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Superconductivity and Magnetism of $Y_{1-x}Pr_xBa_2Cu_4O_8$ Prepared by Nitride Pyrolysis Method

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X-ray diffraction patterns exhibit that samples contain nearly single 124 phase for $x \leqq 0.7$. Lattice parameters a and b increase with Pr concentraion, indicating that Pr is likely trivalent in $Y_{1-x}Pr_xBa_2Cu_4O_8$. Zero resistance temperature T_{co} decreases monotonically from 80K at x=0 to 12K at x=0.65, and superconducting transition widths are inclined to be broader for x>0. The critical concentration x_{cr} is estimated to be 0.7. Effective magnetic moments of $Y_{1-x}Pr_xBa_2Cu_4O_8$ are 3.63, 3.35 and 3.23 μ_B for x=0.2, 0.4 and 0.6, respectively.

I. Introduction

Bulk sample of the high-T_c superconductor $YBa_2Cu_4O_8$ (hereafter referred to as 1-2-4) has been discovered and synthesized by different methods.[1-4] This compound exhibits a superconducting transition at around 80K, and has excellent thermal stability of oxygen content up to 800°C.[1] X-ray[5,6] and neutron diffraction studies[7] revealed that the structure of 1-2-4 is closely related to $YBa_2Cu_3O_{7-y}$ (referred to as 1-2-3) but with one additional Cu-O chain in the unit cell. In particular, its relatively low T_c has been raised up to 90K by partially substituting Ca for Y atoms.[8]

Recently, many studies[9-11] have performed on the characterization of $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ system in order to elucidate the origin for the absence of superconductivity in $PrBa_2Cu_3O_{7-y}$, which is the only compound of the $RBa_2Cu_3O_{7-y}$ (R:lanthanide) with the 1-2-3 phase while not superconducting.[12] Because the structure of 1-2-4 is similar to that of 1-2-3, it is interesting to study the effect of Pr substitution in $Y_{1-x}Pr_xBa_2Cu_4O_8$. In this paper we synthesize the 1-2-4 phase under one atmosphere oxygen pressure by nitrite pyrolysis method[4] and present the structural analysis, electrical resistivity and magnetic susceptibility measurements for $Y_{1-x}Pr_xBa_2Cu_4O_8$ in order to help the understanding of the mechanism responsible for this suppression of superconductivity.

II. Experimental Method

Polycrystalline samples $Y_{1-x}Pr_xBa_2Cu_4O_8$ were synthesized from high purity reagents of Y_2O_3, Pr_6O_{11}, $Ba(NO_3)_2$ and CuO. The powders were weighed into a container with a suitable amount of nitric acid added to it. After the solution dried up under stirring on a heat block, the gray residue was calcined at 750°C under oxygen atmosphere for 6h. Then, black product powder was ground, pressed into pellet and sintered at 800°C for 24h (repeated 3 times with intermediate grinding) in one atmosphere of flowing oxygen. The rate of increasing and decreasing temperature was 60°C/hr. Samples were prepared at the same time in the same furnace as much as possible to ensure the same sample history. X-ray diffraction was carried out with Cu $K\alpha$ radiation. Lattice parameters were determined from least-squares fits of the diffraction lines indexed with the space group Ammm. Electrical resistivity measurements were made by means of standard four-probe method with the data taken from 10K to 300K. A field of 5000 Oe was used to measure the susceptibility above T_c from which the Curie-Weiss temperature Θ and effective magnetic moment μ_{eff} were derived.

III. Results and Discussion

X-ray diffraction patterns exhibit that samples contain nearly single 1-2-4 phase without any 1-2-3 phase for $x \leq 0.7$. The pattern becomes the mixture of $PrBaO_3$, CuO, $BaCuO_2$ and is not the phase of 1-2-4 while $x \geq 0.75$. Therefore the nominal composition of $PrBa_2Cu_4O_8$ can not be synthesized by this method. Figure 1 shows the change of lattice parameters as a function of nominal Pr composition x. Basically the lattice parameters a and b increase with increasing x. Because the ionic radius of Y^{3+} (0.893Å) is smaller than that of Pr^{3+} (1.013Å) and nearly equal to that of Pr^{4+} (0.9Å),[13] the increase of a and b may indicate that Pr is trivalent as a majority in $Y_{1-x}Pr_xBa_2Cu_4O_8$. Lattice parameter c is almost unchange for $x \leq 0.7$. Because the increase of the c axis is less than the difference of ionic radius between Y^{3+} and Pr^{3+}, the separation between rare-earth atoms and $Cu\text{-}O_2$ planes would decrease with increasing Pr concentration.

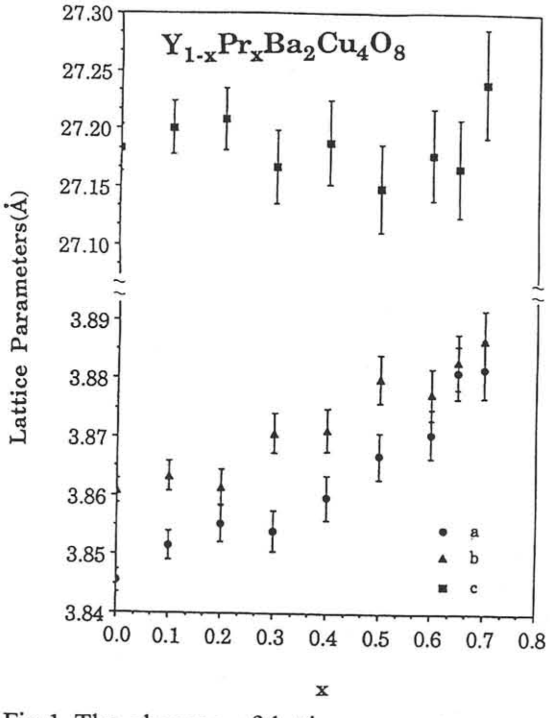

Fig.1 The changes of lattice parameters as a function of the nominal Pr composition x in $Y_{1-x}Pr_xBa_2Cu_4O_8$.

Zero resistance temperature T_{co} and superconducting transition temperatures T_c(90%~10%) versus Pr concentration are shown in Fig.2 and listed in Table I. The dashed line is the room temperature resistivity ρ_{300K} versus x. T_{co} decreases monotonically from 80K at x=0 to 12K at x=0.65, and the superconducting transition widths are inclined to be broader with increasing Pr concentration, especially for x>0.6. This may reflect that solid

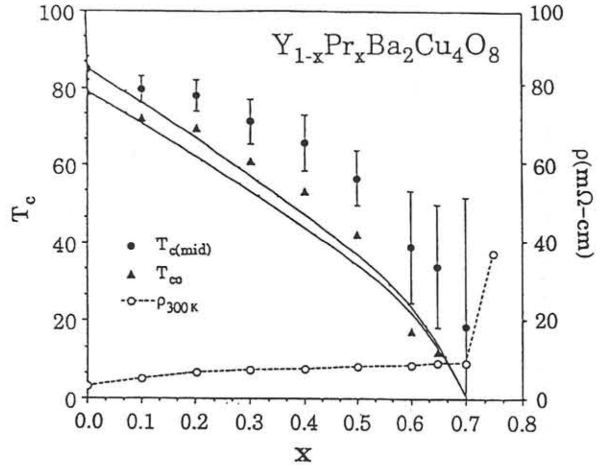

Fig.2 Zero resistance temperature T_{co} and superconducting transition temperature T_c versus Pr concentration in $Y_{1-x}Pr_xBa_2Cu_4O_8$. The dashed line is the room temperature resistivity ρ_{300K} versus x. The upper and lower solid curves are the fits of $T_c(x)$ versus x for A-G theory with $T_c(0)$=85K (midpoint) and 79K (zero resistance), respectively.

x	T_c(K) 90%--10%	T_{co} (K)	μ_{eff} (μ_B)	Θ (K)	χ_0 (emu/mol)
0.0	88 -- 82	79			
0.1	83 -- 76	72			
0.2	82 -- 74	69.5	3.63	-11.37	4.0×10^{-4}
0.3	77 -- 65.5	61			
0.4	73 -- 58.4	53	3.35	- 9.59	6.5×10^{-4}
0.5	63.8 -- 49.6	42			
0.6	53.5 -- 24.4	17	3.23	- 3.80	9.7×10^{-4}
0.65	50 -- 18.1	12			
0.7	51.8 -- ?	?			

Table I. Superconducting transition temperature and magnetic data for $Y_{1-x}Pr_xBa_2Cu_4O_8$.

solution limit occurs at x=0.6~0.7. Room temperature resistivity changes linearly till x=0.7 and increases abruptly at x=0.75, indicating that semiconducting behavior accompanies the destruction of superconducting phase. Thus the critical concentration x_{cr}, at which superconductivity disappears, is estimated to be 0.7.

The Abrikosov and Gorkov[14] (referred to as A-G) pair-breaking theory predicts that the reduced transition temperature $T_c/T_c(0)$ is a universal function of reduced concentration x/x_{cr}

$$\ln[T_c/T_c(0)]=\Psi(1/2)-\Psi(1/2+0.14xT_c(0)/x_{cr}T_c) \text{---(1)}$$

or $$T_c(x)=f(x/x_{cr})T_c(0), \text{---------------(2)}$$

where x_{cr} is the critical concentration of Pr for the complete suppression of superconductivity, $T_c(0)$ is the transition temperature of undoped $YBa_2Cu_4O_8$ and Ψ is the digamma function. The upper and lower solid curves in Fig.2 are the fits of $T_c(x)$ versus x for A-G theory with $T_c(0)$=85K (midpoint) and 79K (zero resistance), respectively. Apparently, the fits are not very successfully for our experimental data. The higher values of $T_c(x)$ than predicted suggest that the pair-breaking mechanism may play weakly in suppressing the T_c of $Y_{1-x}Pr_xBa_2Cu_4O_8$.

Figure 3 shows the inverse magnetic susceptibility versus temperature for x=0.2, 0.4 and 0.6. The magnetic susceptibility data $\chi(T)$ can be approximated by

$$\chi=\chi_o+C/(T-\Theta),\text{-------------------------}(3)$$

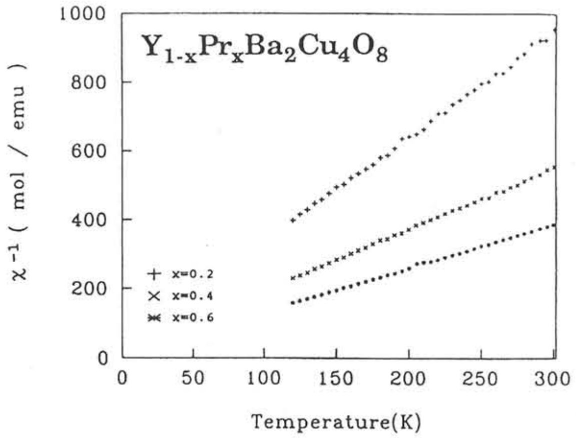

Fig.3 The inverse magnetic susceptibility versus temperature for x=0.2, 0.4 and 0.6 in $Y_{1-x}Pr_xBa_2Cu_4O_8$.

where C is the Curie-Weiss coefficient, which is related to the effective magnetic moment μ_{eff}. Values of μ_{eff}, Θ, and χ_o obtained by a nonlinear least-square fit are also given in Table I. The temperature independent susceptibility χ_o and Curie-Weiss temperature Θ are only weakly concentration dependent. Effective magnetic moment μ_{eff} has the values 3.63, 3.35 and 3.23μ_B for x=0.2, 0.4 and 0.6, respectively. It seems that the μ_{eff} decreases with increasing x. From the valence point of view, the valence of Pr likely changes from 3^+ to 4^+ as Pr concentration is increased.

On the other hand, the separation between rare earth atoms and Cu-O_2 planes would decrease with increasing Pr content in $Y_{1-x}Pr_xBa_2Cu_4O_8$. Therefore the hybridization between extended Pr 4f electrons and conduction bands in Cu-O_2 planes, which is observed in $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$,[11] would also play a role in the suppression of superconductivity in $Y_{1-x}Pr_xBa_2Cu_4O_8$. The studies of ionic radius effect on the superconductivity in $R_{1-x}Pr_xBa_2Cu_4O_8$ are currently in progress to verify this point furthermore.

IV.Conclusion

Structure, superconductivity and magnetism of $Y_{1-x}Pr_xBa_2Cu_4O_8$ have been studied in this work. The nonlinear depression of T_c by the Pr concentration in $Y_{1-x}Pr_xBa_2Cu_4O_8$ is observed with x_{cr}=0.7. The pair-breaking effect can not completely interpret the data for the depression of superconductivity of $Y_{1-x}Pr_xBa_2Cu_4O_8$. In addition, we think the hybridization between extended Pr 4f electrons and conduction bands in Cu-O_2 planes would play a role in the suppression of superconductivity in $Y_{1-x}Pr_xBa_2Cu_4O_8$.

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