

CHANGES IN THE Pr-INDUCED  $T_C$  DEPRESSION OF 123 COMPOUNDS BY CHEMICAL PRESSURE

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We present structural data refined from X-ray spectra for  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  ( $R=Er, Gd, Eu, Sm, Nd$ ) systems with  $x=0, 0.1$ , and  $0.4$ . The evolution of  $T_C$  with the ionic radius of the rare earth for different values of  $x$  can be related to the Cu2-O4 distance. The effect of chemical pressure on  $T_C$  in  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  systems is opposite to that of hydrostatic pressure on the  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  system.

$PrBa_2Cu_3O_{7-\delta}$  is the only member of the series of  $RBa_2Cu_3O_{7-\delta}$  ( $R=rare\ earth$ ) compounds that is non-metallic and non-superconducting. The depression of the superconducting critical temperature,  $T_C$ , in  $RBa_2Cu_3O_{7-\delta}$  compounds by Pr substitution is a puzzling aspect of the physics of these high  $T_C$  oxides. There is a controversy about the mechanism for depression of superconductivity. Hole filling, hole trapping, magnetic pair breaking, or a combination of these effects have been suggested as possible mechanisms. Evidence of hybridization between Pr 4f electrons and those in the  $CuO_2$  valence band has been found in several experiments.<sup>1</sup>

The depression of  $T_C$  by Pr substitution in the R site depends on the particular R ion. The larger the ionic radius of R, the steeper is the  $T_C$  vs  $x$  curve for  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  and, hence, the smaller the critical concentration  $x_{crit}$  for the destruction of superconductivity. The aim of this paper is to point out the subtle structural differences that may be related to this characteristic of the depression of  $T_C$  in  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  systems and also to discuss an apparent contradiction concerning the effect on  $T_C$  of chemical pressure in  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  and hydrostatic pressure in  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ .

Samples of  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  with  $R=Er, Y, Gd, Eu, Sm, Nd$  and  $x=0, 0.1, 0.4$  were prepared by solid state reaction.<sup>1</sup> The final sintering temperatures in flowing oxygen were varied from 950°C to 970°C for

$R=Er$  to  $Nd$ . The  $R=La$  sample was sintered at the higher temperature (970°C) in a  $N_2$  atmosphere, followed by annealing in oxygen. Iodometric titration on representative samples yielded an oxygen content of  $\delta=0.02-0.07$ . The electrical resistivity was measured using a standard four point ac method (16 Hz). The dc magnetization of the  $x=0.4$  samples was measured with a SQUID magnetometer in the temperature range 5K to 80K. X-ray diffraction measurements were performed using a rotating anode Rigaku diffractometer. Intensity data were collected in 0.018° steps for 9 sec in a  $2\theta$  range of 20° to 90°. The structural parameters were obtained with the Rietveld refinement program RIETAN.<sup>2</sup>

Figure 1 shows the superconducting transition temperature obtained from electrical resistivity measurements as a function of the ionic radius of  $R^{3+}$  in  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  systems. The squares in the figure correspond to a 50% drop in resistivity, relative to the extrapolated normal state value, while the transition widths were calculated as the difference between the temperatures of the 10% and 90% resistivity drops. While  $T_C$  increases with the ionic radius of  $R^{3+}$  for  $RBa_2Cu_3O_{7-\delta}$  systems,<sup>3</sup> it decreases for Pr concentrations of  $x=0.1$  and  $x=0.4$ , with the decrease being much more dramatic for  $x=0.4$ . Zero field cooling (ZFC) magnetization data taken in a magnetic field of 10 Oe for the superconducting samples of the series  $R_{0.6}Pr_{0.4}Ba_2Cu_3O_{7-\delta}$

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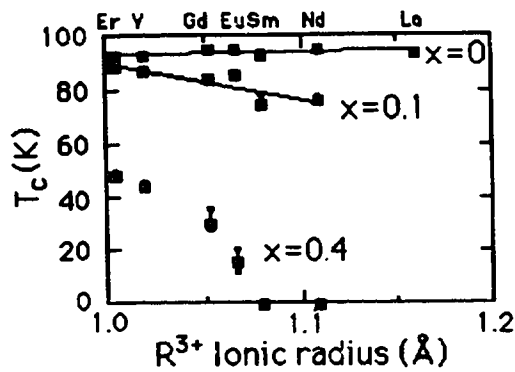


FIGURE 1

Superconducting critical temperature for  $R_{1-x}Pr_xBa_2Cu_3O_{7.6}$  systems as a function of  $R^{3+}$  ionic radius.

showed that the Meissner fraction decreases from 40% to 0.5% in going from  $R=Er$  to  $Eu$ .

The distance between the Cu ion in the  $CuO_2$  plane and the apical oxygen, Cu2-O4, has been shown to be relevant for the charge transfer mechanism from the chains to the planes. In Fig.2 we show the trend of these distances for the  $x=0, 0.1$ , and  $x=0.4$  samples. In spite of large errors in the determination of this distance, a different trend is observed for the samples with and without Pr. A decrease of the distance Cu2-O4 with increasing ionic radius of  $R^{3+}$  for the  $x=0$  samples may indicate more charge transfer to the  $CuO_2$  planes, and this could be related to the increase in  $T_c$ .<sup>3</sup> The opposite behavior is observed for the  $x=0.1$  and  $0.4$  samples where  $T_c$  decreases in going from  $Er$  to  $Nd$ .

A compression of the Cu2-O4 distance with hydrostatic pressure is known to occur in  $YBa_2Cu_3O_{7.6}$ <sup>4</sup> and expected to take place in the  $Y_{1-x}Pr_xBa_2Cu_3O_{7.6}$  system. For  $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_{7.6}$ ,  $T_c$  decreases with hydrostatic pressure<sup>5</sup> and also decreases with negative chemical pressure applied on the Pr ions, i.e.,  $T_c$  decreases in going from  $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_{7.6}$  to  $Eu_{0.6}Pr_{0.4}Ba_2Cu_3O_{7.6}$  (Fig.1). This suggests that the Cu2-O4 distance, which has the same trend for hydrostatic and chemical pressure, is not the only relevant parameter for the samples with  $x=0.4$ . It is reasonable to conclude that the solution for this apparent contradiction is related to the distances

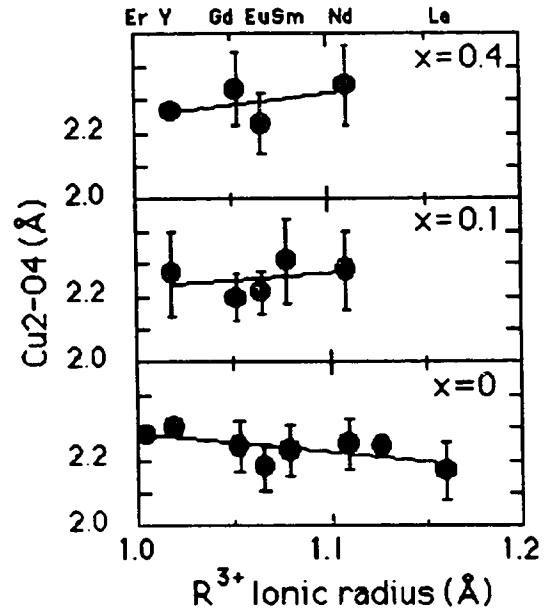


FIGURE 2

Cu2-O4 distances in  $R_{1-x}Pr_xBa_2Cu_3O_{7.6}$  systems as a function of  $R^{3+}$  ionic radius. The data without the error bars are calculated from neutron diffraction data (Ref.6).

between the Pr ions and the ions in the  $CuO_2$  planes. We have studied the Pr-Cu2, Pr-O2 and Pr-O3 distances for  $x=0, 0.1$ , and  $0.4$ . In all cases there is a monotonic increase with the R ionic radius, the Pr-O3 distance showing a steeper slope in the case  $x \neq 0$ .

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