Hybridization in $PrBa_2Cu_3O_7$ and $PrBa_2Cu_4O_8$

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Comparative studies of $R\mathrm{Ba_2Cu_3O_7}$ and $R\mathrm{Ba_2Cu_4O_8}$, with $R=(R'_{1-y}\mathrm{Pr}_y)$ and with $R'=$Y, Yb, Nd, or Gd, exclude the possibility that hybridization of Pr's $4f$ states with cuprate-plane oxygen $2p$ states is responsible for the observed degradation of critical temperatures T_c with increasing Pr content y. [S0163-1829(98)07409-8]

$R\mathrm{Ba_2Cu_3O_7}$ (R123-7) materials have been fabricated for $R=$Y, Cm, and all rare earths except Ce, Tb, and Pm. Almost all of these compounds superconduct with critical temperatures $T_c \approx 90$ K.[1] The one noncontroversial exception is Cm123-7, which does not superconduct.[2] The other exception is controversial: Pr123-7 is the insulator of choice for many Josephson-junction technologies, and is widely believed to not superconduct as conventionally grown, although several authors have recently succeeded in synthesizing *superconducting* Pr123-7,[3–11] using sophisticated methods that minimize the number of Pr-on-Ba-site defects ($\mathrm{Pr_{Ba}}$). Since a few of these demonstrations of superconductivity involve only granular superconductivity,[4–6] some skeptical researchers have claimed that, even in the cases of bulk superconductivity,[7–10] the observed superconductivity is *extrinsic* to Pr123-7, namely, some impurity phase that has nearly the same $T_c \approx 90$ K but necessarily with a new superconducting crystal structure.

Currently there appear to be three general viewpoints of why Pr123-7 is different from most R123-7 homologues: (i) Pr123-7 is an *intrinsic nonsuperconductor* and does not superconduct, primarily due to *hybridization* of the large-radius $\mathrm{Pr^{+3}}$ ions's $4f$ electronic state with a $2p$ state of an adjacent oxygen ion in a cuprate plane;[12] (ii) Pr123-7 is an *intrinsic insulator* because of *hole filling*, namely, the Pr ion is in the $\mathrm{Pr^{+4}}$ state;[13] and (iii) Pr123-7, when synthesized with the sophisticated methods, is an *intrinsic superconductor*, whose failure to superconduct is attributable to a defect formed during conventional synthesis, most likely Pr-on-a-Ba-site ($\mathrm{Pr_{Ba}}$), which forms easily because of $\mathrm{Pr^{+3}}$'s large size.[3,7] This paper deals with hybridization, the first of these viewpoints, which has been the most popular reason given for the failure of Pr123-7 to superconduct.

This hybridization depends critically on the $4f$-$2p$ overlap, namely, on the Pr-O bond length and the spatial extent of the $4f$ electron of the $\mathrm{Pr^{+3}}$. To verify that this effect is responsible for the failure of Pr123-7 to superconduct, Kim *et al.*[14] executed an experiment on ≈ 90 K superconducting Nd123-7, based on the fact that $\mathrm{Nd^{+3}}$ has a $4f$ radius (and hence Nd $4f$-oxygen $2p$ overlap) only slightly smaller than $\mathrm{Pr^{+3}}$'s [0.56 Å vs 0.58 Å (Ref. 15)]: Applying pressure, they squeezed Nd123-7 until the Nd-O bond length contracted by an amount comparable with both the difference in the $\mathrm{Pr^{+3}}$ and $\mathrm{Nd^{+3}}$ radii, and the difference in $4f$ radii, ~ 0.02 Å, and *expected the critical temperature for superconductivity to drop, due to increased* $4f$*-2p hybridization*. Surprisingly, T_c *increased* with pressure. This result has never been satisfactorily explained within the context of any cuprate-plane model of superconductivity.[16]

The main concern with the Kim *et al.* experiment is that it was performed on pressurized Nd123-7, which is different from Pr123-7, both in the size of its $4f$ radius and in its energies. The hybridization mixing coefficient M depends on an energy denominator ΔE as well as on a $4f$-$2p$ matrix element V,

$$M=-V/\Delta E,$$

and both V and ΔE are different for Nd and Pr. Not only does V depend strongly on the $4f$-$2p$ overlap (which is different), but also the chemical difference of $\mathrm{Nd^{+3}}$ and $\mathrm{Pr^{+3}}$ is reflected in the energy denominator ΔE, and either difference might play a role in determining whether T_c increases or decreases with pressure. However, the facts that (i) Cm123-7 does not superconduct,[2] and that (ii) Ce destroys superconductivity in both $(\mathrm{Nd}_{1-u}\mathrm{Ce}_u)$123-7 (Ref. 17) and (iii) in $(\mathrm{Y}_{1-u}\mathrm{Ce}_u)$123-7 (Ref. 17) with increasing Ce content u (to the extent that these materials have been formed), suggest that large *rare-earth* or Cm *sizes*, not *chemical differences* are related to the destruction of the superconductivity. To clarify this point, one would like to have an experiment similar to the Kim *et al.* pressure experiment that involves the same rare-earth cation, rather than the different Pr and pressurized Nd cations—and hence eliminates any differences of the mixing coefficients M.

To do this, we compared the effects of various rare-earth dopants R' on R123-7 and on $R\mathrm{Ba_2Cu_4O_8}$ (R124-8) conventionally grown with $R=R'_{1-y}\mathrm{Pr}_y$. Here the difference being exploited is the extra chain layer of the R124-8 compound: R123-7 and R124-8 are virtually identical structurally in the vicinity of the rare-earth ion R and in the adjacent cuprate planes and Ba-O layers, and differ only in that R124-8 has an extra Cu-O chain. Even the critical temperatures for superconductivity (which are believed to be extremely sensitive to differences in structure) are not too different, being ≈90 K for R123-7 and ≈82 K for R124-8.[18] Moreover, the extra Cu-O chain of R124-8 is remote from the rare-earth site, and so we expect that the hybridization of Pr with cuprate-plane oxygen will be virtually the same in $(R'_{1-y}\mathrm{Pr}_y)$123-7 and in $(R'_{1-y}\mathrm{Pr}_y)$124-8. Consequently, for any rare-earth R' that occupies only the rare-earth sites, the suppression of T_c in R123-7 and R124-8 should be the same for $R=R'_{1-y}\mathrm{Pr}_y$, if hybridization is responsible for the suppression and for the failure of Pr123-7 to superconduct:

$$|dT_c/dy|_{123-7}=|dT_c/dy|_{124-8}.$$

If there is any difference in such hybridization and suppression of T_c, the difference in $|dT_c/dy|$ should be slight and $|dT_c/dy|$ should be larger in the material with the smaller bond length between the rare-earth site and the cuprate-plane oxygen. (There is no difference in ΔE, and only a difference in V related to the larger $4f$-$2p$ overlap associated with the shorter bond length.) But the difference in the Pr-O bond lengths in Pr123-7 and Pr124-8 is only about 0.04 Å,[19] quite a small difference, with Pr124-8 having the *shorter* bond. Therefore, if hybridization is responsible for the failure of Pr123-7 and Pr124-8 to superconduct, then a plot of T_c vs y for $(R'_{1-y}\mathrm{Pr}_y)$123-7 and $(R'_{1-y}\mathrm{Pr}_y)$124-8 should produce lines with the same slopes $|dT_c/dy|$, or a slope for $(R'_{1-y}\mathrm{Pr}_y)$124-8 that is only slightly larger than $|dT_c/dy|$ for $(R'_{1-y}\mathrm{Pr}_y)$123-7: the suppression of T_c by hybridization should be the same for the same local crystal geometry, independent of the choice of R'.

Such experiments have been reported by Horii *et al.*[20] for R'=Y, Yb, Nd, and Gd, and by a number of authors for R'=Y, in both the 123-7 and 124-8 materials. Typical results for $Y_{1-y}Pr_yBa_2Cu_3O_7$ (Ref. 21) and $Y_{1-y}Pr_yBa_2Cu_4O_8$ (Ref. 22) are presented in Fig. 1.[23–26]

The predicted similarities of the slopes due to hybridization are not evident in the data (Fig. 1): dT_c/dy for $(R'_{1-y}\mathrm{Pr}_y)$123-7 and $(R'_{1-y}\mathrm{Pr}_y)$124-8 are not nearly the same; and $|dT_c/dy|$ is not slightly larger for the shorter Pr-O bond length of $(R'_{1-y}\mathrm{Pr}_y)$124-8; but $|dT_c/dy|$ for the 123-7 compounds is roughly two times as large as for the 124-8 compounds, for all choices of R' we have examined: R'=Y, Yb, Gd, and Nd.[20] This is completely contrary to what is expected of a hybridization mechanism of T_c suppression.

Independent confirming evidence of the unimportance of hybridization in these Pr-based compounds is provided by measurements[27] that show that the normal-state resistivity is almost independent of pressure in Pr124-8, indicating that the electronic states participating in transport are insensitive to pressure-induced changes in the hybridization.

Based on comparative analyses of the T_c suppression in $(R'_{1-y}\mathrm{Pr}_y)\mathrm{Ba_2Cu_3O_7}$ and in $(R'_{1-y}\mathrm{Pr}_y)\mathrm{Ba_2Cu_4O_8}$, we conclude that *hybridization is not responsible for the failure of conventionally grown* Pr123-7 *and* Pr124-8 *to superconduct*. That leaves hole-filling (disputed by many authors[3,22,28]) and pair breaking by $\mathrm{Pr_{Ba}}$ (which requires that the primary superconducting condensate not lie in the cuprate planes[3]) as the only well-known remaining current explanations of the anomalous behavior of these materials. Future efforts to understand why Pr123-7 and Pr124-8 do not superconduct when synthesized conventionally should focus on proving or disproving one of these two mechanisms, or on developing a new mechanism.

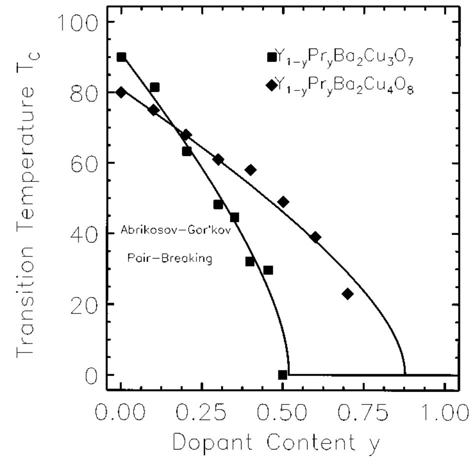

FIG. 1. Onset critical temperatures T_c for $(R'_{1-y}\mathrm{Pr}_y)$123-7 (Ref. 21) and $(R'_{1-y}\mathrm{Pr}_y)$124-8,[22] vs Pr content y, for R'=Y, a small ion that is known to not dissolve on Ba sites. These data are typical of many measurements, which cover quite a range (Refs. 23 and 24). In both cases, we have fit the data to an Abrikosov-Gor'kov pair-breaking curve (Ref. 25), as a matter of convenience, and recognizing its limitations (Ref. 26).

If, as appears to be the case, these materials are both *intrinsic* superconductors when synthesized with the sophisticated techniques, then one must understand how $\mathrm{Pr_{Ba}}$ destroys superconductivity, but $\mathrm{Pr_{Pr}}$ does not—especially if (as many workers believe) the superconducting condensate is in the plane that lies about halfway between the two sites.[3]

Note added in proof. Recent measurements of the effect of pressure on *superconducting* $PrBa_2Cu_3O_7$ show that T_c *increases* with pressure, roughly 2.5 K/GPa, exceeding 105 K at 10 GPa. These data provide some of the strongest evidence confirming the ideas discussed here. [J. Ye, Z. Zou, A. Matsushita, K. Oka, Y. Nishihara, and T. Matsumoto (unpublished)].

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