Superconducting and non-superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_7$

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Abstract. Superconducting properties of Pr123 and microscopic structural differences between the superconducting and non-superconducting Pr123 crystals are reviewed. It is shown that the variety of physical properties of Pr123 is closely related to Cu deficiency at the chain site and our experimental results are consistently explained with a model that the Pr 4*f*–O 2*p* hybridization forms a narrow band and carriers are localized by a kind of atomic disorder in non-superconducting crystals.

Keywords. Pr123; superconductivity; Cu deficiency.

1. Introduction

$\text{RBa}_2\text{Cu}_3\text{O}_7$ (R123) compounds with R = Y or rare earth element are 90 K superconductors except for R = Pr, Ce and Tb (Hor *et al* 1987; Murphy *et al* 1987; Soderholm *et al* 1987). The crystallographic structure has two-dimensional $\text{Cu}(2)\text{O}_2$ planes and one-dimensional $\text{Cu}(1)\text{O}$ chains embedded between Ba and R layers as shown in figure 1. In the cases of Tb and Ce the orthorhombic R123 structure cannot be synthesized. The Pr123 has the orthorhombic R123 structure. However, it has been believed that the Pr123 compound shows neither metallic nor superconducting behaviour (Radousky 1992). In order to make clear the anomalous behaviour of Pr123, the superconducting transition temperature T_c of $\text{Y}_{1-x}\text{Pr}_x\text{123}$ system has been studied by many workers (Peng *et al* 1989; Fink *et al* 1990; Infante *et al* 1990; Neumeier *et al* 1990; Kakinuma and Fueki 1997; Merz *et al* 1997) and several models have been proposed such as (i) filling of mobile holes (Neumeier *et al* 1989), (ii) magnetic pair breaking (Neumeier *et al* 1989; Peng *et al* 1989) and (iii) localization effect mediated through hybridization of Pr 4*f* with O 2*p* states (Fink *et al* 1990; Fehrenbacher and Rice 1993) etc.

Recently, we have found that the stoichiometric Pr123 exhibits superconductivity when it is grown by floating zone method (Zou *et al* 1997, 1998a). Superconductivity or Pr123 is also observed in thin films by Blackstead *et al* (1996) and Usagawa *et al* (1997). These results show that the non-metallic behaviour of Pr123 must be taken into account as also the fact that the Pr123 changes from insulator to superconductor without doping of other rare earth element like Y.

The T_c decrease with increasing Pr concentration in $\text{Y}_{1-x}\text{Pr}_x\text{123}$ system seems to be explained by Abrikosov–Gorkov theory. However, this pair breaking effect does not localize carriers and cannot explain the nonmetallic behaviour of Pr123. The possibility of hole depletion due to four-valent Pr is ruled out by the fact that Pr is trivalent in Pr123. Many experiments such as magnetic susceptibility (Takano *et al* 1995), neutron diffraction (Neumeier *et al* 1990; Lopez–Morales *et al* 1990; Guillaume *et al* 1993), resonant photoemission spectroscopy (Kang *et al* 1989), X-ray absorption (Horn *et al* 1987; Neukirch *et al* 1998), and electron energy-loss spectroscopy (Fink *et al* 1990) etc support a trivalent Pr atom. Merz *et al* (1997) identify the hole states in the CuO_2 planes and the CuO chains by X-ray absorption spectroscopy which lead to the result that models involving hole filling or charge transfer between the planes and the chains can be ruled out. They reported that their data are consistent with approaches based on the idea that Pr 4*f*–O 2*p_π* hybridization produces localization of holes.

Fehrenbacher and Rice (FR) (1993) developed a theory based on hybridization of localized states which accounts for the semiconducting behaviour of Pr123. Liechtenstein and Mazin (1995) noted that this model failed to explain the results of doping studies indicating that the suppression of T_c with Pr concentration levels is dependent on the host rare earth. The recent paper by Mazin (1998) reports that, if handled correctly, the FR model never renders localized states. The FR state forms a band whose dispersion is defined by the Pr–O hopping amplitude. This model explains the conductive state of pure stoichiometric Pr123. In this case, as suggested by Mazin, superconducting carriers are of entirely different character from those residing in the Cu–O bands.

Here, we report superconducting properties of Pr123 and microscopic structural differences between

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the superconducting and non-superconducting Pr123 crystals.

2. Superconducting Pr123

Single crystals of Pr123 were grown by the travelling-solvent floating-zone (TSFZ) and flux methods. Polycrystalline crystals of pure Pr123 and Ca substituted $\text{PrBa}_{2-x}\text{Ca}_x\text{Cu}_3\text{O}_7$ were prepared by solid state reaction in oxygen reduced atmospheres. As starting materials, predried Pr_6O_{11} , BaCO_3 , CaCO_3 and CuO with the purity of 99.99% were used. Details of sample preparations are described elsewhere (Zou *et al* 1997, 1998b; Minawa *et al* 1998; Oka *et al* 1998).

The resistivity of Pr123 shows wide variety, as shown in figure 2, from semiconducting behaviour of flux-grown crystals to superconducting one of TSFZ crystals. All the samples were annealed at 850°C for 24 h and then

at 550°C for 77 h in flowing pure oxygen gas. We find that the value of resistivity of Pr123 changes by 2–3 orders of magnitude depending on the growth condition. The TSFZ crystals have the lowest resistivity and some samples exhibit superconductivity with T_c ranging from about 25–80 K. The growth conditions of the superconducting Pr123 are not completely clear at present (Oka *et al* 1998). The resistivity value of $\text{PrBa}_{1.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_7$ around room temperature is very close to that of superconducting TSFZ crystal with $T_c \sim 55$ K. But this sample shows no superconductivity (Minawa *et al* 1998).

Figure 3 shows the temperature dependence of magnetic susceptibility of the TSFZ crystal with $T_c \sim 80$ K. The magnetic field was applied perpendicular to the *ab* plane. The value of diamagnetism of zero-field cooled magnetization nearly corresponds to the perfect diamagnetism when the demagnetization factor of the sample is taken into account (Zou *et al* 1997). The field cooled magnetization shows the Meissner effect of about 15% of the total volume. The results of the magnetization study show that the superconductivity of this sample is a bulk effect. However, compared with Y123, the superconductivity of this sample is very sensitive to the magnetic field. By the application of the magnetic field of 500 Oe, the superconducting transition temperature decreases down to 40 K. We need a field of over 10 kOe to get the 10 K decrease of T_c in other R123 series. Further study is important to make clear whether this is a true bulk effect of Pr123 or a weak link effect due to a multidomain structure.

Figure 1. Crystal structure of orthorhombic Pr123.

Figure 2. Resistivity of Pr123 single crystals grown by flux and TSFZ methods. Data of polycrystalline samples of Pr123 and $\text{PrBa}_{1.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_7$ are also shown. All these samples are oxygen annealed ones.

The temperature dependence of magnetic susceptibility χ for the superconducting TSFZ crystal and for the semiconducting flux-grown crystal was measured from 5–300 K in magnetic field of 5 kOe. From the fit to the Curie–Weiss law

$$\chi = \chi_0 + C/(T + \theta),$$

we obtain $\chi_0 = 4.5 \times 10^{-4}$ emu/mol and effective magnetic moment $\mu_{\text{eff}} = 2.29 \mu_B$ for the TSFZ crystal (figure 4). For the flux-grown crystal we obtain also $\chi_0 = 4.5 \times 10^{-4}$ emu/mol and effective magnetic moment $\mu_{\text{eff}} = 2.23 \mu_B$ (figure 5). The value of effective magnetic moment of the superconducting sample is nearly equal to that of the semiconducting sample. Many valence studies of Pr in flux-grown crystals reveal that the valence of Pr is +3. Therefore, the results suggest that the Pr in the superconducting sample is also in the same Pr^{3+} state as that in non-superconducting samples.

3. T_c enhancement under pressure

We measured the electrical resistivity under pressure up to 10 GPa using a cubic anvil apparatus and found that the superconducting transition temperature increases by pressure over 105 K (Ye *et al* 1998a). The maximum values of T_c at on-set and zero-resistance point are 109 and 105 K at 9.3 GPa in $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ and 106 and 102 K at 9.7 GPa in $\text{PrBa}_2\text{Cu}_3\text{O}_{6.8}$, respectively. Here, the oxygen contents of the samples were tentatively determined from T_c at zero-pressure. The T_c value at zero-resistance point

Figure 3. Temperature dependence of magnetization for the superconducting Pr123 crystal with $T_c \sim 80$ K.

in both samples exceeds 100 K and still has a potential to increase.

Figure 6 shows the pressure dependence of superconducting transition temperature in the R123 series superconductors. The data are obtained for the samples with nearly optimum oxygen concentration. Except for Yb123, T_c increases with pressure near zero-pressure region. The increasing rate of T_c by pressure increases slightly with increasing rare earth size. However, we can see that the value of dT_c/dP in Pr123 is exceptionally large in the R123 series superconductors. The saturation value of zero-resistance T_c is also large and exceeds 100 K in Pr123. These unusually large saturation values and increasing rate of T_c suggest that Pr123 might have a different electronic structure with the present superconducting compounds.

4. Structural difference between superconducting and non-superconducting Pr123

The crystal structure was investigated using an X-ray precession camera and a four-circle X-ray diffractometer with monochromatized $\text{MoK}\alpha$ radiation. Crystal structures of as-grown samples are tetragonal with space group $P4/mmm$ and those of oxygen annealed ones are orthorhombic with space group $Pmmm$. Since the superconducting sample has a twin structure due to orthorhombicity, the detailed structural difference between TSFZ and flux-grown crystals was studied using as-grown crystals (Ye *et al* 1998b).

The averaged values of lattice parameters for TSFZ crystals are $a = 3.900(1) \text{ \AA}$, $c = 11.856(2) \text{ \AA}$, while for flux ones $a = 3.916(1) \text{ \AA}$, $c = 11.747(2) \text{ \AA}$. The lattice parameter c of TSFZ ones is apparently longer than that

Figure 4. Temperature dependence of magnetic susceptibility for the superconducting TSFZ crystal with $T_c \sim 80$ K.

of flux ones. From the analysis of atomic coordinates and anisotropy of thermal displacement parameters, it has been revealed that the positional parameters z of Ba and Cu(2) atoms differ remarkably between TSFZ and flux crystals, while those of O(2) and O(4) atoms are essentially the same. The parameters z of Ba and Cu(2) are 0.19052(2) and 0.35195(4) for TSFZ crystal and those for flux crystal are 0.18890(2) and 0.35165(3), respectively (Ye *et al* 1998b).

One of remarkable differences between TSFZ and flux crystals is the occupancy parameter of Cu(1) site (table 1). In TSFZ crystals, the Cu(1) deficiency is less than 7%. On the other hand, in flux crystals the deficiency reaches about 30%. Compositional analysis by the inductive coupled plasma method revealed that the chemical compositions of TSFZ crystals are close to the stoichiometry of Pr : Ba : Cu = 1 : 2 : 3. In contrast, the composition of one of the flux-grown crystals was 1.12 : 1.88 : 2.60. The result is consistent with the quantity of Cu(1) deficiency in the flux crystal. Flux crystals grown by different conditions, as reported by Lowe–Ma and Vanderah (1992), have less deficiency (~10%). The crystal grown under reduced atmosphere has the least deficiency in flux-grown crystals. Details of the results will be published elsewhere (Zou *et al* 1998d). We find that the quantity of Cu(1) deficiency is varied with growth condition. In addition to this deficiency, a large thermal displacement parameter of O(4) site is observed in flux crystals (Ye *et al* 1998b). This observation might have a close relation with Cu(1) deficiency of the crystal.

There is a significant difference of ~0.1 Å in the lattice parameter c between TSFZ crystals and flux crystals with Cu(1) deficiency over ~20%. However, the Cu(1)–Cu(2) bond length of the flux crystal is 4.1358 Å

and that of TSFZ one is 4.1657 Å. The Cu(2)–Cu(2) length of the flux crystal is 3.4896 Å and that of the TSFZ crystal is 3.5049 Å. The Pr and O(2) distance (flux crystal : 2.485 Å, TSFZ crystal : 2.482 Å) have little difference between the flux and TSFZ crystals. The bond angles of four O(2)–Pr–O(2) and two O(2)–Cu(2)–O(2) are also slightly different between the flux and TSFZ crystals (Ye *et al* 1998b). Though the difference is small, these slight distortions lead to the c -axis difference and might have some role in appearance of superconductivity.

The c -axis lattice constant of TSFZ crystal is longer than that of the flux crystal. Figure 7 shows the relation between c -axis lattice constant and ionic radius of R^{3+} in the superconducting R123 systems. The values of Pr123 are obtained after oxygen annealing. The values of TSFZ crystal fall in the consistent curve of other superconducting R123 systems (Zou *et al* 1998a). However, the value of c -axis lattice constant of TSFZ crystal scatters from 11.71 to 11.83 Å and the superconducting samples are only a part of them. We could not make clear the relation between T_c and c -axis lattice constant. We can say safely, however, that the flux crystals with smaller lattice constants surely do not show superconductivity.

5. Pressure effect of resistivity

The pressure effect on superconducting transition temperature suggests that the electronic state of Pr123 might be different from other R123 systems (Ye *et al* 1998a). To see the pressure effect on electronic properties, here we compare the pressure effect on electrical resistivity in Pr123 and Y123. The resistivity of superconducting Pr123 decreases with pressure. In Y123 the resistivity ratio at 1 GPa and 0 GPa ($\rho(1 \text{ GPa})/\rho(0)$) around 100 K is ~0.85 both in $T_c = 90$ K and 60 K samples (Murata *et al* 1989). The ratio in superconducting Pr123 is also nearly equal to 0.85 at ~150 K.

Table 1. Lattice parameters of as-grown TSFZ and flux-grown crystals.

	TSFZ crystal	Flux crystal
Lattice parameters (Å)		
a	3.900(1)	3.916(1)
c	11.836(2)	11.747(2)
Positional parameter z		
Ba	0.19052(2)	0.18890(2)
Cu(2)	0.35193(4)	0.35165(3)
Occupancy parameter of Cu(1)		
	0.99(1)	0.79(1)
Bond length (Å)		
Cu(1)–Cu(2)	4.1655(5)	4.1358(4)
Cu(2)–Cu(2)	3.5053(9)	3.4896(8)
Pr–O(2)	2.481(1)	2.485(1)

Figure 5. Temperature dependence of magnetic susceptibility for a flux-grown crystal.

The resistivity of polycrystalline Pr123 sample grown in the atmosphere of 0.5% oxygen is two orders of magnitude smaller than that of flux-grown crystals around 150 K. The resistivity of this sample also shows a large decrease with pressure. The ratio of $\rho(1 \text{ GPa})/\rho(0)$ is ~ 0.6 at $\sim 150 \text{ K}$. But the absolute value of resistivity is larger than the superconducting one by one order of magnitude. On the contrary, the resistivity increases with pressure in Ca doped Pr123, though the resistivity is smaller than the value of the polycrystalline Pr123, as shown in figure 2. It is clear that the conduction mechanism in these two polycrystalline samples is completely different.

6. Discussion: hybridized state of Pr 4f and O 2p orbitals

Our experimental results show that physical properties of Pr123 vary from insulating to superconducting with the growth condition. Two models were proposed to explain the insulating property of Pr123.

One is a hole localization model proposed by Fehrenbacher and Rice (1993). They explained the

insulating state of Pr123 by the existence of a local Pr 4f-O 2p hybridized state which binds the holes to Pr sites. They assumed that the O 2p π orbitals point towards the Pr atom and are rotated by 45° with respect to the CuO₂ planes.

The other is a randomness induced hole localization model proposed by Liechtenstein and Mazin (1995). From the X-ray absorption experiment by Merz *et al* (1997), Mazin (1998) derived that the oxygen p orbitals pointing to the Pr atom forms the angle of $\sim 35^\circ$ with the CuO₂ planes. He concluded that the right geometry of the Pr-O bonds gives a result that the FR state forms a narrow band whose dispersion is defined by the Pr-O hopping amplitude. This band is very narrow and easy to localize.

Figure 7, which shows the relation between *c*-axis lattice constant and R³⁺ ionic radius of superconducting R123 system, seems to support the idea that the hole localization due to strong hybridization between Pr 4f and O 2p orbitals is a main origin of the non-superconductivity of flux-grown Pr123. However, our pressure study revealed that the *c*-axis length is compressed significantly and the *T_c* increases with pressure. If we assume that the angle between O 2p orbitals and the CuO₂ plane is constant under pressure, this result conflicts with the simple expectation that the decrease in *c*-axis leads to stronger hybridization and results in stronger localization of holes.

The *c*-axis lattice constant varies as shown in figure 8 with the quantity of Cu(1) deficiency. These data were obtained for as-grown samples. With decreasing Cu(1) vacancy, the *c*-axis becomes longer. The TSFZ crystal with nearly 100% Cu(1) occupancy shows superconduct-

Figure 6. Pressure dependence of superconducting transition temperature in the R123 series superconductors (Benischke *et al* 1992; Klotz *et al* 1991; Lin *et al* 1995).

Figure 7. Rare earth ionic radius vs *c*-axis lattice constant in oxygen annealed R123 systems.

tivity after oxygen annealing. This figure suggests that the superconductivity of Pr123 does not depend on the preparation technique or *c*-axis length but strongly depends on the quantity of Cu(1) deficiency.

The model proposed by Mazin (1998) seems to be more plausible for our experimental results. According to his model, the FR band is very narrow and is easily localized by weak randomness. As for the origin of disordering, Blackstead *et al* (1996) predicted that substitution disorder due to Pr on Ba sites exists in Pr123 and destroys superconductivity. Very recently, Shukla *et al* (1998) measured the electron momentum density in Pr123 and Y123. They explained the observed difference between Pr123 and Y123 with the model that substitution disorder due to Pr on Ba sites exists locally in non-superconducting Pr123. As far as we know, however, there is no direct observation by neutron or X-ray diffraction on this disordering between Pr and Ba.

In our experiments we observed a clear deficiency of Cu(1) atoms in non-superconducting Pr123. Most of the Pr123 samples have Cu(1) deficiency. The quantity of deficiency amounts to 30% in flux-grown crystals. In the TSFZ crystals it is small and less than 7%. We cannot deny the possibility that the Cu(1) vacancy is closely related to presence of Pr on Ba sites. We think, however, even if there is no substitution between Ba and Pr, existence of Cu(1) vacancy will be enough to localize the narrow FR band.

by pressure may be interpreted with a movement of carriers from the Cu–O band to the localized Pr–O band.

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