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Detection of the nearly invisible defect that disrupts bulk superconductivity in $Pr_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$

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Neutron diffraction measurements on $Pr_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ (Pr222Nb-10) show that the defect previously predicted as responsible for the lack of superconductivity Pr_{Sr} (Pr on a Sr site), is present in the material in sufficient content to destroy the bulk superconductivity by magnetic scattering of Cooper pairs. Microwave power dissipation shows that the material, although previously thought to be an insulator, is in fact a granular superconductor with a superconducting transition temperature of ≈ 28 K. A Cu impurity electron spin resonance (ESR) is also detected. Mössbauer spectra show that some grains of the material contain ordered magnetism at the ^{57}Fe site (Cu site), while others are superconducting. These results are interpreted in the context of recent observations on the similar-structure compound $PrBa_2Cu_3O_7$, and indicate that in both materials Pr ions occupying alkaline-earth sites quench the superconductivity.

I. INTRODUCTION

Recently it was predicted that $PrBa_2Cu_3O_7$ (Pr123-7) would superconduct with $T_c \approx 90\,\mathrm{K}$ if it were grown without a significant concentration of Pr-on-Ba-site (Pr_{Ba}) defects.[1] Although there have since been numerous confirming reports of superconducting Pr123-7 (Refs. 2–14) with critical temperatures in the $85\,\mathrm{K} < T_c \leqslant 90\,\mathrm{K}$ (Refs. 5 and 10) range, and a great deal of evidence that Pr_{Ba} is the culprit destroying the superconductivity[1,10,13,15–21] in conventionally grown Pr123-7, a more definitive experiment correlating the presence of Pr_{Ba} with the destruction of superconductivity in a Pr123-7 sample has not yet been reported—primarily because Pr and Ba have almost identical neutron scattering lengths, making the Pr_{Ba} defect almost indistinguishable from Ba by neutrons. Consequently, it would be desirable to have a superconducting material with almost the same crystal structure as Pr123-7, but with Sr replacing the Ba, because neutrons can distinguish between Sr and Sr-site Pr. $PrSr_2Cu_3O_7$ is difficult to fabricate, and so we study instead $Pr_{2-z}Ce_zSr_2Cu_2NbO_{10}$ (Pr222Nb-10). Neutron-scattering experiments from Pr222Nb-10, exploiting the difference in scattering lengths of Pr and Sr, are expected to have sufficient sensitivity to detect a few percent of Pr_{Sr} defects. (On the order of 7% Pr_{Sr} defects should destroy superconductivity in otherwise-superconducting grains of the material.[22,23]) If microwave studies of Pr222Nb-10 suggest that it is a granular superconductor, as was the case in Pr123-7 at first,[2] and if such neutron diffraction experiments are successful in detection of Pr_{Sr}, then we would have strong and convincing evidence that Pr readily occupies alkaline-earth sites, and destroys superconductivity—both in the Sr-based material Pr222Nb-10, and, by inference, in its sister compound Pr123-7.

II. STRUCTURE OF Pr222Nb-10

There are at least two interesting ways of looking at the material Pr222Nb-10: (i) as a sister of Pr123-7 and (ii) as a superlattice containing $Pr_{2-z}Ce_zCuO_4$ which is a subset of the layers in its fundamental supercell.

A. Similarity of Pr222Nb-10 to Pr123-7

Pr222Nb-10 is a material with almost the same layers as found in Pr123-7, but with Sr in place of Ba: it has a crystal structure featuring (i) a rare-earth layer ($Pr_{1-(z/2)}Ce_{(z/2)}$), (ii) a cuprate-plane below the rare earth (in the negative c-axis direction), (iii) a SrO layer below the cuprate plane (analogous to the BaO layer of Pr123-7), and (iv) further below, a NbO_2 layer in place of the CuO chain layer of Pr123-7 (see Fig. 1). On the other (positive c) side of the rare-earth layer is an O_2 layer, followed by rare-earth ($Pr_{1-(z/2)}Ce_{(z/2)}$), CuO_2, SrO, and NbO_2 planes, displaced in the **a** and **b** directions so that a rare-earth ion lies directly above a Cu ion

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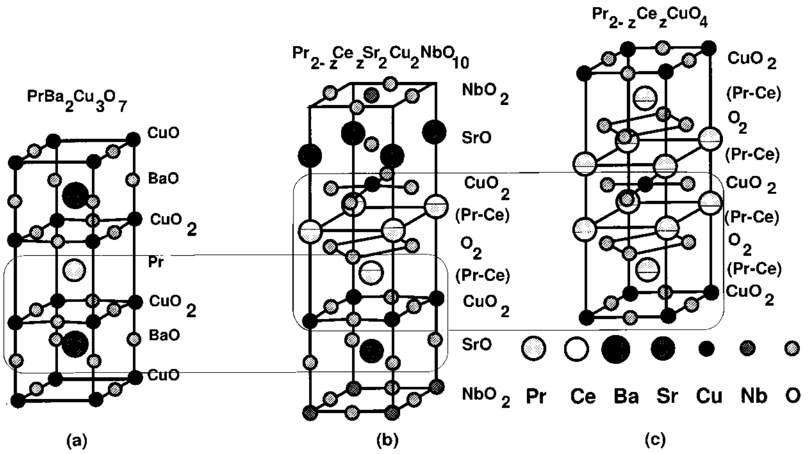

FIG. 1. Crystal structures of (a) Pr123-7, (b) Pr222Nb-10, and (c) Pr21-4. Note that Pr222Nb-10 is a 1×1 superlattice of Pr21-4 and $/CuO_2/SrO/NbO_2/SrO/$ layers, but with optimal Ce doping $z\approx0.5$, instead of $z\approx0.15$ (as in Pr21-4). Pr222Nb-10 also has similar layers to Pr123-7: (i) a rare-earth ion, (ii) a cuprate plane, (iii) a SrO layer (in place of BaO), and (iv) a NbO_2 layer (in place of Pr123-7s CuO chain layer). It also has an extra O_2 layer, displacement of its crystal structure in the [1,1,0] direction, and then a repeat of the same layers.

of its second closest cuprate-plane. From this viewpoint, Pr222Nb-10 should superconduct with a critical temperature not too different from that of Pr123-7, $T_c\approx90$ K, if one adopts a cuprate-plane model of the superconductivity—because the nearest-neighbor planes to a cuprate-plane are a rare-earth layer and a SrO layer, the same as in Pr123-7, except that alkaline-earth Sr replaces fellow alkaline-earth Ba.

An indication of the expected effect of Ba replacement by Sr on this $T_c\approx90$ K estimate can be obtained by noting that T_c of $YBaSrCu_3O_7$ is 83 K,[24] although $YBaSrCu_3O_7$ is $YBa_2Cu_3O_7$ with half of its Ba replaced by Sr. This suggests that full replacement of the Ba in $YBa_2Cu_3O_7$ should degrade T_c about twice as much, giving $T_c\geqslant73$ K for hypothetical superconducting $YSr_2Cu_3O_7$ and its homologues such as $PrSr_2Cu_3O_7$. Hence, if the primary superconductivity occurs in the cuprate-planes, we expect that Pr222Nb-10 will have a critical temperature in excess of 73 K, because it has the same layers next to the cuprate-planes as Sr-replaced Pr123-7.

B. Pr222Nb-10 is a superlattice of $Pr_{2-z}Ce_zCuO_4$ and $/SrO/NbO_2/SrO/CuO_2/$ layers

Pr222Nb-10 is also a natural superlattice of $Pr_{2-z}Ce_zCuO_4$ (Pr21-4) with the metal oxide layers $/SrO/NbO_2/SrO/CuO_2/$. If we adopt a cuprate-plane model of the superconductivity and if we assume that the role of the oxide layers is solely to confine the superconducting Pr21-4, then we expect that Pr222Nb-10 will also superconduct—perhaps with a critical temperature near that of Pr21-4's $T_c\approx24$ K,[25–31] and with a somewhat different ''optimal doping'' z. In fact the optimal doping in the stand-alone compound Pr21-4 is $z\approx0.15$, and in the superlattice compound Pr222Nb-10 is expected to be $z\approx0.5$, as it is for the superconducting R222Nb-10 homologues.

C. Expected T_c in each model

Therefore, from both viewpoints, we expect Pr222Nb-10 to superconduct in a cuprate-plane model, (i) because $Pr_{2-z}Ce_zCuO_4$ superconducts and Pr222Nb-10 is a superlattice containing Pr21-4 (but doped with $z\approx0.5$ instead of 0.15) and $/SrO/NbO_2/SrO/CuO_2/$ layers, suggesting a T_c near the 24 K of Pr21-4;[31] or (ii) because Pr123-7 now superconducts[2–11] and has the same structure on either side of its cuprate planes as found in Pr222Nb-10 (except that Sr replaces Ba), suggesting a T_c nearer to 90 K (or at least $\geqslant73$ K expected for Sr having replaced Ba).

Indeed, if the cuprate-planes are the primary superconductors, then we expect the material whose nearest-neighbor environment to those planes is most similar to that of Pr222Nb-10 to have the nearest T_c: namely, ≈90 K, as in Pr123-7, or $\geqslant73$ K as in $PrSr_2Cu_3O_7$, not ≈24 K, as in Pr21-4. [Pr21-4 has neighboring layers to its cuprate-planes that are both Pr/Ce layers, while Pr222Nb-10 has one rare-earth layer (Pr/Ce or R) and one SrO layer as the neighbors to its cuprate planes, as in $RSr_2Cu_3O_7$.] This argument implies that T_c for Pr222Nb-10 should certainly be greater than 73 K—if the primary superconductivity inhabits the cuprate planes.

Since we shall find that Pr222Nb-10 is a granular superconductor with $T_c\approx25$ K, closer to T_c of Pr21-4 than to T_c of Pr123-7, something must be wrong with the assumption that the cuprate planes are the primary superconductors.

D. Superconductivity of Pr222Nb-10

If the cuprate planes of the crystal structures of Nd21-4 and Nd222Nb-10 are the primary superconductors, then it should be the case that replacement of the Nd by some other rare-earth will cause either both compounds or neither to super-conduct. In other words, since Pr21-4 superconducts, then either (i) Pr222Nb-10 *must* superconduct or else (ii) *different layers* of the homologues of Nd21-4 and Nd222Nb-10 must be the superconducting layers. This argument can be applied to the Pr compounds and their homologues to show that either (i) Pr222Nb-10 must superconduct (but has not done so because of some superconductivity-destroying defect, such as Pr_{Sr}) or else (ii) the superconducting condensates in Pr21-4 and in Pr222Nb-10 are located in different layers (e.g., not both in the cuprate planes).

The fact that Pr123-7 now superconducts (as predicted in Ref. 1), although it was long thought to be an intrinsic insulator,[32,33] lends further support to the notion that Pr compounds, when carefully fabricated, superconduct if their rare-earth homologues do superconduct—and provides a hint about what causes Pr222Nb-10 to *not superconduct*: Pr_{Sr} defects, which are analogous to the pair-breaking Pr_{Ba} defects responsible for killing the superconductivity in Pr123-7. If this picture is correct, Pr222Nb-10, although a bulk insulator, should exhibit *granular* superconductivity (detectable by rf

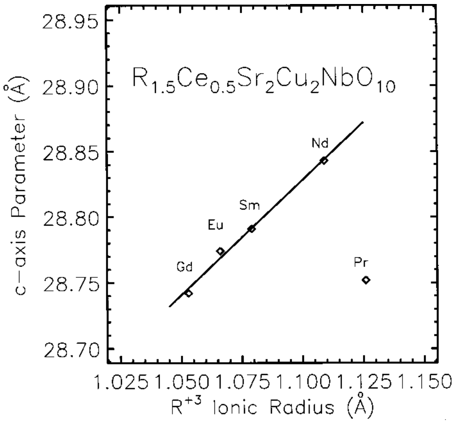

FIG. 2. Plot of the *c*-axis lengths (in Å) of $R_{2-z}Ce_zSr_2Cu_2NbO_{10}$ (Refs. 43 and 44) (which are qualitatively similar to those of $RBa_2Cu_3O_7$) (Refs. 41 and 45) *versus* trivalent-rare-earth radii (in Å) (Refs. 40 and 41). Note that the *c*-axis is anomalously short for $R = \mathrm{Pr}$ (in both materials), and material with an anomalously short *c* axis does not superconduct. This is symptomatic of Pr occupancy of the Sr (or Ba) sites.

surface resistance measurements[2]) and should contain >5% Pr_{Sr} (which can be detected by neutron diffraction).

Therefore, we set out (i) to observe Pr_{Sr} defects and (ii) to detect granular superconductivity in Pr222Nb-10. Not only did we accomplish both goals, but we also saw direct evidence in Mössbauer data of a superconducting phase in Pr222Nb-10 that coexists with an ordered magnetic phase, confirming by an independent method the presence of grains of superconductivity embedded in magnetically ordered material.

III. SAMPLE PREPARATION AND TESTS FOR BULK SUPERCONDUCTIVITY

Our Pr222Nb-10 was fabricated by standard means,[34] which routinely produced bulk nonsuperconducting Pr222Nb-10, although its homologues with the rare-earth ions Nd, Sm, Eu, and Gd all superconducted[25–30] when fabricated similarly. The Pr222Nb-10 was very similar in behavior to our early Pr123-7 samples: no evidence of *bulk* superconductivity (diamagnetism) was apparent in them when they were probed by a superconducting quantum interference device (SQUID), and the *bulk* resistivity was semiconductor-like, increasing as the temperature was lowered.[35,36] Clearly, the Pr222Nb-10 we studied *did not exhibit bulk superconductivity*.

IV. EVIDENCE OF Pr_{Sr} DEFECTS

The proposal that a pair-breaking defect in Pr222Nb-10 kills the superconductivity causes us to search for such a defect. By analogy with Pr123-7,[1] where Pr_{Ba} is almost certainly the pair-breaking defect, we proposed that Pr_{Sr} is the culprit defect in Pr222Nb-10.[37–39]

If Pr occupies Sr sites in our Pr222Nb-10, then the *c*-axis lattice constant should be shorter than in material without such defects, much as occurred for Pr_{Ba} in Pr123-7 and Cm_{Ba} in Cm123-7.[19] Figure 2 shows such *c*-axis contraction for $R = \mathrm{Pr}$ in the $R_{2-z}Ce_zSr_2Cu_2NbO_{10}$ compounds, which is comparable with the *c* axes contraction observed in the $RBa_2Cu_3O_7$ compounds.[40–45]

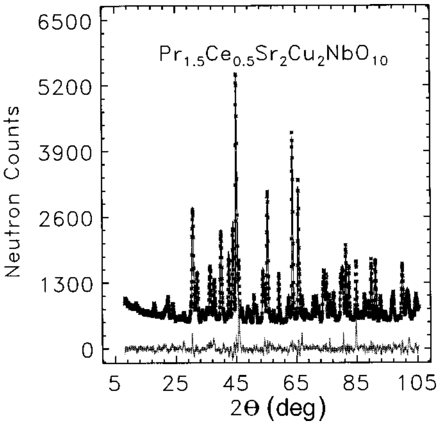

FIG. 3. Neutron diffraction spectrum of Pr222Nb-10 (number of counts vs 2θ, where θ is the diffraction angle). The solid line is the fit, and the residuals are the bottom curve.

Note that in both Pr compounds that originally *did not exhibit bulk superconductivity*, Pr123-7 and Pr222Nb-10, the *c*-axis length was short in comparison with the trends, but that in the version of Pr123-7 that did superconduct, the *c* axis was what the trends predicted. We propose that the same will be the case for superconducting Pr222Nb-10.

V. NEUTRON DIFFRACTION

A. Main results

Neutron diffraction data on Pr222Nb-10 were collected on a high-resolution powder diffractometer at the University of Missouri Research Reactor, and analyzed with the GSAS program (see Fig. 3). Refinement with this phase alone showed a number of residual peaks, and the program TREOR was used to search for high-symmetry unit cells with interplanar spacings matching the residuals. A second, nonsuperconducting phase was identified, having a cubic unit cell with $a = 3.97$ Å, the cell parameter of the simple phase-separated perovskite $SrNbO_3$.[46] Most of the residual peaks were successfully fit with this structure, which was found to account for 14% of the sample by volume. Pr222Nb-10 accounts for the balance (~85%), except for two small residual peaks that remain unidentified (<2%). These residuals do not affect the refined results significantly, but do control the minima in the goodness-of-fit parameters reported. The presence of $SrNbO_3$ (Ref. 47) implies that the Pr222Nb-10 phase must be Pr rich, with significant numbers of Pr ions occupying non-rare-earth sites.

The rare-earth sites are found to be fully occupied by Pr or Ce, and the data are incompatible with more than a few percent Sr on those sites. The best refinement gives 23% Pr on Sr sites, the expected pair-breaking defects. However, the minimum χ^2 obtained from fitting the data is shallow as a function of the Pr_{Sr} occupancy, and the results are consistent with an occupancy value between roughly 15 and 30%. Clearly there are more than enough Pr_{Sr} defects to account for the failure to observe bulk superconductivity in Pr222Nb-10.

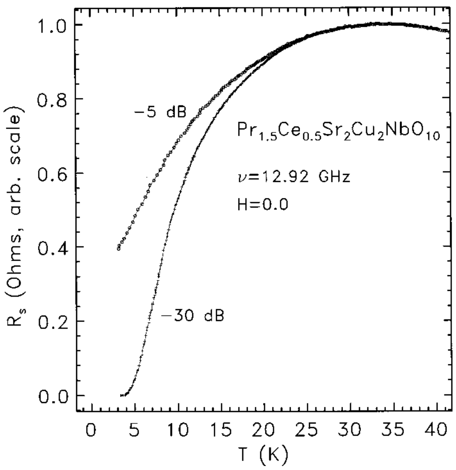

FIG. 4. Surface resistance R_S (in ohms) on an arbitrary scale *versus* temperature T (in K). The microwave frequency employed was $\nu = 12.92\,\mathrm{GHz}$, and the measurements were in zero applied field **H** with a power levels of ≈32 mW (−5 dB) and ≈0.1 mW (−30 dB). The data with a power level of −5 dB indicate a partial breakdown of the superconductivity at this higher power level. This breakdown results from the relatively low J_c of parts of the superconducting material.

B. A new distortion

The neutron refinement also reveals a distortion of the structure from the ideal structure shown in Fig. 1(b). The oxygen atoms in the NbO_2 planes, O(1), were originally thought to reside at the midpoint $(0,\frac{1}{2},0)$ between the Nb atoms at the origin of the unit cell. However, the refinement gave anomalously large anisotropic thermal factors for O(1) with this model, and it was clear from the refined thermal factors that significant-ionic density was located off the ideal site and in the basal plane, in a direction perpendicular to the cell edge. Reanalysis of the data with a disorder model[48] in which the oxygen atoms were split into two partially occupied sites at $(\pm x,\frac{1}{2},0)$, with $x = 0.138$ (or $xa = 0.487 \pm 0.31$ Å) produced a better fit and more reasonable thermal factors for the partially occupied sites.[49] Both the original model and the disorder model show that the NbO_2 plane is oxygen deficient, with its sites about 20% empty. The remaining oxygen sites appear to be fully occupied (to within ±3%) and so the actual stoichiometry is $O_{9.6}$ rather than O_{10}.[46,50]

VI. MICROWAVE MEASUREMENTS

A. Surface resistance

As in the case of Pr123-7, Pr222Nb-10 is expected to exhibit granular rf superconductivity even if it is not a *bulk* dc superconductor. This granular superconductivity was evident in the microwave surface resistance (measured for a frequency $\nu = 12.92\,\mathrm{GHz}$), which dropped rather suddenly at 25–30 K (Fig. 4). These data indicated either a metal-insulator transition or a superconductor-insulator transition. We also found that the rf surface resistance was power dependent, consistent with a granular material. In our rf experiments, the current densities ranged from roughly 10^3 to $10^5\ \mathrm{A/cm^2}$; high rf current densities can drive a bulk superconducting sample normal.[51] Since metal-insulator transitions are at least rare and perhaps unknown in the cuprates, we interpret the power dependence of the surface resistance (Fig. 4) as indicative of granular superconductivity. Note that the temperature of the drop in surface resistance coincided with the drop in bulk resistance, also observed at 25–30 K, detected in R222Nb-10 for $R =$ Nd, Sm, Eu, and Gd. Thus we conclude that Pr222Nb-10 exhibits granular superconductivity for $T_c \approx 25-30\,\mathrm{K}$.

We obtained a crude estimate of the Meissner fraction by comparing the size of the signal obtained here with that of a bulk superconductor; we estimate a volume fraction of order ~10%. Our attempts to directly measure a (bulk) Meissner effect and diamagnetism in the granular Pr222Nb-10 failed, presumably because a SQUID is expected to detect flux expulsion only if the size of the superconducting grains exceeds the penetration depth λ and if the grains percolate to form continuous superconducting paths. We have demonstrated the ability to detect vortex dissipation with microwaves in grains that are larger than λ, but fail to percolate. Materials with small superconducting grains exhibit superconductivity without displaying either a Meissner effect or vortex dissipation.

B. Meissner screening

One way to measure a mesoscopic Meissner effect is with electron spin resonance (ESR) of Cu in an impurity phase or by a substitution such as Gd for Pr.[3,52] The integrated intensity of the resonance varies inversely as the temperature T, and the coefficient of this variation is proportional to the number of unscreened spins. The number of unscreened spins should decrease suddenly as the sample temperature drops through the superconducting critical temperature T_c, due to Meissner screening, and due to a decrease in the effective microwave penetration depth.

We did observe a $g = 2$ ESR associated with Cu. Since Cu does not normally resonate when the Cu lies *in* a cuprate plane, we assign this resonance to defects either in the nonsuperconducting parts of the Pr222Nb-10 matrix containing the superconducting grains, or in some other undetected nonsuperconducting impurity phase which is near superconducting grains. For example, the defect phase responsible for this resonance could be $SrCuO_2$ or Pr_2SrCuO_5.

VII. MÖSSBAUER SPECTRA

The low-temperature Mössbauer spectra of ^{57}Fe substituted for cuprate-plane Cu in Pr222Nb-10 and Eu222Nb-10 (for comparison) are given in Fig. 5.[34] A sextet spectrum is characteristic of ordered magnetism at the Fe site, namely, antiferromagnetism or weak ferromagnetism, at the Cu site in the cuprate planes.[53,54] (Weak ferromagnetism associated with canted antiferromagnetic Cu spins has been reported in Pr222Nb-10.[55,56]) A doublet spectrum signals the lack of magnetic order at the Fe site, and hence, in a cuprate-plane model, is consistent with superconductivity there. The expected type of spectrum for a superconducting compound similar to pure Pr222Nb-10 is given in Fig. 5(b), and is the spectrum of superconducting Eu222Nb-10. The spectrum of Pr222Nb-10 is different from that of Eu222Nb-10 in two important ways: (i) the spectrum of Pr222Nb-10 in Fig. 5(a) features *both* a doublet *and* a sextet, suggesting that the

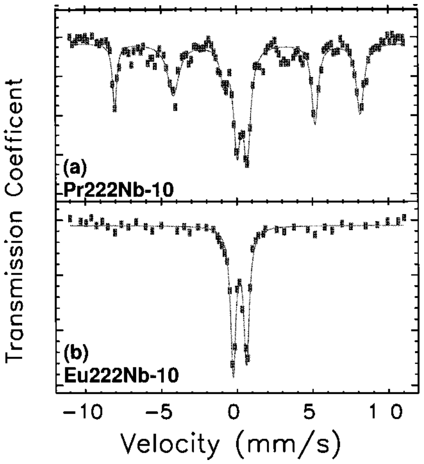

FIG. 5. Low-temperature (4.1 K) Mössbauer γ-ray absorption spectra of (a) Pr222Nb-10 and (b) Eu222Nb-10, after Ref. 34. Note that Pr222Nb-10 features *both* a doublet and a sextet, while Eu222Nb-10 has only a doublet. Furthermore the sextet in Pr222Nb-10 has a slightly larger splitting indicative of a slightly different hyperfine field. We interpret these data as indicating that the Pr222Nb-10 sample is inhomogeneous and that the sample contains at least two kinds of grains—one kind that superconducts (producing the doublet) and another that contains an ordered magnetic structure (e.g., weak ferromagnetism). The slightly larger splitting of the sextet in Pr222Nb-10 than in Eu222Ru-10 or in $(La_{1-x}Pr_x)_{2-\beta}Sr_\beta CuO_4$, is an indicator that the crystal structure in the vicinity of the ^{57}Fe on the Cu sites in the cuprate planes of the nonsuperconducting grains contains a defect (such as Pr_{Sr}). The lines are guides to the eye.

Pr222Nb-10 sample contains *both* superconducting grains and magnetic grains (and is inhomogeneous[57])–consistent with the picture provided by surface resistance measurements of granular superconductivity (namely, some grains that superconduct and others that do not);[58] and (ii) slightly larger splittings are detected of the sextet in Pr222Nb-10 than in either Eu222Ru-10 or $(La_{1-x}Pr_x)_{2-\beta}Sr_\beta CuO_4$ (Refs. 59–62)—suggesting that the ^{57}Fe site of the granular material sees a different hyperfine field from that of the bulk superconductors.

An analysis of the Pr222Nb-10 Mössbauer spectrum assuming (i) that the doublet comes form Fe-containing regions or from grains that are locally nonmagnetic and superconducting and (ii) that the sextet is associated with nonsuperconducting and magnetic regions, reveals that 32% of the sample by volume is from the nonmagnetic and superconducting phases. This 32% is therefore an approximate upper bound to the superconducting volume fraction, being an overestimate because we do not know how much Fe is on grain boundaries, in microphases such as Fe_2O_3, or in other impurity phases. It should be compared with the crude estimate of ~10% superconducting volume fraction, and is not inconsistent with that value—given the uncertainties involved in both estimates.

VIII. SUMMARY

In summary, the samples that we have studied of Pr222Nb-10 contain the predicted Pr_{Sr} defects in amounts sufficient to destroy the *bulk* superconductivity of Pr222Nb-10. We also provide evidence that Pr222Nb-10 is a granular superconductor, with a critical temperature of ≈28 K, and so the superconducting grains are similar in structure to Pr222Nb-10's superconducting homologues, such as Eu222Nb-10. The lack of superconductivity in the majority of the sample is doubtless due to defects that break Cooper pairs and destroy the superconductivity: The continuous superconducting paths across the sample needed to produce *bulk* superconductivity do not occur, and the Mössbauer data indicate that parts of the CuO_2 planes are doped, and hence are nonmagnetic and superconducting. The pair-breaking defect that we predicted,[37] Pr_{Sr},[37–39] is present in ample quantities, but its twin defect, Sr_{Pr}, whose presence we had also predicted, has been detected, but in smaller quantities than Pr_{Sr}. Therefore the relevant defect is not the antistructure defect (Pr_{Sr}, Sr_{Pr}), but is the pair-breaking half of that antistructure defect, Pr_{Sr}.[50] Furthermore, the observed crystal structure of Pr222Nb-10 contains an unexpected distortion of its NbO_2 planes from the expected square planar structure.

The implications of these results for the overall theory of high-temperature superconductivity are significant.

(i) We have presented evidence that the magnetic defect Pr_{Sr} is a pair breaker in Pr222Nb-10 and implicit evidence (the fact of granular superconductivity) that Pr_{Pr} is not. Since the cuprate plane is approximately midway between the Pr and Sr sites, and since the magnetic environments of the two sites are virtually the same, it is difficult to understand on symmetry grounds how Pr on one side of a cuprate plane (on a Sr site) can be a pair breaker, but Pr on the other side, on a regular Pr site in about the same location with respect to the cuprate plane, is not. If the primary superconducting condensate occupies the cuprate plane approximately midway between the two sites, then Pr on both sites should have the same effect on the superconductivity. Hence we conclude on symmetry grounds that the primary superconducting condensate is likely *not in the cuprate planes*, and that ''clean'' Pr222Nb-10 is a ≈28 K superconductor. This general picture is confirmed by the fact that no pair-breaking Eu_{Sr} defects were observed in the neutron diffraction spectra of the homologous superconductor Eu222Ru-10.[63] A consequence of this logic is the prediction that Pr222Nb-10 will be a bulk superconductor if it can be grown with few Pr_{Sr} defects.

(ii) These conclusions add to existing evidence that Pr_{Ba} is the pair-breaking defect in Pr123-7. Although we disagree with the authors of Ref. 55 on a number of central issues,[46,64] we heartily endorse their conclusion that the same physics is responsible for the lack of superconductivity in both Pr123-7 and Pr222Nb-10, while pointing out that the pair-breaking defects responsible for destroying the superconductivity are Pr_{Ba} and Pr_{Sr}, respectively. The difficulty with the Pr_{Ba} defects is that unpolarized-neutron diffraction cannot detect Pr_{Ba} because the neutron scattering lengths of Ba and Pr are so similar.

(iii) The 23% Pr_{Sr} defects are more of these pair-breaking defects than we expected. However, this large concentration of Pr_{Sr} is consistent with a paucity of large superconducting granules (i.e., with sizes as large as a penetration depth λ), as indicated by our microwave measurements in an applied field, which featured neither observable vortex dissipation nor field dependence. Since the coherence length in the *a-b* plane is very likely ~20 Å, the 32% doublet/sextet Mössbauer ratio, the 10% Meissner volume fraction, and the 23% Pr_{Sr} defects are probably not mutually inconsistent. The rare-earth excess in the Pr222Nb-10 phase is compensated in the overall chemistry by the rare-earth-free $SrNbO_3$.

(iv) Although the local environments of the cuprate planes in Pr222Nb-10 and Pr123-7 are almost the same (except that Sr replaces Ba), the critical temperatures of the two compounds are very different, with T_c for Pr222Nb-10 being only about one-third the size of T_c expected for Sr-replaced $PrSr_2Cu_3O_7$. This means that the cuprate planes probably are *not the primary superconducting elements* of these compounds, as widely assumed.

(v) The logical anomaly that Pr21-4 superconducts, while its superlattice compound Pr222Nb-10 does not, has been removed; both compounds superconduct, with almost the same critical temperature. This, however, may be somewhat accidental; see the following paragraph (vi). Also Pr123-7 and Pr-PSYCO ($Pb_2Sr_2Pr_{0.5}Ca_{0.5}Cu_3O_8$) superconduct, as expected, showing that the Pr ion is not an anomalous pair breaker. Nor is there any indication from the high-pressure experiments that Pr is in any way unusual.[5,14,19]

(vi) The enigma presented by the substitution of the rare earths $R = Pr$, Nd, and Gd into the R222Nb-10 and R21-4 structures has been recently discussed in some detail in Ref. 65. In brief, the apparent lack of superconductivity in some of these structures is due either to a substitutional defect such as Pr_{Ba} (in the Pr structures) or to the intrinsic $L=0$, $S=\frac{7}{2}$ character of Gd, which is a pair-breaker (in the Gd structures[66]). R222Nb-10 and R123-7 structures which dissolve significant numbers of Pr_{Ba} pair-breaking defects, may not superconduct. But Cm in $Cm_{2-z}Th_zCuO_4$, is an $L=0$ actinide ion, and $Cm_{2-z}Th_zCuO_4$, much as $Gd_{2-z}Ce_zCuO_4$, cannot superconduct at all. The attendant implication for R21-4 homologues of either Gd21-4 or Cm21-4 is that the primary R21-4 superconductivity is exterior to the cuprate planes (i.e., in the R-O_2 layers,[67] where the holes are found, according to a bond-valence-sum analysis[68]) and cannot be in the same regions as in R222Nb-10, where we have identified the SrO layers as holding the superconductivity.

Finally, we note that the two-layer double perovskite Ba_2GdRuO_6, when Cu-doped on the Ru site, does not superconduct, but that homologous materials, such as Cu-doped Sr_2YRuO_6, do.[69] This is another example of $L=0$ Gd^{+3} functioning as a pair breaker. We predict that other homologous compounds will superconduct.

It is our position that Gd, not Pr, is the unusual ion of the rare-earth series, and that this is due to its being magnetic with $L=0$, and hence not crystal-field split—which allows it to break pairs. Pr, being large, merely has a large solubility on the Ba site, where it breaks pairs and disrupts the superconductivity, whenever enough Pr is off site.

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[18] Symptoms of nonsuperconducting Pr123-7 (as opposed to superconducting material) include (i) the presence of $\mathrm{Pr_{Ba}}$ defects, (ii) the attendant shorter *c*-axis lattice constant than expected from the trends as a function of rare-earth size (Ref. 19), (iii) excess $\mathrm{BaCuO_2}$ in the sample, (iv) antichain oxygen between the CuO chains, and (v) a high Néel temperature (of order 20 K) (Ref. 1). These symptoms can be reduced by reacting the material at high temperatures in low oxygen pressure with subsequent annealing at lower temperatures, because Pr moves off site more readily at high temperatures and when nearby oxygen occupies antichain sites.

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[57] Reference 59 presents evidence that the superconductivity is rather homogeneous in Gd222Ru-10, as detected by current-voltage scans with a scanning tunneling microsope, but does not rule out the possibility of significant inhomogeneity on an atomic scale.

[58] Another interpretation of the Pr222Nb-10 Mössbauer spectrum has been advanced: that Fe on both cuprate plane and Nb sites contribute to the spectrum, providing both the doublet and the sextet (Ref. 54). This point will be dealt with in some detail in a subsequent publication.

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