Superconductivity in Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ with metallic double chains

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Abstract

We report superconductivity with $T_{c,\text{onset}} \approx 10$ K in polycrystalline samples of Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ possessing metallic double chains. A reduction treatment on as-sintered samples causes not only the enhanced metallic conduction but also the appearance of superconductivity, in strongly contrast with the oxygen removal effect of superconducting Y$_2$Ba$_4$Cu$_7$O$_{15-\delta}$.

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1. Introduction

Since the discovery of high-$T_c$ copper-oxide superconductors, extensive studies on strongly electron correlated system have been in progress on the basis of physical properties of two-dimensional (2D) CuO$_2$ planes. Moreover, from the viewpoint of low-dimensional physics, particular attention is paid to the physical role of one-dimensional (1D) CuO chains included in some families of high-$T_c$ copper oxides such as Y-based superconductors with the transition temperature $T_c \approx 92$ K. It is well known that the Pr-substitution for Y-sites in YBa$_2$Cu$_3$O$_{7-\delta}$ (Y123/7) and YBa$_2$Cu$_4$O$_8$ (Y124/8) compounds dramatically suppresses $T_c$ and superconductivity in CuO$_2$ planes disappears beyond the critical value of Pr, $x_c \approx 0.5$ and 0.8, respectively [1,2]. Such a
suppression effect due to Pr-substitution on superconductivity has been explained in terms of the hybridization model with respect to Pr-4f and O-2p orbitals [3]. Y124/8 compound with double chains is thermally stable up to 800 °C, while in Y123/7−δ oxygen deficiencies are easily introduced at lower annealing temperatures [4]. Intermediate between PrBa$_2$Cu$_3$O$_{7−δ}$ (Pr123/7−δ) with single chains and PrBa$_2$Cu$_4$O$_8$ (Pr124/8) with double chains is the Pr$_2$Ba$_4$Cu$_7$O$_{15−δ}$ (Pr247/15−δ) compound with an alternative repetition of the single and double chains along the c-axis, isomorphic with superconducting Y$_2$Ba$_4$Cu$_7$O$_{15−δ}$ (Y247/15−δ) [5,6]. The crystal structure of orthorhombic Pr247 is schematically shown in Fig. 1 (space group Ammm). In Pr247, it is possible to

Fig. 1. Schematic view of the Pr$_2$Ba$_4$Cu$_7$O$_{15−δ}$ structure with a repetition of the corner-sharing CuO single chain and the edge-sharing CuO double chains. Also shown is the direction of the orthorhombic principal axes. The inset indicates models of parallel resistors along the b direction, where $R_p$ and $R_c$ denote resistances of CuO$_2$ planes and CuO chains, respectively.
examine physical properties of metallic double chains varying oxygen contents along single chains [6,7].

In this paper, we report superconductivity in Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ compound possessing metallic double chains.

2. Experimental

Polycrystalline samples of Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ were synthesized using a powder sintering method under high pressure oxygen [2,6]. The Pr$_6$O$_{11}$, BaO$_2$ and CuO powders with high purity were mixed to the stoichiometric composition and were then pressed into a cylindrical pellet. The pellet was calcined at 850–900 °C in air and was then sintered at 975 °C for 18 h with P(O$_2$) = 5 atm. As-sintered samples were annealed in argon gas at 650 °C. The resistivity measurement was performed by a conventional four-probe technique. The magnetization measurement was carried out down to 2 K under zero-field cooling (ZFC) and field cooling (FC) conditions using a SQUID magnetometer.

3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns for as-sintered and Ar reduced Pr$_{247}$/15 – $\delta$ at room temperature. All diffraction lines were indexed in terms of the Pr$_{247}$ majority phase, except for a small amount of the BaCuO$_2$ phase. Here, we give some comments on impurity phases in Pr$_{247}$. From our previous studies on synthesis of Pr$_{247}$ compounds, we have pointed out possible impurity phases such as PrBaO$_3$, BaCuO$_2$ and Pr$_{124}$/8, except for the starting materials [6,2]. X-ray diffraction patterns on both as-sintered and reduced Pr$_{247}$ reveal at a small amount of the BaCuO$_2$ impurity phase although the precipitation of PrBaO$_3$ and Pr$_{124}$/8 is strongly suppressed in this sintering process. It is truly expected that in the present samples, the PrBaO$_3$ and Pr$_{124}$/8 phases may be included as a very small volume fraction hardly detectable by X-ray diffraction. However, the lower-$T$ heat treatment never causes superconductivity for the PrBaO$_3$, BaCuO$_2$ and Pr$_{124}$/8 phases. The oxide materials of PrBaO$_3$ and BaCuO$_2$ are highly insulator. Moreover, the Pr$_{124}$/8 phase is thermally stable under lower temperature annealing and the resistivity data of metallic Pr$_{124}$ single crystals exhibit no superconductivity down to 2 K [8]. Therefore, we believe that even if there exist minor impurity phases hardly observed by X-ray probe, low-$T$ reduction process induces no superconductivity for the impurity phases in Pr$_{247}$.

The lattice parameters of the as-sintered sample are estimated from the least-squared fitting to the X-ray diffraction data to be $a = 3.8880(3)$, $b = 3.9037(3)$ and $c = 50.660(4)$ Å, respectively. The oxygen deficiency $\delta$ of as-sintered Pr$_{247}$ is
taken as almost zero because pure Y247 prepared under the same sintering condition as Pr247, exhibits a sharp superconducting transition with $T_c = \sim 89$ K [2]. In fact, Tallon et al., reported that the resistivity of Y247/15 shows a superconducting transition near $T_c = \sim 92$ K [9]. For comparison, the unit length of $c$-axis in Pr247/15 [=2×(Pr123/7 unit) + (Pr124/8 unit)] is estimated to be 50.77 Å from $c = 11.73$ Å for Pr123/7 and $c = 27.308$ Å for Pr124/8 [6,10]. This estimation is almost comparable with the $c$-axis lattice constant of Pr247/15. For the sample reduced in Ar for 4 days, the lattice parameters are determined to be $a = 3.8923(5)$, $b = 3.9020(3)$ and $c = 50.814(6)$ Å, respectively. The oxygen deficiency $\delta$ of Pr247 due to Ar annealing is estimated to be $\delta = \sim 0.5$ from the thermogravimetry and results in a substantial elongation of the $c$-axis length up to $\sim 0.3\%$, keeping its orthorhombic structure. These results are similar with a variation in the lattice parameters of Y247 as a function of oxygen deficiency. Irizawa et al., reported that the $c$-axis length of Y247/15–$\delta$ reaches an increase by 0.36% over the range of oxygen deficiency from $\delta = 0.05$ to 0.6 [11].

Fig. 3(a) shows the temperature variation of electrical resistivity in sintered Pr247/15–$\delta$. The value of $\rho$ of the as-sintered sample exhibits a semiconducting behavior at high $T$, it reaches a broad maximum at $T_m = \sim 150$ K and gradually decreases down to 4 K. This finding has been well explained on the basis of the parallel circuit model (the inset of Fig. 1) composed of both the semiconducting CuO$_2$ planes and metallic CuO double chains, as first proposed by Bucher et al., in YBCO system [7,12]. A previous study on both sintered Pr124 and Pr247 implicated that the negative temperature dependence of the resistivity above $T_m$ is ascribed to the CuO$_2$ plane conduction, while the positive $T$-dependence of the resistivity below $T_m$ to the CuO double-chain conduction [7]. On the other hand, the $T$ dependence of $\rho$ of the reduced samples follows a strongly metallic conduction up to 300 K. For the 4-days reduced sample, the superconducting transition evidently appears around 10 K and the zero-resistivity temperature $T_{c, \text{zero}}$ is determined to be 3.8 K from low-$T$ resistivity data. The value of $\rho$ of the superconducting sample is proportional to $T^2$ below 150 K, which is the same temperature dependence of $\rho$ along the $b$-axis of Pr124 single crystal [8]. Accordingly, the oxygen defects in Pr247 system cause not only the enhanced metallic state but also the appearance of superconductivity, in strongly contrast with the oxygen removal effect of Y247 on its resistivity [11].

Next, the temperature dependence of magnetic susceptibility ($\chi$) in Pr247 is shown in Fig. 4. For the 4-days reduced sample, the value of $\chi$ gradually increases with decreasing $T$, then exhibits a hump near 10 K and finally a clear diamagnetic signal is detected below $\sim 9$ K on both ZFC and FC data. The superconducting volume fraction is estimated to be about 4% at 2 K from the ZFC data. Moreover, for 2-days reduced one, a sharp drop in the $\chi$...
data is also observed below 10 K. On the other hand, the value of $v$ for the as-sintered one shows a Curie–Weiss like behavior and a slight anomaly is observed at $/C24\ 3 \text{K}$ indicating the formation of a superconducting state. The Curie–Weiss plot suggests that the Néel temperature of Pr spins $T_N$ is nearly 16 K almost the same as $T_N$(17 K) in Pr124 [2]. Furthermore, the $(\chi - \chi_0)^{-1}$ data in the inset of Fig. 4(b) show a nonlinear deviation near $\sim 160 \text{K}$ associated with the Néel ordering of Cu spins, which is not far from $T_N(=200 \text{K})$ in Pr124 [13]. This finding is consistent with the evidence for an antiferromagnetic order of the planar Cu spins in the NQR experiment [14].

Here, we would like to comment on superconductivity with $T_c = 85 \text{K}$ in a Pr123 single crystal reported by Zou et al. [15]. Surely, the origin of bulk superconductivity in Pr123 has not been made clear, but several authors claimed that the superconductivity originates from the inhomogeneities in the chemical composition such as the Ba-rich Pr123 [16]. The partial substitution of Ba for Pr-site gives rise to a strong suppression of the hybridization between Pr-4f and O-2p orbits, resulting in doping mobile carriers into CuO$_2$ planes and the appearance of superconductivity. This issue seems to depend on the criterion whether the orbital hybridization leading to carrier localization is retained or not. The negative T-dependence of resistivity for as-sintered Pr247 (Fig. 3(a)) demonstrates a clear contribution from the insulating CuO$_2$ planes as well as the insulating Pr123. Moreover, Matsushita et al. showed that the value of $\rho$ in as-sintered Pr247 gradually rises at high temperatures with applied pressure, indicating the enhancement of the hybridization state between Pr and O orbits [7]. It is easily understood that a reduction process does not alter the electronic state of the Pr–O hybridization because a lower temperature annealing in Ar hardly causes the Ba substitution for Pr sites in the Pr247 composition. In fact, a previous work on stoichiometric Pr123/7 reported that its resistivity increases by more than three orders of magnitude as the oxygen content $7 - \delta$ is reduced from $6.93$ to $6.46$ [10]. In this study, the c-axis elongation due to oxygen deficiency gives no changes on the Pr–O hybridization state in Pr123 system. In a similar way, it is expected that there also exists the hybridization in the reduced Pr247 accompanied by the c-axis elongation due to oxygen removal. In the view point of sample preparation, we have to point out outstanding differences between Pr123 and Pr247. As-grown crystal of Pr123 was annealed in flowing pure oxygen gas for over 4 days under two steps of annealing temperatures in order to realize superconductivity. Zou et al., reported that the c-axis lattice constant of the annealed crystal is shorter than that of the as-grown one. Therefore, it is
difficult to identify the observed superconductivity in reduced Pr247 with the bulk superconductivity in oxidized Pr123 crystal.

Recently, we have found out that a low-T reduction treatment in a vacuum causes a higher superconductive sample of Pr247, as shown in Fig. 5, through our seeking for more suitable annealing conditions. It should be noted that superconductive samples are obtained reproducibly under the similar annealing procedure from starting materials. Moreover, Hall coefficient measurement [17] on reduced Pr247 reveals that \( R_H(T) \) clearly shows its negative sign below 100 K, which is probably related to the enhanced metallic state due to oxygen removal. A systematic study on the pressure effect on both transport and magnetic properties in the superconducting Pr247 is in progress [18]. A microscopic research such as the NMR will be also carried out, in order to specify the superconducting regions.

In summary, we have reported superconductivity in polycrystalline samples of Pr\(_2\)Ba\(_4\)Cu\(_7\)O\(_{15\,-\,\delta}\) possessing metallic double chains. Both resistivity and magnetization measurements exhibit the superconducting transition temperature \( T_{c,\text{onset}} \approx 10 \) K and the superconducting volume fraction is estimated to be about 4% at 2 K. The reduction treatment causes not only the enhanced metallic conduction but also the realization for superconductivity, accompanied by the \( c \)-axis elongation due to oxygen deficiency.

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References