

Fig. 1 Temperature dependence of the resistance of $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample (curve *b*) and including a silver contact (dashed curve *a*). Right inset: the four-point measurement configurations *a* and *b*. Left inset: vertical scale expanded 100 times. The contact resistance has a room-temperature value of $2.4 \text{ m}\Omega \text{ mm}^{-2}$ and drops to less than $10 \mu\Omega \text{ mm}^{-2}$ at 77 K. Sample size: $1 \times 1 \times 20 \text{ mm}^3$; current-contact area: 1 mm^2 ; $\rho(300 \text{ K}) = 1.2 \text{ m}\Omega \text{ cm}$; density = 5.4 g cm^{-3} ; $I = 6 \text{ mA}$. Sample densities in all experiments ranged from 3.5 to 5.4 g cm^{-3} .

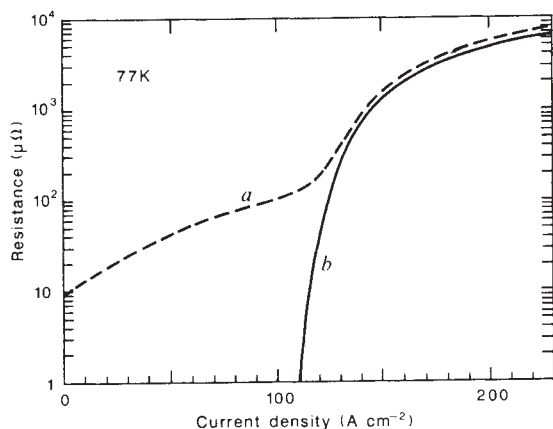


Fig. 2 The resistance of the sample alone (curve *b*) and including a silver contact (dashed curve *a*) as a function of current density in sample and contact at 77 K. Meaning of *a* and *b* as in Fig. 1. Below the critical current the contact resistance essentially saturates at the low value of $\sim 10 \mu\Omega \text{ mm}^{-2}$.

Several groups discussed different types of contacts on copper-oxide superconductors including silver-paint and silver-epoxy⁶, platinum leads attached with gold-paste and pressed indium contacts⁷, and ultrasonic soldering⁸. We have tested several of these contacting techniques but the contact resistance is always $\sim 1 \Omega \text{ mm}^{-2}$. On the other hand, whenever a silver coating has been baked onto the ceramic at 900°C , the contact resistance, and therefore the contact heating, were systematically reduced by several orders of magnitude. Indeed, through some of the contacts we passed more than $2,000 \text{ A cm}^{-2}$ (77 K) without burn-out. Scanning electron micrographs show that at the highest current densities it is the ceramic Y-Ba-Cu-O side of the contact area that burns out, rather than the mixed interface material of the contact itself.

Finally, we note that once the described silver contact has been prepared one can easily solder copper wires onto the contact area. But repeated soldering at 350°C increases the current dependence of the contact resistance, so that these soldering temperatures are better avoided.

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Incorporation of Pr in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: electronic effects on superconductivity

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Considerable excitement has been generated by the report of superconductivity above 90 K in a multi-phase Y-Ba-Cu oxide¹. The superconducting phase was subsequently identified as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ^{2,3}. The complete replacement of Y by the trivalent rare-earths La-Lu, with the exception of Ce, Pr and Tb, yields a superconducting phase with a critical temperature (T_c) almost identical to that reported for the yttrium compound⁴⁻⁷. This is somewhat surprising as most of these ions carry significant magnetic moments, the presence of which rapidly decreases T_c in ordinary superconductors. The three exceptions noted, Ce, Pr and Tb, are the rare-earth ions which have a stable tetravalent state. Here we present the results of a study of the structure and transport properties of the series of compounds $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($x = 0-1.0$), in which we observe a monotonic decrease in T_c and eventually a metal-insulator transition with increasing Pr concentration. To date, this is the only rare-earth ion which has been found substantially to alter T_c upon partial substitution for Y.

Samples were prepared by grinding and mixing Y_2O_3 , Pr_6O_{11} , BaCO_3 and CuO in the correct metal stoichiometries, and firing at 975°C , followed by annealing at 650°C and slow cooling in flowing oxygen. The samples were then reground and refired to improve homogeneity. Powder diffraction data were obtained using GE-XRD5 and SCINTAG-PADV X-ray diffractometers and the special-environment powder diffractometer (SEPD) at the intense pulsed neutron source (IPNS) at Argonne National Laboratory. Resistivities were measured in a closed cycle refrigerator from 300 to 8.5 K using Si-diode thermometry by the standard four-probe technique.

Diffraction measurements show this series of compounds to be predominantly a perovskite phase which is tripled along the *c*-direction. The majority phase in all samples can be roughly indexed according to the well-known orthorhombic *Pmmm* $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure^{8,9}. Although the structure can be indexed as orthorhombic through the full concentration range, the *a*- and *b*-axes converge with increasing *x*, indicating a tendency toward a tetragonal cell. The volume increases monotonically with Pr concentration consistent with solid solution formation. Preliminary Rietveld refinement of high-resolution neutron data indicates the presence of secondary phases (<5% of BaCuO_2 and CuO) together with a possible subtle structure change which complicates the analysis of oxygen site

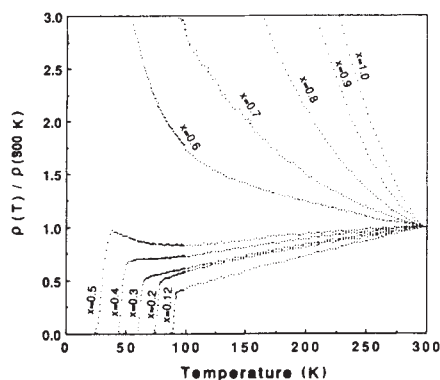


Fig. 1 Relative resistivity, ρ (normalized to room temperature) as a function of temperature for selected samples of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. $x = 0.1, x = 0.2, x = 0.3, x = 0.4, x = 0.5, x = 0.6, x = 0.7, x = 0.8, x = 0.9$ and $x = 1.0$.

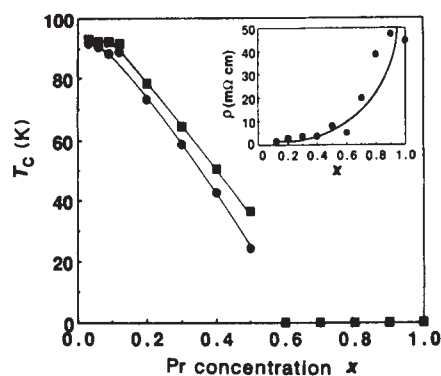


Fig. 2 Superconducting transition as a function of Pr concentration, x . (■) Indicates the onset in the resistivity while (●) shows the temperature at which the resistivity becomes zero. The inset shows the room temperature resistance as a function of Pr concentration.

occupancy. For this reason we have not included an analysis of the oxygen stoichiometry and its consequences.

Figure 1 shows relative resistivities as a function of temperature for selected Pr concentrations. The normal state resistivity exhibits a systematic metal (positive temperature coefficient of resistivity TCR) to non-metal (negative TCR) transition as a function of x for all samples. The superconducting transition temperature decreases monotonically, with samples above $x \approx 0.5$ becoming non-superconducting (Fig. 2). The absolute room-temperature resistance (inset Fig. 2) increases dramatically as the samples become non-metallic.

Changes in resistivity could occur if changes in grain sizes, special geometric arrangements of other phases, or general changes in microstructure are present. But while not studied as a function of x , the microstructure is not expected to vary in a fashion which could account for the observed systematic behaviour. Moreover, the fraction of minority phase present is always far from the three-dimensional percolation threshold.

The metal-insulator transition at $x \approx 0.5$ occurs at a much higher resistivity than commonly observed in most disordered systems¹⁰. This indicates that superconducting metal oxides behave in some sense as ordinary metals with a low carrier density, in contrast to a number of disordered two- and three-dimensional metals which show a universal metal-non-metal transition as a function of absolute resistivity (Mooij correlation)¹¹ for resistivities orders of magnitude lower ($\approx 150 \mu\Omega \text{ cm}$). Ordinarily the metal-insulator transition has been thought to occur close to the Ioffe-Reggel limit¹², where the electronic mean free path becomes comparable to the interatomic spacing. But in these materials, one might argue that the metal-insulator transition arises from the very low carrier density (assuming a constant mean free path), as the transition occurs when the resistivity is several orders of magnitude higher than the Ioffe-Reggel limit. By scaling the resistivity at which the metal-insulator transition occurs with that of simple metals one obtains a carrier density of 10^{20} – 10^{21} electrons cm^{-3} . The same kind of arguments about the resistivity have been invoked to claim low carrier density in $LaNi_{1-x}M_xO_3$ ($M = Cr, Mn, Fe$ and Co) perovskite systems¹³.

Similar trends in T_c and resistivity were observed on quenched samples of $YBa_2Cu_3O_{7-\delta}$ ^{14,15}, where the decrease in the transition temperature and resistance ratio along with an increase in the resistivity correlates with a decrease in oxygen stoichiometry. The lower oxygen content results in a decrease in the average oxidation state of Cu, with Cu^{3+} reduced to Cu^{2+} . As the behaviour of the resistivity and critical temperature of Pr-doped samples are much the same as that observed in quenched

samples, we postulate that doping with Pr is equivalent to decreasing the oxygen stoichiometry in undoped samples. With constant oxygen content the reduction of the formal charge state of Cu from Cu^{3+} to Cu^{2+} can be accounted for by incorporation of Pr in its tetravalent state. This hypothesis is supported by the increase in the unit cell volume with increasing Pr concentration, as the reduction of Cu results in an increase in the average Cu–O bond distance as electrons are added.

It was previously found that $YBa_2Cu_3O_{7-\delta}$ undergoes a phase change from orthorhombic (with ordered Cu–O chains) to tetragonal (without the chains) when $\delta = 0.5$, as all the copper in the sample is reduced to Cu^{2+} (ref. 16). Equivalently, in the Pr samples $x = 0.6$ corresponds to the absence of Cu^{3+} (assuming $\delta = 0.2$), as each Pr^{4+} adds one electron to the structure. If the structural phase transition in the undoped samples is electronically driven, this might explain the possible subtle structural changes observed. Neutron diffraction experiments at high temperatures¹⁶ and on quenched samples (J. D. Jorgensen, unpublished data) show that the reduction in T_c , the trend toward a tetragonal structure¹⁴ and the decrease in oxygen stoichiometry are accompanied by a disordering of the sub-lattice containing the Cu–O chains. We therefore expect a similar disordering with increasing Pr concentration. It appears that the formal charge state of Cu and the oxygen vacancy ordering are intimately linked and therefore they both play a key role in the underlying superconducting mechanism in compounds which are isostructural with $YBa_2Cu_3O_{7-\delta}$.

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