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Observation of superconductivity in $PrBa_2Cu_3O_7$

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Inhomogeneous superconductivity in $PrBa_2Cu_3O_7$ at $\approx$92 K is observed in surface resistance measurements (at microwave frequencies) and in diamagnetism (Meissner effect) detected by ESR of trace amounts of Cu impurity spins. These observations are interpreted in terms of the oxygen model. [S0163-1829(96)03433-9]

The purported lack of superconductivity in $PrBa_2Cu_3O_7$, in contrast with almost all other (rare-earth)-$Ba_2Cu_3O_7$ compounds, is a perplexing anomaly with a variety of explanations, none of which is generally accepted: direct pair breaking by Abrikosov-Gor'kov exchange scattering,[1,2] magnetic hybridization leading to pair breaking,[3] subtle magnetic interactions,[4] and charge compensation (hole-filling).[5,6] Most of these theories of nonsuperconductivity in $PrBa_2Cu_3O_7$ (i) are *homogeneous*, featuring the same physics in every unit cell, (ii) have rare-earth Pr ions occupying only rare-earth sites, and (iii) assume that the superconductivity originates in the cuprate planes adjacent to the rare-earth sites [Fig. 1 (Refs. 7 and 8)]. These three signatures are susceptible to experimental investigation.

In this paper we report observation of *inhomogeneous* superconductivity with a critical temperature $T_c \approx 92$ K in $PrBa_2Cu_3O_7$, superconductivity that was *predicted* on the basis of the oxygen model[9–11] which locates the origin of superconductivity *in the vicinity of the chain layers* of (rare-earth)$Ba_2Cu_3O_7$ (Fig. 1) and assigns the nonsuperconductivity of $PrBa_2Cu_3O_7$ to pair breaking by *Ba-site magnetic Pr* (Refs. 8 and 12)—an inhomogeneous phenomenon. In this model, Pr often occupies Ba sites, where it breaks pairs and destroys superconductivity that originates in the adjacent charge-reservoir oxygen, e.g., in the vicinity of the Cu-O chains. Statistically, some regions of the material that are larger than a coherence volume have no Ba-site Pr, and the model predicts that these regions superconduct. To our knowledge, there have been few, if any, previous successful theoretical predictions of superconductivity in a new material;[13] most new superconductors have been discovered using empirical rules. This particular prediction is especially satisfying because so many theories[14,15] have predicted that $PrBa_2Cu_3O_7$ *cannot superconduct*.

We assume that the two keys to observing superconductivity in $PrBa_2Cu_3O_7$ are (i) samples prepared under growth conditions that minimize the amount of Ba-site Pr (Pr is known to be rather soluble on Ba sites, where the magnetic Pr ions break pairs and destroy superconductivity in the adjacent layers;[16–21] in general, rare-earth ions with radii larger than the radius of Gd^{+3} are commonly found on Ba sites[7,15,16,22–29]), and (ii) detection schemes sensitive to the small *regions* of superconducting $PrBa_2Cu_3O_7$ *that contain no Ba-site Pr*. To superconduct, these defect-free regions must be larger than a coherence volume $V_\xi \sim \xi_a \xi_b \xi_c$.[30]

Our samples were of two types: (i) thin films prepared by pulsed-laser deposition,[31] and (ii) powders prepared in a low oxygen-pressure environment. In both cases, the sample-preparation schemes involved features that were not favorable to the formation of large quantities of Ba-site Pr.

The films were deposited onto MgO substrates as part of a study to determine optimized growth conditions for *c*-axis $PrBa_2Cu_3O_7$, with substrate temperatures ranging from 923 to 1023 K. The films deposited at 1023 K were single-phase, and exclusively *c*-axis oriented, but the 923 K films were a complex mixture of phases. The laser deposition permitted us to fabricate material at relatively low temperatures (compared with other materials-growth schemes), and so led to conditions conducive to superconductivity: growth temperatures as high as necessary to obtain films primarily of the $PrBa_2Cu_3O_7$ phase, but low enough to minimize Pr diffusion to Ba sites.

The powders were prepared in low-oxygen environments, because of our belief that oxygen on an antichain site (between two Cu ions along the *a* axis in Fig. 1) causes higher Ba-site occupancy by (rare-earth)$^{+3}$ ions in general, and by Pr^{+3} ions in particular. The powders were also prepared with trace amounts of an impurity phase that exhibits a Cu electron-spin resonance (ESR)—most likely Pr_2BaCuO_5 or

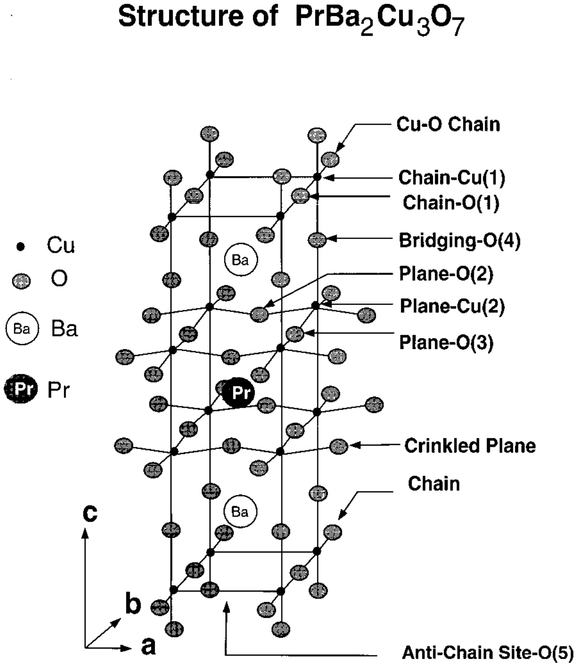

FIG. 1. Crystal structure of $PrBa_2Cu_3O_7$. Note that a magnetic impurity on a Ba site should break Cooper pairs in an adjacent chain layer, in a BaO layer, or in an adjacent cuprate plane *via* the exchange interaction, which has a range of about the nearest-neighbor distance. However, a magnetic ion at the rare-earth (Pr) site is adjacent to two cuprate planes, but remote from the charge-reservoir chains. The observation that Ba-site magnetic ($J \neq 0$) rare-earth ions such as Pr destroy superconductivity, while the same magnetic rare-earth ions on rare-earth sites do not (Refs. 7 and 8), indicates that the superconductivity originates in the vicinity of the chains, not in the planes.

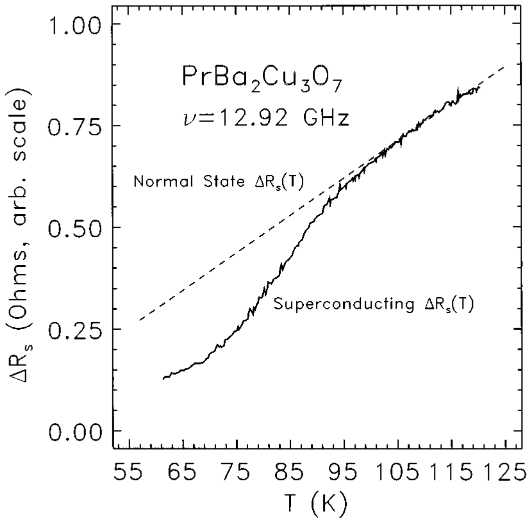

FIG. 2. Observed change in surface resistance (in ohms with a scale that is arbitrary to within a factor of about 2) of $PrBa_2Cu_3O_7$ film *versus* temperature (in K). The dashed line is the extrapolated curve for nonsuperconducting material. Note the lower surface resistance for $T<92$ K associated with superconductivity of ~7% of the sample, which was fabricated at 923 K.

barium cuprate. The purpose of introducing these trace impurity phases (which are difficult to avoid, anyway) is to measure with sufficient sensitivity the diamagnetic screening (Meissner effect) associated with the regions of superconductivity: the intensity of the ESR signal is proportional to the number of resonating or unscreened Cu spins.[32] Thus, as the sample temperature is reduced through the superconducting transition temperature, the ESR signal intensity should drop dramatically, reflecting the sudden onset of diamagnetism in the superconducting regions. It does.

The proposed mechanism of pair breaking by Ba-site Pr has not been previously taken seriously because Rietveld refinements of ordinary neutron-scattering spectra have not detected significant amounts of Pr on Ba sites. The neutron-scattering lengths of Ba and Pr are almost equal, however, making it very difficult to discriminate Pr from Ba.[33] However, other spectroscopies, most notably spin-polarized neutron scattering,[20] magic-angle spinning nuclear magnetic resonance,[19] x-ray measurements,[17] and chemical analyses[16] have all provided evidence of Ba-site Pr in $PrBa_2Cu_3O_7$. Furthermore, oxygen occupying antichain sites is a good indicator of Ba-site occupancy by (rare-earth)$^{+3}$ ions:[18,25] Pr occupies Ba sites approximately in proportion to its total concentration. Thus the data taken together suggest that $PrBa_2Cu_3O_7$ commonly contains of order several percent Ba-site Pr.[16,17,19–21] Such Pr ions are expected to be in the $+3$ ionic state,[34,35] and could be magnetic pair breakers if they are nearest neighbors to the oxygen ions whose Cooper-paired holes superconduct.

The possible *magnetic* nature of the pair breaking in $PrBa_2Cu_3O_7$ can be inferred by comparison with data for $LaBa_2Cu_3O_7$, a material which can be prepared with up to $\approx 50\%$ of the nonmagnetic La^{+3} on the Ba site by growth in an oxygen-rich environment.[36] While both $(La_{Ba})^{+3}$ and $(Pr_{Ba})^{+3}$ replacing Ba^{+2} produce defect levels, and the accompanying antichain O(5) does also, the experimental evidence (for $Y_{1-y}Pr_yBa_2Cu_3O_7$, for example[5]) indicates that considerably smaller concentrations (a few percent) of magnetic Pr_{Ba} are required to quench superconductivity by pair breaking than the concentrations of nonmagnetic La_{Ba} or (magnetic) Pr_{Ba} required to generate enough carrier traps to make the material insulating by charge trapping.[5] Indeed, for Ba-site concentrations of La less than 0.5, the critical temperature is scarcely degraded by the carrier trapping of Ba-site nonmagnetic La^{+3}.[8,25]

Figure 2 shows the observed temperature-dependent changes in the surface resistance of a single film. These data, which are typical of five films examined, feature a transition with an onset temperature of $T_c \approx 92$ K, and a 90–10 % transition width of approximately 20 K. The data have three features: (i) a background, linear in temperature with a small positive slope, that is associated with an empty microwave cavity; this signal has been measured (immediately following sample removal from the cavity) and subtracted from the data, with the difference displayed in Fig. 2; (ii) a background, linear in temperature, which is characteristic of the material in its normal state, and is extrapolated as a dashed line in Fig. 2; and (iii) a drop in surface resistance as the sample is cooled through ≈ 92 K, characteristic of superconductivity in about ~7% of the sample. We have observed similar drops in surface resistance in superconducting $YBa_2Cu_3O_7$, with the main difference being that 100% of the $YBa_2Cu_3O_7$ sample superconducts (a larger deviation from the dashed line). In $YBa_2Cu_3O_7$ we have observed transition widths of 1 to 30 K, depending on sample preparation. Since the substrate is insulating MgO, the $PrBa_2Cu_3O_7$ observations must come from superconductivity in the film, not in the substrate.

We consider unlikely the possibility that $\sim 7\%$ of the sample contained regions of contaminant that superconducted at ≈ 92 K for the following reasons: First we showed that the 92 K superconductor is an oxide that loses its superconductivity when deoxygenated. To accomplish this, we took one of our samples with a large response, cut it approximately in half (to an area of ~ 9.7 mm^2), and deoxygenated one half in a vacuum oven at ~ 600 K for 2 h. The deoxygenated half no longer superconducted, and the unaltered half did—implying that the only possible ≈ 92 K superconducting contaminants are of the (rare-earth)$Ba_2Cu_3O_7$ type. Then we checked the purity of one sample with x-ray photoemission spectroscopy, and found no contaminants with an accuracy better than 1%.[37] Finally we tried to detect Y or rare earths other than Pr in two of our samples, using sputter-secondary-ion-mass-spectroscopy (SIMS) measurements.[38] The SIMS did find very small traces of Y in one sample. Taking the sum of the mass spectra signals of Pr^{+1} and PrO^{+1} as unity, and assuming that the ion yields of Y and the lanthanides are close to the ion yield of Pr, we found no evidence of La or any other rare earth at levels of even 10^{-4}.[39] In the sample studied by Charles Evans and Associates,[38] we found the only observable contaminant, 4×10^{-3} Y^{+1}. Then we estimated the maximum surface-resistance signal to be expected from such a concentration of Y: we assumed that this Y formed $YBa_2Cu_3O_7$ which segregated from the $PrBa_2Cu_3O_7$ and formed a contaminant superconductor—although the miscibility of Y and Pr is strong evidence against such segregation. Even in this extreme segregated limit, the $YBa_2Cu_3O_7$ volume would be about half our noise level (and therefore undetectable by our apparatus), more than an order of magnitude below our detected $PrBa_2Cu_3O_7$ signal level. To reach these conclusions, we measured the drops in surface resistance *versus* temperature for similarly fabricated $YBa_2Cu_3O_7$ films of different areas, found the surface resistance to be a linear function of the area, and determined by extrapolation the amounts of $YBa_2Cu_3O_7$ required to produce superconducting signals of the sizes (i) observed in our $PrBa_2Cu_3O_7$ samples, namely $\sim 7\%$ of the $PrBa_2Cu_3O_7$ film volume (compared with an upper bound of 0.4% detected in SIMS), and (ii) at our noise level, namely $\sim 1\%$ of the volume. Our $PrBa_2Cu_3O_7$ superconductivity signal is more than 9 times our noise level. We concluded that the observed superconductivity [which has $T_c \approx 92$ K, disappears when the samples are deoxygenated, and is not attributable to any other (rare-earth)$Ba_2Cu_3O_7$ compound] is associated with $PrBa_2Cu_3O_7$—as predicted.[10]

While the drop in surface resistance was strong evidence of superconductivity, observation of diamagnetism (Meissner effect) at ≈ 92 K constituted stronger proof. In the thin films (thickness ~ 3000 Å), a conventional Meissner-effect measurement is difficult because of the strong paramagnetic background of Pr, the small thin-film volume, and the granular character of the $\sim 7\%$ superconducting fraction of this volume.[40] Accordingly we employed a more sensitive scheme based on electron-spin resonance (ESR) of Cu spins in trace amounts of an (unknown) impurity phase, deliberately incorporated into bulk 99.9% pure powders of $PrBa_2Cu_3O_7$. The ESR signal of this phase, which is most likely either Pr_2BaCuO_5 or barium cuprate, is absent in pure $YBa_2Cu_3O_7$. On the basis of measurements of the g factors and ESR linewidths of Pr_2BaCuO_5 and barium cuprate, we believe that the impurity phase is Pr_2BaCuO_5 (which has a much narrower linewidth than barium cuprate). The Cu ESR signal intensity is proportional to the number of *resonating* or unscreened spins; therefore, with decreasing temperature, the ESR signal intensity should drop suddenly at ≈ 92 K, as the Meissner effect of the suddenly superconducting and diamagnetic regions shifts the nearby paramagnetic Cu spins out of resonance.[40,41] Figure 3 shows such behavior, suggestive of inhomogeneous superconductivity.

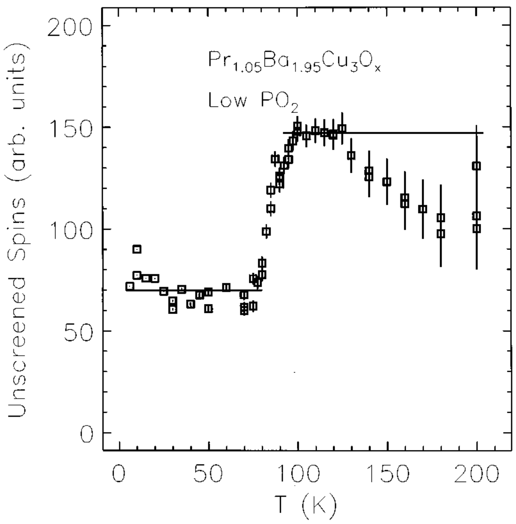

FIG. 3. Observed change in the number of resonating or unscreened spins (in arbitrary units) *versus* temperature (in K). The number of unscreened spins in this powder is the product of temperature and the observed intensity of the ESR signal of trace amounts of Cu spins having the g factor of Pr_2BaCuO_5 or barium cuprate. The sudden drop in the number of unscreened spins upon cooling through ≈ 92 K reflects the onset of diamagnetic shielding of the Cu paramagnetic spins by the regions of superconducting $PrBa_2Cu_3O_7$ (Meissner effect).

These results, although novel, in retrospect should not be very surprising. Norton *et al.* reported superconductivity in thin films of $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_7$, but not in bulk material, which was insulating.[42] Furthermore, their superconductivity depended rather critically on the *substrate temperatures* of their films. Such data are clear indications of a kinetic effect, and suggest that the Pr solubility on Ba sites is controlled sensitively by the substrate temperature and the sample preparation scheme[43]—which may be why Norton *et al.* observed superconductivity at all. Their film samples probably contained modest amounts of pair-breaking Ba-site Pr—which is why their superconducting transition temperature was considerably lower than ≈ 92 K, namely 43 K, but was not zero (as in their bulk samples).

Therefore, our experiments provide evidence that (i) fully oxygenated $PrBa_2Cu_3O_7$ (presumably when mostly in its ideal crystal structure) superconducts at ≈92 K, and that the superconductivity is inhomogeneous and disappears with deoxygenation. In addition, they suggest that schemes which minimize the amount of Pr on Ba sites favor the formation of superconductivity, and that different substrate temperatures affect the superconductivity, possibly by controlling the occupancy of Ba sites by magnetic rare-earth ions. All of these notions fit the general picture of the oxygen model.[9,10]

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[39] The only detected elements or oxides in the mass range from 80 to 100 and 130 to 190 amu were Ba^{+1}, Pr^{+1}, their oxides, and traces of Y^{+1} (4×10^{-3}) and Sr^{+1} (6×10^{-4}). Cu^{+1} was also observed. Ce^{+1}, Nd^{+1}, Pm^{+1}, Sm^{+1}, Gd^{+1}, Tb^{+1}, Ho^{+1}, Er^{+1}, and Yb^{+1} ions were all well below the 10^{-4} level. Eu^{+1}, Tm^{+1}, and Lu^{+1} may conceivably have been hidden by host oxides, but this is unlikely since no EuO^{+1}, TmO^{+1}, or LuO^{+1} was observed. Furthermore, no peaks were observed that are characteristic of their isotopic abundances.

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