.1	2.073	− 10.86	8.83	2.82	+ 3.73
0.2	2.196	− 9.80	8.17	2.86	+ 3.69
0.3	2.304	− 8.30	7.54	2.97	+ 3.60
0.4	2.116	− 10.88	7.44		

and erbium ions do not influence the magnetic moment for each other. Such a result was proved for the case of gadolinium with large magnetic moment (8.0 μ_B) [22].

4. Conclusions

The present study suggests that the superconducting properties of the $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system are very similar to those of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, even though the erbium ion has a very large magnetic moment. In our $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, it is shown that T_c decreases non-linearly and the lattice parameters increase slightly with praseodymium concentration, x. From thermoelectric power measurements, it is shown that our system loses its metallic property by praseodymium substitution, which means reduction of mobile carrier density. From the tendency of the thermopower changes and the modified Heikes formula, we have verified that the $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system is a strongly correlated system, as proposed by Anderson. The average praseodymium valency + 3.67 is obtained by magnetic susceptibility data. Although it appears that still further study is necessary to pinpoint the praseodymium suppression mechanism of superconductivity, we believe that the dominant mechanism is due to the reduction of carrier density and structural changes.

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