

PRASEODYMIUM 1-2-3:
INTRINSIC STRUCTURE, OXYGEN CONCENTRATION EFFECTS,
AND SOLID SOLUTIONS, WITH YTTRIUM, CALCIUM AND ZINC

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$\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ is probably the most enigmatic member of the 1-2-3 family of compounds. It is the only non-superconducting example in this lanthanide series of isomorphous structures. We have studied its structural details, and dependence of its physical properties on oxygen concentration and solid solutions with Y, Ca and Zn, with the objective of understanding its peculiar behavior and the role Pr plays in suppressing superconductivity.

1. Introduction

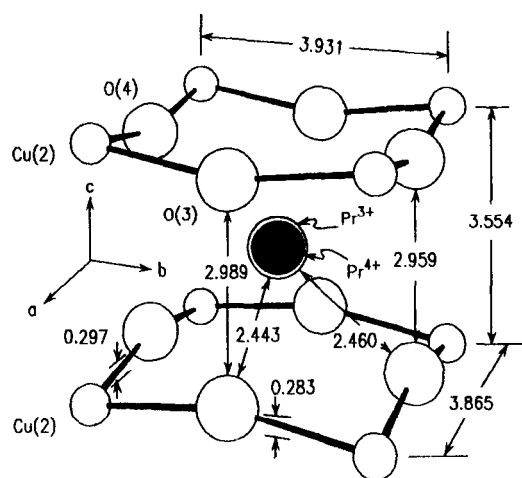
Quite a large number of studies of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ and its solid solutions with other elements now exist in the literature. The parent compound itself is insulating even though it is isomorphous to the other lanthanide 1-2-3 compounds all of which exhibit superconductivity. This bizarre behavior immediately drew attention to the possibility that the ionic state of Pr might be $4+$, which occurs in some of its oxides. If Pr were tetravalent, this would provide a convenient explanation for its lack of superconductivity, inasmuch as no free carriers would exist to form the metallic and superconducting states. However attractive, this picture is *not* without difficulty. There is substantial evidence from core level spectroscopy, Raman, and unit cell dimensions that indicate Pr in 1-2-3 to be far more trivalent than tetravalent. Space does not permit the discussion of this issue in depth here (*vide* Ref. 1). In this paper we will present a brief report on oxygen content effects in Pr 1-2-3 and how Pr interacts with other cations in determining carrier concentration and critical temperature properties in 1-2-3 compounds.

2. Sample Synthesis

All compounds reported herein were synthesized using standard solid state reaction techniques. The principal departure from usual methods was the use of multiple regrindings and lengthy reaction times, sometimes three weeks, to assure single phase product in the face of very slow Pr diffusion rates. To the limit detectable by powder x-ray diffraction, our samples were single phase. Oxygen content analysis was performed by iodometric techniques. Unique values of the excess positive charge per CuO unit could not be obtained because of the unknown mixed valent character of Pr.

3. Structural Details

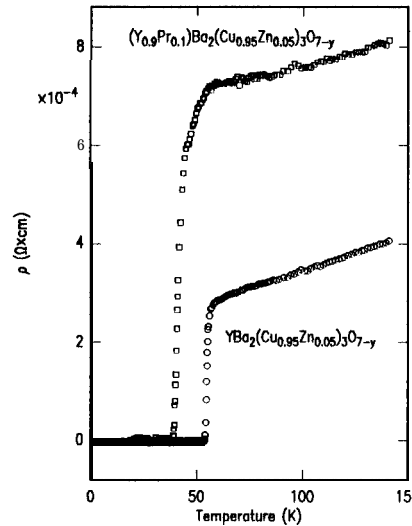
X-ray and neutron powder diffraction structural refinement methods were used to determine the elemental atomic positions in the Pr 1-2-3 unit cell. The figure below summarizes the resulting interatomic distances found for the central Pr-Cu-O "cage" of this structure. Comparison of these distances with the other Ln 1-2-3 compounds and ionic radii of rare earths and oxygen reveals key insights into the Pr valence state. The inter-CuO planar distance is remarkably consistent with a Pr^{3+} ionic radii and with the trend set by the rest of the trivalent lanthanide series. On the other hand, the Pr-O bond distances are much shorter than that expected for Pr^{3+} , reflecting hybridization of the Pr 4f electronic levels with the surrounding O 2p orbitals, but with the charge $3+$ remaining in the central cage.



4. Oxygen and Cation Effects

The main effects on removing oxygen from $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ are 1) to induce an orthorhombic-tetragonal transition, 2) an increase in resistivity by 10^3 , and 3), no change in the Pr magnetic moment. This last fact, and the low value of the moment, supports a strongly hybridized Pr-O bond in agreement with the above structure data. Thus the paradoxical situation regarding Pr valency is resolved: those experiments which probe properties of the Pr-O bond (e.g., χ_{para}) will indicate Pr^{4+} , while those sensitive to charge contained in the cage (e.g., Raman, XPS) would have Pr trivalent. The appropriate picture for no-T, in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ is then one of Pr mixed valency based on the periodic Anderson model² where holes in the CuO planes become trapped on the time scale of carrier transport.

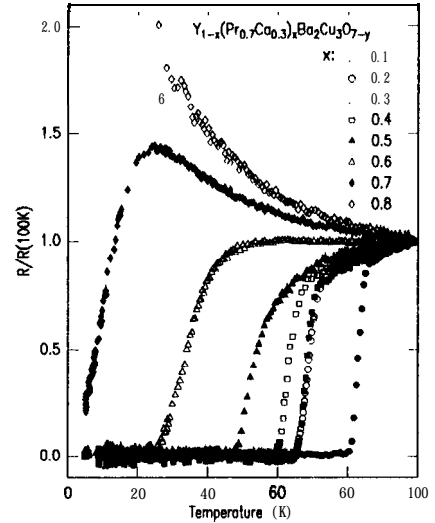
The next figure shows the result of putting small amounts of Pr in $\text{YBa}_2(\text{Cu}_{1-z}\text{Zn}_z)_3\text{O}_{7-y}$.



It has been suggested the reason T_C is depressed in $\text{YBa}_2(\text{Cu}_{1-z}\text{Zn}_z)_3\text{O}_{7-y}$ is due to excessive hole concentration.³ If so, one would expect adding Pr to increase T_C by trapping holes, whereas the opposite is observed.

Our last figure shows the variation in T_C with x in $\text{Y}_{1-x}(\text{Pr}_{0.7}\text{Ca}_{0.3})_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$. Ca is believed to substitute in the Y position⁴ resulting in an increase in the CuO planar hole concentration above the optimum value, thus decreasing T_C as in the Zn doping case.³ For 0.1 Ca per 1-2-3 formula unit, T_C drops to roughly 75 K.⁴ This amount of Ca corresponds to our $x \approx 0.3$ sample which

also contains 0.2 Pr per formula unit. On the assumption these cations are 2+ and 4+, respectively, there results a net removal of 0.1 holes per formula unit in this sample. This is equivalent to an oxygen reduction $7-y = 6.85$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ for which $T_C = 80-90 \text{ K}$.⁵



However, we see a much lower $T_C = 65 \text{ K}$ for sample $x \approx 0.3$, not in accord with the excess hole concentration picture. On the other hand, as can be seen in the above figure, Ca does partially offset the deleterious effect of Pr, allowing superconductivity to persist to Y levels as low as $1-x = 0.3$.

5. Summary

In summary, the structure and oxygen concentration properties of Pr 1-2-3 can be explained by an Anderson lattice model, while the decrease in T_C observed on substituting Pr for Y in Zn and Ca doped Y 1-2-3 casts doubt on present interpretations about the behavior of high- T_C materials containing large amounts of holes. The Mexican authors (MEL-M, DR-J) gratefully acknowledge financial support from Programa Universitario de Superconductores Ceramicos de Alta Temperatura.

6. References

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