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Magnetic and superconducting properties of Pr in $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ system with $0.0 \leq x \leq 1.0$

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We report the results on structural aspects, magnetic, and superconducting properties of the $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ system. Both x-ray and neutron diffraction studies reveal that Pr substitutes isostructurally in the tetragonal $\text{LaBaCaCu}_3\text{O}_7$ (La:1113) system until the complete replacement of La by Pr. The superconducting transition temperature, T_c , determined from ac susceptibility measurements decreases, with increasing x . The relative T_c depression due to Pr in the $\text{LaBaCaCu}_3\text{O}_7$ superconductor is less in comparison to that found for La-site Pr substituted $\text{LaBa}_2\text{Cu}_3\text{O}_7$ (La:123). While the critical Pr concentration (x_{cr}) to completely suppress the superconductivity in the former is around 70 at. % of Pr at La site, the same is reported as only 30 at. % for the latter. For nonsuperconducting samples, i.e., for $x=0.70$ and 1.0, possible antiferromagnetic ordering with Neel temperatures, T_N , of 4 and 8 K, respectively, are observed from both dc magnetic and heat capacity measurements. Interestingly in the $\text{La}_{1-x}\text{Pr}_x:1113$ system the x_{cr} of Pr is 0.70, and T_N of Pr:1113 is 8 K, while for the $\text{La}_{1-x}\text{Pr}_x:123$ system x_{cr} is 0.30 and T_N of Pr:123 is 17 K. The results are explained on the basis of distribution of Pr at both RE and Ba sites in the RE:1113 structure. This leads to a lower T_N and a less deleterious effect of Pr on superconductivity of La:1113 compared to La:123. © 1998 American Institute of Physics. [S0021-8979(98)17411-X]

I. INTRODUCTION

High temperature superconductivity (HTSc) above 90 K is observed in nearly all RE (rare earth) based $\text{REBa}_2\text{Cu}_3\text{O}_7$ (RE:123) compounds, except Ce, Pr, and Tb.¹ The structure of RE based 123 perovskite compound consists of two dimensional Cu–O planes and one dimensional Cu–O chains embedded between Ba and RE layers.² Both Ce and Tb based RE:123 compounds do not crystallize in the required structure: instead they form a multiphase system.³ The situation is more interesting in the case of Pr:123 ($\text{PrBa}_2\text{Cu}_3\text{O}_7$). This compound crystallizes in ideal orthorhombic RE:123 structure, similar to that of other superconducting compounds of this family, yet with no superconductivity.^{4–15} In fact, $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is an antiferromagnetic insulator, with Cu spins in CuO_2 planes ordered near room temperature and Pr moments ordered at nearly 17 K.¹⁵ However, as far as we know, three reports exist in literature which claim superconductivity of Pr:123: one on laser ablated $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$ thin film,⁶ another on bulk $\text{Pr}_{1-x}\text{Ca}_x\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_7$ ⁷ and one on recently reported $\text{PrBa}_2\text{Cu}_3\text{O}_7$ single crystals.⁸ Unfortunately, none of these results have been confirmed till now. The most promising one is the latest⁸ by Zou *et al.* [Jpn. J. Appl. Phys., Part 2 **36**, L18 (1997)]. These authors show bulk superconductivity of 80 K for $\text{PrBa}_2\text{Cu}_3\text{O}_7$ single crystals. These results have been greeted with considerable criti-

cism since the structure of superconducting Pr:123 compound reveals an anomalously long c axis questioning whether this material is truly isostructural with the superconducting RE:123 materials. Moreover, like other reports on superconducting Pr:123 compounds,^{6,7} the latest one,⁸ also lacks the universal reproduction of the same by other groups.

There are several models in the literature which try to explain the nonobservation of superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_7$. The most widely discussed are the hole filling model,^{4,9,10} and pair breaking mediated by the hybridization of Pr 4*f* with O 2*p* states.^{11,12} The hole filling model is based on the existence of Pr in a valence state of more than +3, and whereby the extra electrons from Pr neutralizes mobile holes and brings the compound to near insulating regime. This model also accounts for the restoration of superconductivity in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$, where the holes are restored by lower valence Ca substitution at Pr site in the compound.⁶ The main drawback of this model is that a valence state of more than 3+ could never be detected in the $\text{PrBa}_2\text{Cu}_3\text{O}_7$ compound. In fact the detailed magnetic susceptibility,^{13,14} photoemission spectroscopy,¹⁵ x-ray absorption,¹⁶ and electron energy loss spectroscopy¹⁷ results altogether favor a +3 valence state of Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_7$.

While the pair breaking model appeared to be promising, in that it could explain the suppression of superconductivity

in $\text{RE}_{1-x}\text{Pr}_x:123$ systems,^{11,12} pair breaking itself could not account for the insulating behavior of the $\text{PrBa}_2\text{Cu}_3\text{O}_7$ compound.

Two more recent and better understood models are given by Fehrenbacher and Rice (FR) and Liechtenstein and Mazin (LM).^{18,19} Both models involve the transfer of holes from superconducting $pd\sigma$ state to the $pd\pi$ state. In the FR model, the $p\pi$ orbitals of the planar oxygens neighboring a Pr ion, form a hybrid with the $\text{Pr-}f_{z(x^2-y^2)}$ orbital, which is strongly localized.¹⁸ Further in this model, the $p\pi$ holes are predominantly planer (p_{xy}), according to LM,¹⁹ the same have comparable amounts of $p_{x,y}$ and p_z character. The FR and LM models could also gain credence from recent x-ray absorption spectroscopy results on the $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ system.²⁰ Although both the FR and LM models explain the insulating behavior of $\text{PrBa}_2\text{Cu}_3\text{O}_7$, they do not successfully account for the T_N of nearly 17 K for Pr moments in this compound.

With more and more experimental results appearing in the literature the mystery of nonsuperconducting $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is becoming increasingly complicated. In the present study we report an interesting result on two different types of Pr doped RE:123 compounds, with the same rare earth, La. These results suggest that both T_c suppression and the antiferromagnetic ordering of Pr moments are closely related to each other. We study the compound $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ with several x values and compare the same with reported data²¹ on $\text{La}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$. Our structural, magnetic and thermal measurements on this system show that the critical concentration of Pr (x_{cr}) to quench superconductivity in this system is 0.70 which is double of that found earlier for $\text{La}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ ($x_{cr}=0.30$).

II. EXPERIMENT

Samples of the series $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$, with $x=0.0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60$, and 1.0, were prepared by a solid state reaction from La_2O_3 , BaCO_3 , CaCO_3 , Pr_6O_{11} , and CuO each of 4N purity with the procedure, as reported in Ref. 22. The samples were characterized for their phase purity by x-ray diffraction (XRD) measurements. Alternating current magnetic susceptibility measurements were carried out on a Quantum Design SQUID magnetometer, in an applied r.m.s. field of 0.01 mT and 31 Hz. Neutron diffraction patterns at room temperature were obtained for the samples with $x=0.0$ and 1.0 using the research reactor facility of the University of Missouri. The experimental details are similar to those reported earlier for RE:123 ceramic samples.²³

III. RESULTS AND DISCUSSION

X-ray diffraction studies show that $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ samples are nearly single phase materials. All the samples crystallize in a $P4/mmm$ tetragonal RE:123 phase with a decrease in the c parameter with increasing x .²² The $\text{LaBaCaCu}_3\text{O}_7$ compound is known to crystallize in the tetragonal RE:123 structure, despite having an oxygen content close to 7.0, due to the intermixing of La, Ba, and Ca sites which gives rise to equally occupied O(1) and O(5) sites in CuO chains, resulting in $a=b$.^{24,25}

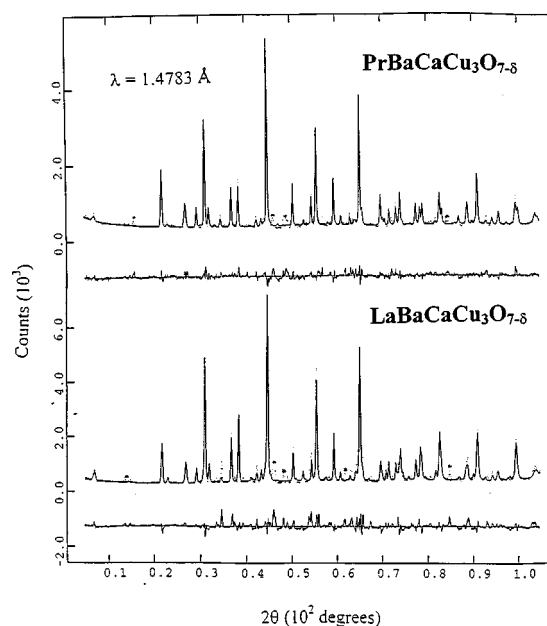


FIG. 1. Fitted and observed Neutron diffraction patterns for $\text{LaBaCaCu}_3\text{O}_7$ and $\text{PrBaCaCu}_3\text{O}_7$ samples, taken at room temperature.

Room temperature observed and fitted neutron diffractions patterns for $\text{PrBaCaCu}_3\text{O}_7$ and $\text{LaBaCaCu}_3\text{O}_7$ compounds are shown in Fig. 1. In addition to the lines from main phase, both the samples show a few diffraction lines from unreacted species in their respective spectra, similar to those observed earlier in x-ray diffraction patterns of these compounds.^{22,26} The results of the Rietveld refinement procedure using the Generalized Structural Analysis System (GSAS) for $\text{LaBaCaCu}_3\text{O}_7$ sample reveal that part of La occupies Ba site with a corresponding amount of Ca occupying the nominal RE site. Quantitatively 46% of Ca atoms occupy the usual La site, and the remaining 54% are at the Ba site. It is presumed that a similar situation occurs when Pr is substituted at La site, i.e., part of Pr occupies the Ba site. Unfortunately, the neutron scattering cross sections of Pr and Ba are very similar preventing accurate determination of their occupancies. The oxygen contents of the two samples were found to be 7.01 and 6.86, respectively, for $x=0.0$ and 1.0.

In Fig. 2 are shown the real and imaginary parts of ac susceptibility versus temperature plots for the $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ system with various x values. The inset shows the T_c vs x behavior for the presently studied system and that reported in $\text{La}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ system.²¹ The superconducting transition temperature, T_c , is defined as the onset of the diamagnetic transition, which is around 70 K for the unsubstituted sample. T_c decreases with creasing x in both $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ and $\text{La}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ systems. In RE:123, the depression of T_c depends strongly on the ionic radius of the host rare earth. Hence a comparison of the $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ system can be made with the Pr substituted La:123 system only. As seen from inset of Fig. 2, the critical Pr concentration (x_{cr}) for destroying superconductivity is 0.70 in the $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ system, while the same is nearly 0.30 for the $\text{La}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ system. This shows that Pr is less effective in destroying the superconductivity.

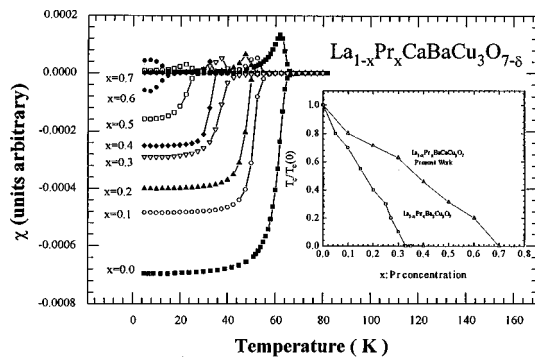


FIG. 2. ac susceptibility (both real and imaginary parts) vs temperature plots for $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ system with various x values, the inset shows the T_c vs x behavior for presently studied and reported (Ref. 21) $\text{La}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ systems.

tivity of $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ than that of $\text{La}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$.

The susceptibility (χ) of both $x=0.70$ and 1.0 samples showed deviations from the standard Curie–Weiss behavior at 4 and 8 K, respectively. Heat capacity measurements²² also show humps at these temperatures. These results indicate the possibility of magnetic ordering of Pr moments at these temperatures in the two compounds. Incidentally, similar deviation in dc magnetic susceptibility measurements and a broad hump in C_p occurs at 17 K for the $\text{PrBa}_2\text{Cu}_3\text{O}_7$ compound (see, for instance, Ref. 5). Interestingly, while the x_{cr} is higher, the T_N of Pr is lower for the presently studied system than for $\text{La}_{1-x}\text{Pr}_x$:123. The lower T_N of Pr in the $\text{La}_{1-x}\text{Pr}_x\text{BaCaCu}_3\text{O}_7$ system, perhaps explains the less deleterious effect of the Pr on superconductivity.

The high T_N of Pr in Pr:123 type compounds is presumed to arise from the strong hybridization of Pr 4*f* orbital with the neighboring Cu–O conduction band.⁵ Decreased oxygen content in Pr:123 compounds, decreases the number of charge carriers in the Cu–O conduction band and increases the Pr to Cu–O distance, which results in a decreased T_N . For example, a T_N of 12 K is reported for $\text{PrBa}_2\text{Cu}_3\text{O}_{6.4}$.²⁷ This shows that the small decrease of oxygen content in our sample of composition $\text{PrBaCaCu}_3\text{O}_{6.86}$ cannot explain solely the lowering of T_N to 8 K. Another possible and more viable reason for the decreased T_N may be the distribution of Pr at both the usual Pr site (sandwiched between two Cu–O planes) and the Ba site. This may result in a lower T_N and a less destructive effect of Pr on superconductivity in the present system.²⁸

In conclusion our study indicates that superconductivity can be induced in $\text{RE}_{1-x}\text{Pr}_x$:123 compounds for higher x values by separating the Pr from Cu–O conduction band. In this way one can decrease the magnetic interaction of Pr 4*f* with the Cu–O conduction band and induce superconductivity in Pr:123 type compounds.

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