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Citation: *J. Appl. Phys.* **80**, 6884 (1996); doi: 10.1063/1.363758

View online: <http://dx.doi.org/10.1063/1.363758>

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# Oxidation state and superconducting properties of $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$

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(Received 8 April 1996; accepted for publication 28 August 1996)

Superconductivity exists in orthorhombic  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$  up to a critical concentration ( $x_{cr}$ ) of 0.65. A progressive decrease in  $T_c$  occurs as  $x$  increases from 0 to 0.65. A further increase in  $x$  leads to a tetragonal transformation and as a consequence the  $T_c$  vanishes; however, the orthorhombicity of these Sr-based compounds is much lower than that observed for the Ba analog,  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  and, hence, the  $T_c$ . On the one hand, crystal chemistry correlations indicate that the Pr ion is in trivalent state while on the other hand, the stabilizing cation, viz., Re, is in hexavalent state which accounts for the excess oxygen ( $>7.0$ ) in the system. The high  $x_{cr}$  value of the Sr series compared to the Ba series ( $x_{cr}=0.55$ ) is attributed to the much reduced orbital overlap of the trivalent Pr( $4f$ ) state with the Cu( $3d_{x^2-y^2}$ )-O( $2p$ ) conduction band, via hole localization and/or pair breaking, and is not due to the much discussed hole filling by tetravalent Pr. © 1996 American Institute of Physics. [S0021-8979(96)05823-9]

## INTRODUCTION

The superconducting  $YSr_2Cu_3O_z$  (YSCO), analogous to the widely studied  $YBa_2Cu_3O_{7-\delta}$  (YBCO), can only be stabilized<sup>1</sup> under high pressure (7 kPa) at 1350 °C. On the one hand, the solubility limit of Sr in  $YBa_{2-x}Sr_xCu_3O_{7-\delta}$  is about 60% and  $T_c$  decreases with increase of Sr content.<sup>2-4</sup> On the other hand, the partial substitution of Cu by  $d$ -block elements has proven to be an effective route for synthesizing such metastable YSCO phases under normal preparative conditions.<sup>5-9</sup> While the increase of Ln (=Pr) concentration in  $Y_{1-x}Ln_xBa_2Cu_3O_{7-\delta}$  suppresses the superconductivity, and at  $x>0.55$  superconductivity vanishes, the other lanthanides have practically no influence on the superconductivity and the  $T_c$  is highly insensitive.<sup>10</sup> This singular nature of Pr attracted a great deal of research and inspired a large amount of work in the  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  (YPrBCO) system.<sup>11-14</sup> Although a large number of articles have appeared on the YPrBCO system, only a few reports are available on the  $Y_{1-x}Pr_xSr_2Cu_{3-y}M_yO_{7+\delta}$  series.<sup>15-20</sup> In view of the importance and the interest on the understanding of the  $T_c$  depression mechanism, in particular the detrimental effect of Pr on  $T_c$ , we have undertaken the present study. Moreover, this is also an attempt to stabilize these metastable Sr-based 123 phases by Re, viz.,  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$  (YPrSCO).

## EXPERIMENT

Nominal compositions of  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$  ( $0\leq x\leq 1.0$ ) were synthesized by a conventional solid-state method from stoichiometric mixtures of high-purity

(99.99%)  $Y_2O_3$ ,  $Pr_6O_{11}$ ,  $SrCO_3$ ,  $CuO$ , and  $ReO_3$ . The powder mixture was well ground, calcined at 1000 °C for 24 h followed by sintering at 1050 °C for 5 h with a final annealing at 500 °C in flowing oxygen for 24 h. Further details can be seen elsewhere.<sup>21,22</sup> The samples were systematically characterised by powder x-ray diffraction (XRD;  $Cu K\alpha$ ; JEOL JDX-8030) and energy-dispersive x-ray (EDX; KeveX-8000 microanalyzer) analysis. All the reflections were indexed on the basis of orthorhombic symmetry ( $P/mmm$ , Y-123 type), the tetragonal phases are indexed by  $P4/mmm$ , and the unit-cell parameters were derived using the least-squares-fit method. The oxygen content in the samples was found to be  $\geq 7.3$  from our neutron-diffraction studies.<sup>23</sup> Superconducting measurements were made both by dc electrical resistivity (four probe) and ac magnetic susceptibility (Sumitomo superconducting properties measurement system) methods. A superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc.) was used to get the dc magnetic susceptibility data in a field of 10 Oe. Table I summarizes the cell parameters, superconducting transition temperatures of various YPrSCO samples. X-ray photoelectron spectroscopy (XPS) data were recorded in VG Scientific ESCALAB Mark-II spectrometer using monochromatized  $Mg K\alpha$  radiation (1253.6 eV) with a base pressure of  $<10^{-9}$  mbar. The surface was cleaned *in situ* prior to the analysis by scrapping. The binding energy values are given relative to C (1s) core level at 284.5 eV.

## RESULTS AND DISCUSSION

The powder XRD patterns of YPrSCO are presented in Fig. 1. As can be seen from the figure, a single phase composition exists up to  $x=0.5$  and beyond this impurities start to appear. More important, with  $x>0.65$  the structure changes from orthorhombic to tetragonal symmetry. For example, the characteristic splitting of (020) and (200), (213)

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TABLE I. Structure and superconductivity data of  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$ 

Pr content $x$	Lattice constants				$e = (b-a)/(b+a)$ ( $\times 10^{-3}$ )	$T_{c(\text{on})}$ (K)	$T_{c(\text{zero})}$ (K)
	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )			
0.00	3.821 (8)	3.849 (9)	11.521 (4)	169.4 (5)	3.66	47.0	42.0
0.25	3.826 (5)	3.852 (9)	11.528 (2)	169.9 (3)	3.43	39.0	32.0
0.50	3.834 (4)	3.860 (4)	11.549 (7)	170.5 (4)	3.37	30.0	18.0
0.60	3.838 (8)	3.863 (5)	11.557 (6)	171.3 (4)	3.14	23.0	11.0
0.65	3.839 (7)	3.862 (7)	11.559 (8)	171.4 (5)	2.98	21.0	...
0.75	3.852 (1)	...	11.565 (5)	171.6 (4)	...	...	...
1.00	3.859 (1)	...	11.570 (4)	172.3 (3)	...	...	...

and (123) lines reduces and vanishes completely. Figure 2 shows the behavior of the lattice constants as a function of  $x$ . The cell parameters of the orthorhombic phase increases linearly up to  $x=0.65$  and above this  $a$  and  $c$  increase almost linearly but  $b$  decreases sharply, converging into the  $a$  of the

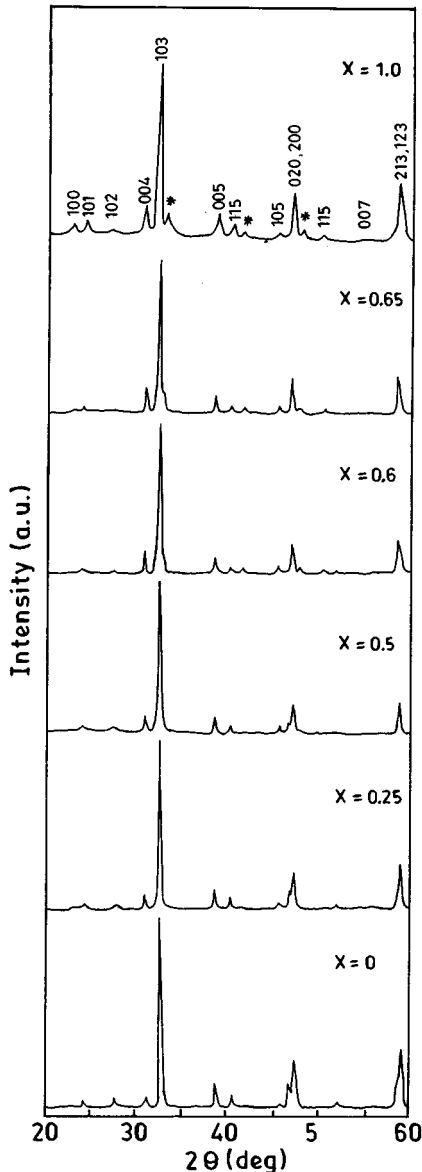


FIG. 1. Powder XRD patterns of  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$ . The impurity phase is marked by an asterix.

tetragonal phase; however, an overall increase in the cell volume can be observed (Table I). This change is consistent and scales with the ionic radii (eight fold coordination) of the elements ( $Pr^{3+}=1.126$  Å;  $Y^{3+}=1.019$  Å).<sup>24</sup> A similar trend is noticed for<sup>14,25</sup> YPrBCO ( $0 \leq x \leq 1.0$ ) indicating that the Pr ion is in the trivalent state rather than tetravalent. On the other hand, from the structural point of view, had Pr been in tetravalent state there should have been a trend of decreasing unit-cell volume (ionic radius:  $Pr^{4+}=0.96$  Å).<sup>24</sup> It is also to be noted here that as the Pr concentration increases both the  $T_c$  and the orthorhombicity,  $e = (b-a)/(b+a)$ , decrease up to  $x=0.65$  (Fig. 3). Interestingly, the magnitude of  $e$  is considerably smaller compared to YPrBCO,<sup>14</sup> which may account for the lower  $T_c$  than the YPrBCO. Two other compositions, viz.,  $YSr_2Cu_{2.8}Re_{0.2}O_{7+\delta}$  and  $PrSr_2Cu_{2.8}Re_{0.2}O_{7+\delta}$ , were also prepared and characterized. The former crystallizes in orthorhombic structure [ $a=3.825(7)$  Å;  $b=3.851(6)$  Å, and  $c=11.524(5)$  Å] with a  $T_{c(\text{on})}$  45 K and  $T_{c(\text{zero})}$  41 K; while the latter adopts a tetragonal symmetry [ $a=3.861(2)$  Å and  $c=11.572(4)$  Å] and exhibits a semiconducting behavior down to 10 K.

The temperature dependence resistivity plots for YPrSCO are displayed in Fig. 4. For  $x > 0.65$ , the samples show

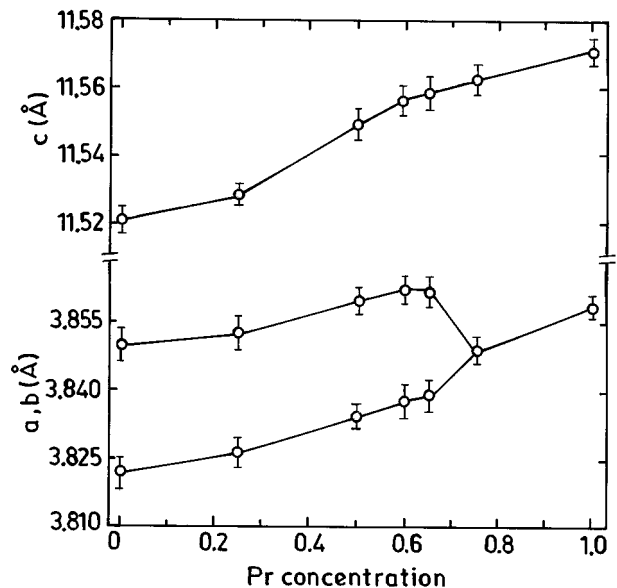


FIG. 2. Unit-cell parameters of  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$

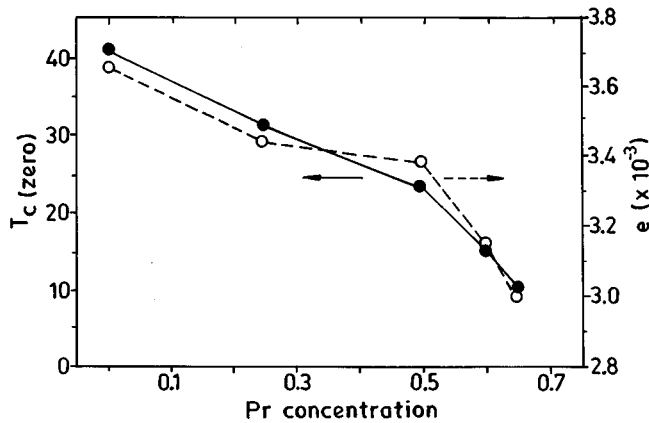


FIG. 3. Superconducting transition temperature and orthorhombicity of  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$

a typical semiconductive temperature dependence and at low temperatures it becomes an antiferromagnetic insulator, while all the samples for  $x \leq 0.65$  are metallic at high temperatures and showing superconducting transition at low temperatures. A similar trend in the  $T_c$  values was also noticed from the ac susceptibility measurements. The  $T_c$  steadily decreases and the transition width increases moderately with increasing  $x$  and vanishes at  $x > 0.65$ . For  $x=1$  it retains semiconductivity down to 10 K, like  $PrBa_2Cu_3O_{7-\delta}$ ; however, the room-temperature resistivity of the former is smaller than the latter by over three orders of magnitude. Although the transition is not complete for  $x=0.65$ , due to a low superconducting volume fraction, the SQUID measurements show a weak transition (Fig. 5). As can be seen from the figure, the superconducting volume fraction increases with decreasing Pr content in the samples. A remarkable feature of the YPrSCO system is that  $T_c$  can be preserved up to a concentration of  $x=0.65$  compared to  $x=0.55$  for YPrBCO system. The high  $x_{cr}$  value in YPrSCO could be due to a

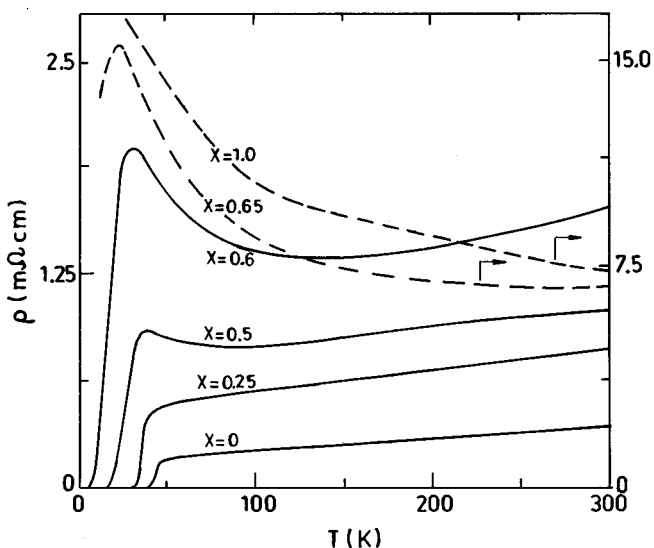


FIG. 4. Temperature-dependent resistivity of  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$

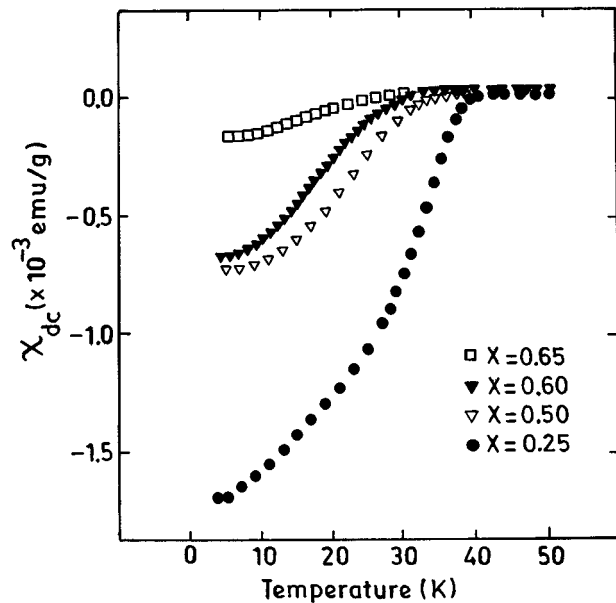


FIG. 5. Temperature dependence of field-cooled dc susceptibility of  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$

much reduced overlap of the  $Pr(4f)$  orbital with the  $CuO_2$  conduction band,  $Cu(3d_{x^2-y^2})-O(2p)$ , which may be attributed to the lesser buckling of  $Cu(2)-O$  bond. It is well supported by our preliminary neutron-diffraction study<sup>23</sup> that the observed  $Cu-O$  bond distances in a Sr-based system [ $Cu(2)-O(2)=1.918 \text{ \AA}$  and  $Cu(2)-O(4)=2.206 \text{ \AA}$ ] is relatively much shorter than the Ba-based [ $Cu(2)-O(2)=1.958 \text{ \AA}$  and  $Cu(2)-O(4)=2.306 \text{ \AA}$ ] 123 phases.<sup>26</sup> The large reduction in bond lengths can cause less buckling of  $Cu-O$  bonds and makes the  $CuO_2$  conduction plane more planar and, hence, the reduction in the orbital overlaps.

Figure 6 depicts the  $Re(4f)$  photoelectron spectra of YPrSCO. The  $Re$  binding energies, for all the samples, are centered around 45.1 eV corresponding to the hexavalent (6+) state.<sup>27-29</sup> This is in excellent agreement with the excess oxygen ( $>7.0$ ), as deduced from neutron-diffraction studies;<sup>23</sup> however, the increase of Pr concentration in the phase does alter the spectra significantly. That is, a broadening is actually taking place at higher Pr content ( $x \geq 0.65$ ). Deconvolution of spectra indicates the presence of both hexavalent and heptavalent (7+)  $Re$ , and that the latter appears at 46.5 eV.<sup>27-29</sup> This is further supported by the  $O(1s)$  levels (the spectra are not given here due to the complication involved in resolving the various species) which show an additional feature characteristic of heptavalent  $Re$  ( $\sim 535.6 \text{ eV}$ ).<sup>29</sup> Such species are also noticed with the increase in  $Re$  concentration, viz,  $PrSr_2Cu_{2.8}Re_{0.2}O_{7+\delta}$  (see Fig. 6). Since  $Re_2O_7$  is volatile, it is likely that the interaction of  $Re$  with the constituent oxides may well be responsible for the formation of heptavalent  $Re$  phases,<sup>28,29</sup> such as  $Pr(ReO_4)_3$  and/or  $Sr(ReO_4)_2$ . In the case of  $Pr(3d)$  core-level results, the  $3d_{5/2}$  region is broader due to a direct overlap of  $Cu(2p_{3/2})$  level and, hence, it is difficult to analyze the data; however, it can be derived that  $Pr$  is in trivalent state but the result is approximate. At this point it is worth mentioning

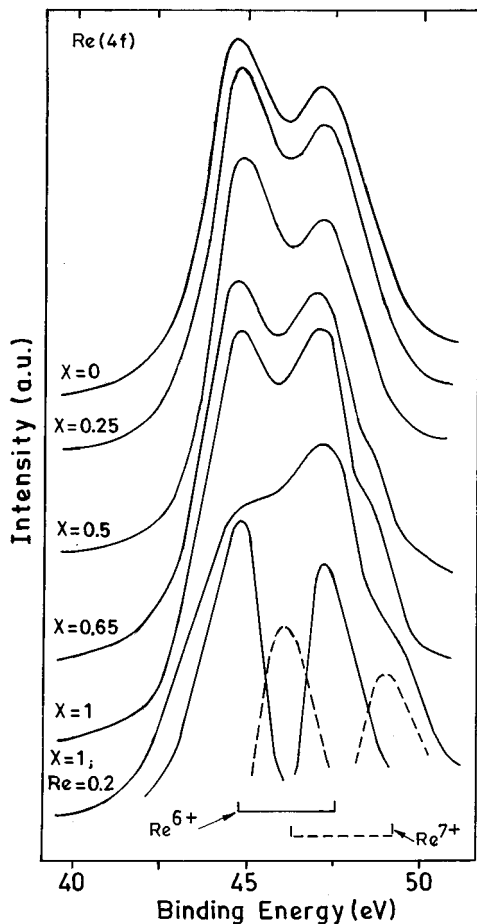


FIG. 6. XPS core-level of  $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$

that one of the lanthanides, viz, Tb like Pr, is known to exhibit ambivalent character ( $Tb^{3+}$  and  $Tb^{4+}$ ),<sup>30</sup> but in superconducting cuprates it is reported to be stabilized in trivalent state.<sup>22,31-33</sup> This is substantiated by the fact that the reduction potential of Tb ( $Tb^{4+} + e^- \rightarrow Tb^{3+}$ ;  $E^0 = 3.1$  V) is close to that of Pr ( $Pr^{4+} + e^- \rightarrow Pr^{3+}$ ;  $E^0 = 3.2$  V).<sup>30</sup> On this basis it may be argued that Pr would also be in trivalent state in YPrSCO/YPrBCO. These findings are well supported by the diffraction results wherein an increase in the lattice parameter which is in accordance with the structural correlations. Hence, it may be concluded that the depression of  $T_c$  by Pr, in general, can be of trivalent origin in YPrBCO/YPrSCO systems.

#### ACKNOWLEDGMENT

One of the authors M.M. is grateful to University Grants Commission for providing a senior research fellowship.

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