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Implications for the origin of the pseudogap: Microwave spectroscopy of $PrBa_2Cu_4O_8$

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Using techniques of microwave spectroscopy at 13 GHz, we have observed antiferromagnetic resonance arising from the magnetically ordered cuprate planes of conducting $PrBa_2Cu_4O_8$; the Cu Néel temperature is approximately 80 K. In addition, we have detected a Cu electron spin resonance which is due either to Cu in chain fragments or more likely to Cu in a minority impurity phase, $BaCuO_2$, a phase also detected by x-ray diffraction. Although this sample was conducting to the lowest temperatures, no indication of even granular superconductivity was detected. The *c*-axis parameter of $PrBa_2Cu_4O_8$ is dependent on processing and varies more than in other Ln124 materials; we propose that the lack of superconductivity is a consequence of a defect, namely, substitution of a variable content of smaller Pr on the Ba site. Such substitution also results in the formation of the minority phase $BaCuO_2$. Our observation of cuprate-plane antiferromagnetism coupled with evidence that the cuprate planes are insulating (provided by Horii *et al.* [Phys. Rev. B **6**, 6327 (2000)]) indicates that any conductivity is associated with the CuO chains, not with the CuO_2 planes. These results imply that the existence of the pseudogap detected at 150 K in Pr124 by Bäckström *et al.* [Phys. Rev. B. **61**, 7049 (2000)] is unrelated to either carriers or spin fluctuations in the cuprate planes.

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I. INTRODUCTION

Of the five well-known oxide materials containing Pr whose homologues routinely superconduct e.g., $PrBa_2Cu_3O_7$ (Pr123), $PrBa_2Cu_4O_8$ (Pr124), $Pr_{2-z}Ce_zCuO_4$, $Pr_{2-z}Ce_zSr_2Cu_2NbO_{10}$, and $Pb_2Sr_2Pr_{0.5}Ca_{0.5}Cu_3O_8$, only two, $Pr_{2-z}Ce_zCuO_4$ and $Pb_2Sr_2Pr_{0.5}Ca_{0.5}Cu_3O_8$, *routinely* exhibit bulk superconductivity,[1–4] while $Pr_{2-z}Ce_zSr_2Cu_2NbO_{10}$, heavily defected by Pr substituted for Sr (Pr_{Sr}), has been shown to exhibit granular superconductivity.[5] Pr124 has received rather less attention than its closely related material Pr123, in large part because of the relative difficulty in preparation of the double chain-layer material Pr124. (The transition temperatures of the double chain-layer Ln124 (Ln=lanthanide) materials are generally lower than those with single chain layers.) To date, we know of no reports of superconductivity in Pr124, while improved processing techniques, which limit the content of Pr_{Ba} defects, now yield superconducting Pr123.[6–21] These two closely related structures are compared in Fig. 1; it is useful to note that the neighborhood environments of the cuprate planes of the two materials are identical. The only structural difference between Pr123 and Pr124 is associated with the chain layers between neighboring BaO layers. Since Pr123 superconducts with limited defect content, either the superconductivity is associated with the chain layer, the neighboring BaO layers which may have been impacted by the different chain-layer structures, or else Pr124 is defected. Since materials without CuO chains are known to superconduct,[22] e.g., the homologue $YSr_2Cu_2RuO_8$, in which the CuO chain layer of the parent "123" compound has been replaced by a magnetically ordered RuO_2 layer, it is clear that the chain layer is not the primary host of superconductivity. Thus, either the presence of the second chain layer (which may have impact on the electronic properties of the BaO layers) or a defect is involved, which disrupts pair formation and/or charge transfer. Because the several other known Ln124 homologues superconduct, disruption of some property of the BaO layers by the differing chain-layer structure can be eliminated as a cause of the nonsuperconductivity of Pr124. As a result, efforts to discern the reason for the lack of superconductivity in Pr124 are necessarily focused on the attributes of possible defects. For example, it has been established that variations of the *c*-axis lattice parameter of Pr123 are associated with a variable content of Pr_{Ba}.[5] In the following, we argue that a similar defect limits the superconductivity of Pr124.

In Fig. 2, data for the *c*-axis parameters of several Ln124 homologues are given.[23–32] These data have substantially more scatter than the corresponding data for the Ln123 homologues. The remarkable scatter associated with the Pr124 data suggests that the same lattice anomalies associated with conventionally prepared nonsuperconducting $PrBa_2Cu_3O_7$ and $Pr_{2-z}Ce_zSr_2Cu_2NbO_{10}$ are present in $PrBa_2Cu_4O_8$; we interpret the scatter in the *c*-axis parameter as evidence for Pr_{Ba} defects in this material. The smallest *c*-axis datum, denoted

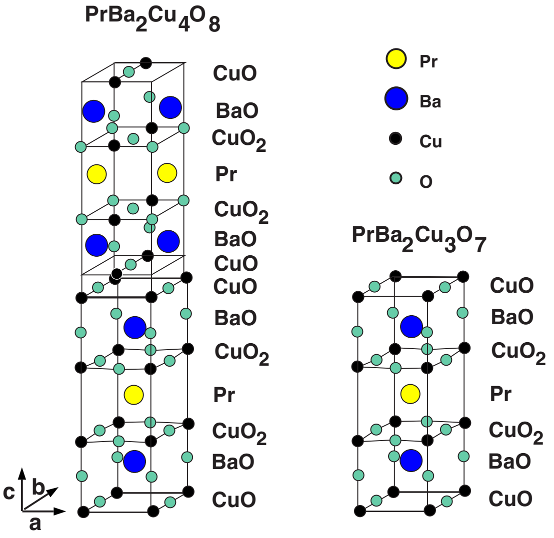

FIG. 1. (Color online) Structures of $PrBa_2Cu_4O_8$ (left) and $PrBa_2Cu_3O_7$ (right). These two structures are closely related, since $PrBa_2Cu_4O_8$ can be viewed as resulting from the stacking of two $PrBa_2Cu_3O_7$ cells with an offset of $\mathbf{b}/2$ in the chain layer. The local environments of the cuprate planes are essentially identical in the two structures; the only structural difference lies in the chain layers separating the BaO layers.

by the asterisk in Fig. 2, was reported for single crystal Pr124. It is our position that this datum is the most reliable for its indication of *c*-axis contraction consistent with a significant content of the defect Pr_{Ba}.

Because recent advances in the preparation techniques[23] of Pr124 have yielded material which at low temperatures is conducting (as opposed to insulating), we have sought to investigate the material's microwave properties. The microwave probe has been proven to be more sensitive[6,7] than superconducting quantum interference device or resistivity measurements for detection of granular superconductivity, which results from the failure of superconducting grains to achieve percolation. Magnetic resonance is also more effective in identifying cuprate-plane magnetic order than neutron diffraction. Recently, Fujiyama *et al.*[33] have employed another Cu resonance technique, nuclear magnetic resonance (NMR), to show that the planar Cu in their conventionally prepared samples, with insulating planes which ordered at temperatures near 220 K, producing a local field of ~6 T at the planar Cu sites at 1.5 K. Additionally, they have found that the Cu moments $\sim 0.5\mu_B$ lie within ~5° of the *a*-*b* plane.[34] Yamada *et al.*[35] employed μ^+SR to detect the development of an internal field below 220 K, also identifying the onset of antiferromagnetism. Because of the substantial similarities of Pr124 and Pr123, in the following, we will discuss consequences of preparation details and relevant experience with both of the related materials which may serve to illuminate critical aspects of defects in Pr124.

A. Role of oxygen pressure

Although bulk superconductivity has been observed in crystals of $PrBa_2Cu_3O_7$ (Pr123) prepared using a traveling solvent floating zone furnace,[8–15] and in a polycrystalline material prepared with a sol-gel process,[20] conventional preparation procedures almost invariably yield insulating material. One common feature of the preparation procedures which have yielded superconducting Pr123 is the use of low pressure oxygen during critical high temperature processing. However, this procedure is well known to reduce the substitution of La on the Ba site of $LaBa_2Cu_3O_7$ (La123), and the same procedure applied to $NdBa_2Cu_3O_7$ (Nd123) yields enhanced transition temperatures as high as 98.7 K,[36] also through the reduction of the Nd_{Ba} content.[37]

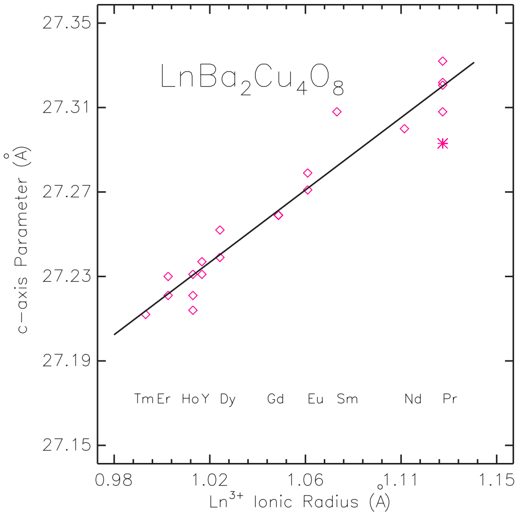

FIG. 2. (Color online) *c*-axis parameter as a function of Ln ionic radius. The data for Pr have a great deal of scatter; the smallest datum plotted with an "*" is for single crystal Pr124. This scatter, much larger than *any possible* experimental errors, is consistent with a variable defect content, Pr on the Ba site. The straight line is a least-squares fit to the data, ignoring the Pr points.

While processing Nd123 in low pressure oxygen yields a material with an enhanced transition temperature, processing in oxygen yields a material with dramatically enhanced flux-pinning properties;[38] however, the same flux-pinning enhancement is not known to occur for similarly prepared La123. This difference in the response to the defects of nonmagnetic La_{Ba} as compared to magnetic Nd_{Ba} implies that a magnetic as opposed to an electronic mechanism is the dominant mechanism responsible for the depression of the transition temperature.[39] This magnetic pair-breaking mechanism, due to magnetic Ln_{Ba}, also leads to the creation of small normal regions, centered on the pair breaker, which serve as flux-pinning centers. In agreement with Hume-Rothery, it is well known that the solubility of lanthanides on the Ba site diminishes rapidly with decreasing size. This solubility can be limited by careful processing. The transition temperature of La123, processed in N_2 at high temperatures, yielded critical temperatures as high as 101 K.[40–42] It was also shown for La123 that La may substitute for Ba, but that Ba is too large to substitute for La.

Unfortunately, it is the case that the use of *low pressure* oxygen during the high temperature processing of Pr124 does not have the desired effect of reducing the Pr_{Ba} defect density without also introducing a high density of various chain-layer defects. Low pressure oxygen leads to the breakdown of the material. In fact, processing in very *high oxygen pressure* is the norm[24] for Ln124 materials, yielding superconductors, except for Pr124. One exception is the processing procedure involving a sol-gel technique, which was employed for the samples studied here.[23] Processing at lower oxygen pressures can also be successful[43] if small amounts of Ln are replaced by Ca. Thus, it is expected that the light lanthanide Ln124 materials will be more difficult to prepare than the heavy ones, a result confirmed by the experiment.

B. Charge compensation

In the case of Ln123, the potential at the Ba site is substantially insufficient to ionize any Ln to Ln^{3+}. Thus, substitution of $\mathrm{Ln}_{\mathrm{Ba}}$ apparently occurs in conjunction with negatively-charged oxygen added on an adjacent O(5) site in the chain layer, explaining why limitation of oxygen during critical high temperature processing serves as a control of $\mathrm{Ln}_{\mathrm{Ba}}$ substitution. An oxygen vacancy, similar to the O(5) site in Pr123, does not appear to be available in Ln124, due to the additional chain layer, see Fig. 1. However, there is another detail in which Ln123 and Ln124 differ; the addition of an oxygen and copper in the second chain layer substantially modifies the potential at the Ln124 Ba site. The bond length data of Mori *et al.*[44] were used to determine the bond valence sum[45,46] charges for the several ions of Y124;[47] the computed Ba-site potential is −21.37 V, while the ionization potential of Pr^{3+} is −21.62 V. This small difference indicates that, while Pr may substitute for Ba, Pr124 should exist as a stable, undefected, compound. However, taking this result literally means that successful fabrication of La124 (La^{3+} has an ionization potential of −19.18 V, ~2.4 V smaller in magnitude than that of Pr^{3+}) appears unlikely, except possibly with techniques which grow materials layer by layer, such as molecular beam epitaxy (MBE). Hence, conventional solid state reaction techniques for La124 appear extremely unlikely to be successful. We can find no evidence in the literature that La124 has ever been successfully prepared.

If, as we suspect, Pr^{3+} substitutes for Ba^{2+} in Pr124 without incorporation of additional oxygen, the resulting defect will have both hole-filling and pair-breaking characters. Since the Ln124 materials ideally are underdoped, the consequences of the combination of pair breaking and charge compensation will be difficult to overcome. These two effects should have different impacts on the material; pair breaking should produce a localized defect, with suppression of the superconducting transition temperature, while hole filling will modify the doping. It is somewhat surprising that the *typical* impact of pair breaking in HTSC materials is to yield an *insulator, not* a nonsuperconducting *metal*.

C. Pr substitution for Sr

Recently, it has been shown that $\mathrm{Pr}_{2-z}\mathrm{Ce}_z\mathrm{Sr}_2\mathrm{Cu}_2\mathrm{NbO}_{10}$ exhibiting granular superconductivity also contained a surprisingly large concentration (~23%) of Pr substituted for Sr ($\mathrm{Pr}_{\mathrm{Sr}}$) defects but rather less (~4%) of the reverse substitution, namely, Sr on the Pr site[48] ($\mathrm{Sr}_{\mathrm{Pr}}$). This result demonstrated that site exchange, even for comparatively similarly sized Pr^{3+} and Sr^{2+}, is less likely than previously thought.[49] The neutron diffraction experiments which found $\mathrm{Pr}_{\mathrm{Sr}}$ were made possible by the difference in neutron cross sections[50] of Pr and Sr. In this case, Pr^{3+} replaces Sr^{2+}, also suppressing superconductivity by two mechanisms: pair breaking and hole filling. Unfortunately, Pr and the common isotope of Ba have nearly the same neutron cross sections, and so are not easily distinguished.[50] Markvardsen *et al.*[51] carried out *polarized neutron* diffraction on nonsuperconducting single crystal Pr123 and found ~5% $\mathrm{Pr}_{\mathrm{Ba}}$ defects. Earlier observations are discussed in Ref. 52. Recent NMR measurements[53,54] have identified $\mathrm{Pr}_{\mathrm{Ba}}$ defects through the detection of the O(5)-site oxygen in Pr123. The proposition advanced[52] that $\mathrm{Pr}_{\mathrm{Ba}}$ (and $\mathrm{Pr}_{\mathrm{Sr}}$) breaks pairs, while Pr on the Pr site has no impact on the superconductivity, remains as the only explanation consistent with all the data.

D. Pr substitution for Ba in Ln123 materials

Shukla *et al.*[18] succeeded in the preparation of superconducting Pr123 and concurred with the Blackstead-Dow position that $\mathrm{Pr}_{\mathrm{Ba}}$ is responsible for the suppression of superconductivity but erroneously argued that the suppression is a result of hole filling by tetravalent $\mathrm{Pr}_{\mathrm{Ba}}$. Subsequent standing-wave x-ray measurements confirmed[55] the inelastic neutron diffraction data of Soderholm *et al.*[56] showing that Pr is present exclusively as Pr^{3+}, negating the Pr^{4+} hole-filling argument of Shukla *et al.* Kazimirov *et al.* also showed that ~20% Pr was present on the Ba site of Pr123, while they found no evidence (10% uncertainty) that Sm substituted[57] for Ba in Sm123, confirming again the experimental result that the large Ln ions substitute readily, while the smaller ones have very limited solubility. Tagami and Shiohara[58] reported the growth of $\mathrm{Pr}_{1+z}\mathrm{Ba}_{2-z}\mathrm{Cu}_3\mathrm{O}_{7-\delta}$ crystals with $0.06 \leqslant z \leqslant 0.29$, finding that with $z=0.06$, the material failed to exhibit superconductivity, even though the c-axis parameter (11.768 Å) approached that found by Zou *et al.* (11.77 Å) for relatively pure ($z \sim 0$) material. Thus, material with a defect content of a few percent may have nearly the lattice parameters of the undoped material but will still fail to exhibit superconductivity. These authors also compared the temperature dependent resistivity for three compositions and found that each exhibited semiconducting behavior; the crystal with $z=0.29$ at 70 K had a resistivity 6 *orders of magnitude larger* than that of the crystal with $z=0.06$. The sample with $z=0.14$ had an intermediate resistivity at 70 K, roughly 2 orders of magnitude larger than that of the crystal with $z=0.06$. Thus, increasing $\mathrm{Pr}_{\mathrm{Ba}}$ content correlates with dramatic increases in resistivity.

Several authors including Harris *et al.*,[59] Usagawa *et al.*,[60] and Xu *et al.*[61] have expressed views differing from ours above. Harris *et al.*[59] claimed that their *nonsuperconducting* Pr123, prepared with conventional processing techniques, contained 1% or less of $\mathrm{Pr}_{\mathrm{Ba}}$ defects, while the short c axis of their sample was consistent with a content of approximately $0.13\mathrm{Pr}_{\mathrm{Ba}}$. Previously, two of us estimated that as little as 5% $\mathrm{Pr}_{\mathrm{Ba}}$ would be sufficient to destroy superconductivity.[52] While an ~1% $\mathrm{Pr}_{\mathrm{Ba}}$ impurity level may be thought of as insignificant by some investigators, Usagawa *et al.*[60] argue that such a small content may be sufficient to eliminate superconductivity in Pr123.

A recent paper by Xu *et al.*[61] argues that $\mathrm{Pr_{Ba}}$ suppresses the superconductivity through an unknown electronic mechanism exclusive to Pr. Thus, there still exists controversy in the community as to how $\mathrm{Pr_{Ba}}$ may suppress superconductivity and the size of the critical dopant content, even though the predicted[52] superconductivity of Pr123 has been conclusively demonstrated in suitably prepared (low defect density) material.

Recent measurements[11,13,14] of the pressure dependence of the superconducting transition temperature of Pr123 *exclude* explanations that the presumed lack of superconductivity is a consequence of hybridization, in particular, arguments such as those advanced by Fehrenbacher and Rice.[63]

E. *c* axis length contraction in Pr123

Pr123 with a *c*-axis length less than 11.70 Å has never been reported to superconduct, while material with a longer *c* axis, near 11.77 Å, does. Substitution of the smaller $\mathrm{Pr^{3+}}$ ion for $\mathrm{Ba^{2+}}$ leads to a contraction of the *c* axis, and the rejected ions form impurity phases, especially $\mathrm{BaCuO_2}$, which is difficult to detect by x-ray diffraction but has a clear and easy-to-detect $g=2$ electron spin resonance (ESR) signature. Thus, detection of a $g=2$ ESR signal, coupled with an anomalously short *c*-axis lattice parameter, may be regarded as indicative of the partial substitution of Pr for Ba. In the case of Pr124, a sufficient content of $\mathrm{BaCuO_2}$ is present and has been detected by x-ray diffraction in polycrystalline materials, while some Pr occupies the Ba site.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $\mathrm{PrBa_2Cu_4O_8}$, prepared with a sol-gel process described in detail elsewhere,[23] were mounted on the bottom of a rectangular $\mathrm{TE_{101}}$ microwave cavity. In this position, the rf magnetic field (H_{rf}) is nearly uniform. The external applied magnetic field H could be rotated in the plane of the cavity bottom, to orientations either parallel to or perpendicular to the rf magnetic field. In the configuration $H \| H_{rf}$, the rf torque on paramagnetic spins vanishes. As a result, it is expected that the ESR intensity should also vanish. Of course, with $H \perp H_{rf}$, the ESR resonance intensity is maximized. In the case of ordered materials, if the *ferromagnetic* magnetization is parallel both to the applied field and to the rf magnetic field, the ferromagnetic resonance intensity also vanishes. However, for both *antiferromagnetic* and *weakly ferromagnetic* spin systems, the selection rules for the excitation of magnons are different. Generally, there are two degenerate magnon modes at $H=0$: one is excited with $H \| H_{rf}$ and the other is excited with $H \perp H_{rf}$. The degeneracy is lifted by the application of a magnetic field, and a superposition of these magnon modes may be excited for arbitrary orientations of H relative to H_{rf}. Thus, the selection rules allowed the identification of ferromagnetic ordering versus antiferromagnetic ordering.

The microwave spectrometer we employ does not utilize magnetic field modulation; as a result, the detected signals are proportional to the absorption, not to the derivative of the absorption signal with respect to magnetic field. This feature was especially useful in the studies presented below because several of the observed signals exhibited extremely large linewidths and would almost certainly have been undetectable with conventional modulation techniques.

III. EXPERIMENTAL RESULTS

Figure 3 illustrates the power dissipation observed at 10 K in Pr124 with $H \perp H_{rf}$, in the resonance configuration, and also for $H \| H_{rf}$. These data have two features: the first is the broad dissipation observed even at $H=0$, which falls off with increasing H; the second with $H \perp H_{rf}$ is a comparatively narrow $g=2$ resonance observed superimposed on the broad signal. This narrow signal is consistent with paramagnetic Cu in the impurity phase $\mathrm{BaCuO_2}$. It is well established that the *paramagnetic* Cu in Ln123 and other cuprate materials generally does not exhibit a resonant microwave response, a result believed due to extremely rapid relaxation which broadens any potential resonance to undetectability at conventional microwave frequencies. Several reports of Cu resonance have been attributed to a variety of sources[62] but have likely resulted from impurity phases.

The broad lines are characteristic of antiferromagnetic resonance in magnetically ordered cuprate planes. The magnon energy gap exceeds the microwave photon energy, so only the high-field part of the lines is observed. At a sufficiently high excitation frequency (here only 13 GHz), the entire line would be in evidence. In addition to the data, Fig. 3 includes nonlinear least-squares fits to the two lines and the composite response. It was necessary to use a Dysonian lineshape function to describe the ESR because the anisotropic response was characteristic of resonance in a *conducting* material. The anisotropic line shape $[y(H)]$ used here was introduced by Dyson,[64] and Poole[65] and is expressed as

$$y(H) = \frac{1 + T_2\gamma(H - H_0)}{2[1 + T_2^2\gamma^2(H - H_0)^2]}.$$

Here, γ is the gyromagnetic ratio, H_0 is the field for resonance, T_2 is a relaxation time, and H is the applied field. The superimposed (summed) ESR and antiferromagnetic resonance (AFMR) line shapes represent the data, with very small errors.

In Fig. 3, the dissipation data with $H \| H_{rf}$ at 10 K are also presented along with the fits to the two magnetic resonances and the composite response; in this case, the ESR signal is greatly reduced in intensity but is still detectable. What this implies is that the Cu exists in an environment in which the local field has two sources, the applied field and a field due to neighboring ordered moments which are not parallel to the applied field. The little-changed broad resonance confirms its origin in either antiferromagnetism or weak ferromagnetism. The anisotropic response characteristic of a conductor, combined with the presence of a local field, suggests that some of the detected Cu may be part of the Pr124 lattice in chain segments, as opposed to part of a distinct chemical impurity, $\mathrm{BaCuO_2}$.

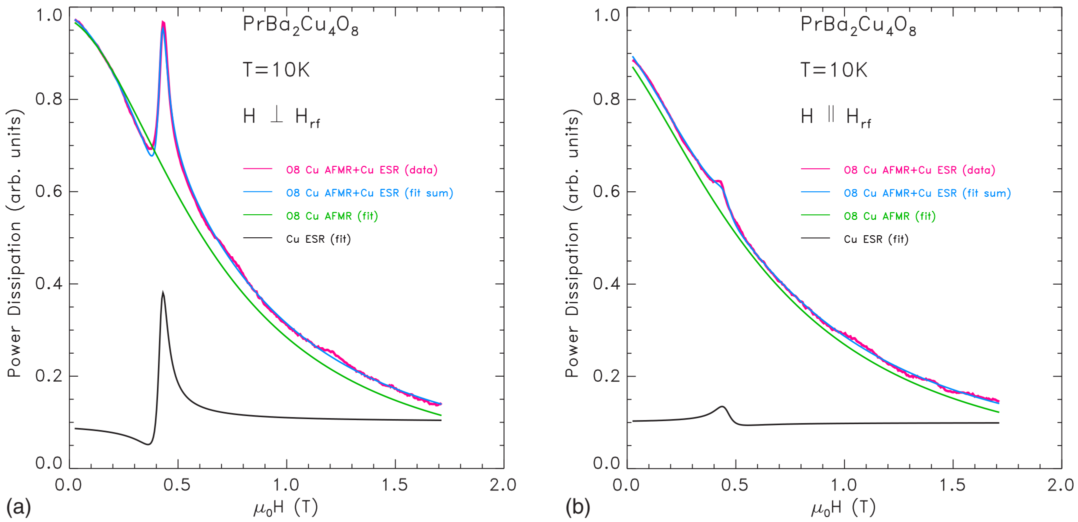

FIG. 3. (Color online) Microwave (13 GHz) power dissipation at 10 K in two configurations: in the left panel, $H_{rf} \perp H$ in the conventional resonance configuration, while in the right panel we have $H_{rf} \| H$ in a configuration for which the rf torque normally vanishes, except for antiferromagnets. The data include a narrow ESR attributed to Cu in $BaCuO_2$, while the broad resonances are due to the antiferromagnetic resonance in the ordered cuprate planes. In each case, the individual fits to the lines and the composite (summed) fits are displayed. The asymmetry of the ESR response indicates metallic behavior, while the small resonance in the case with $H_{rf} \| H$ indicates that these spins also experience a *local field* which is not parallel to the applied H. This suggests that the $BaCuO_2$ is in intimate contact with the O8 material, likely on grain boundaries.

Figure 4 presents magnetic resonance data for both magnetic field configurations at 20 K. The broad antiferromagnetic lines are little changed from the 10 K data, a consequence of an ordering temperature much higher than 20 K. The ESR response is substantially reduced, by ~50%, since it arises from a paramagnetic response with a characteristic $1/T$ intensity. The maximum temperature to which this antiferromagnetic resonance could be observed, see Fig. 5, was ~80 K; as a result, we estimate the Cu Néel temperature to be $T_N \sim 80$ K. The data of Fig. 5 are compiled with a common gain scale, so that the several scans at different temperatures can be directly compared. These data are organized with a common offset at $H=0$ because the available field is insufficient to determine a no-signal base line at high fields. The signal at low temperatures is large, and as the signal tends to vanish with increasing temperature, this presentation yields a roughly field-independent scan for temperatures above the magnetic transition temperature. Since the impurity Cu ESR signal intensity varies as $1/T$, it is prominent only at low temperatures.

IV. DISCUSSION

These several results confirm the conducting character of Pr124, while eliciting no evidence for even granular superconductivity. The (insulating) cuprate-plane antiferromagnetic response was also identified. This is a surprise, since according to typical phase diagrams, conductivity and antiferromagnetism are expected to be mutually exclusive. What this suggests to us is that the observed conductivity arises in, or in the vicinity of, the double chain layers, and any claimed charge transfer to the cuprate planes was insufficient to produce a fully conducting state. This conclusion appears to be completely in agreement with the results of single crystal resistivity measurements by Horii *et al.*[25] Their resistivity measurements on single crystals of Pr124 yielded remarkable results; the conductivity parallel to the chains (σ_b) is as much as 2 orders of magnitude higher than the conductivity perpendicular to the chains (σ_a). The c-axis conductivity (σ_c) is smaller than σ_a. It seems reasonable to conclude that this anomaly, nearly one-dimensional conductivity, is associated

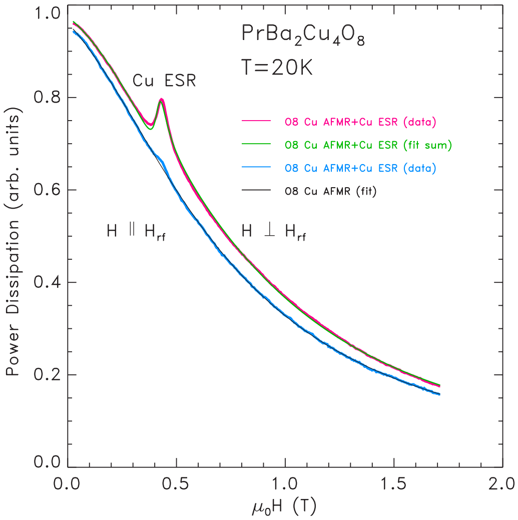

FIG. 4. (Color online) Resonance data at $T=20$ K with $H \perp H_{rf}$ (upper curve) and with $H \| H_{rf}$ (lower curve). These data show that the antiferromagnetic responses are little different in the two configurations. In addition, the ESR is substantially reduced in intensity, relative to the $T=10$ K data, as expected for a paramagnet. Fits to the data are plotted as well as the data.

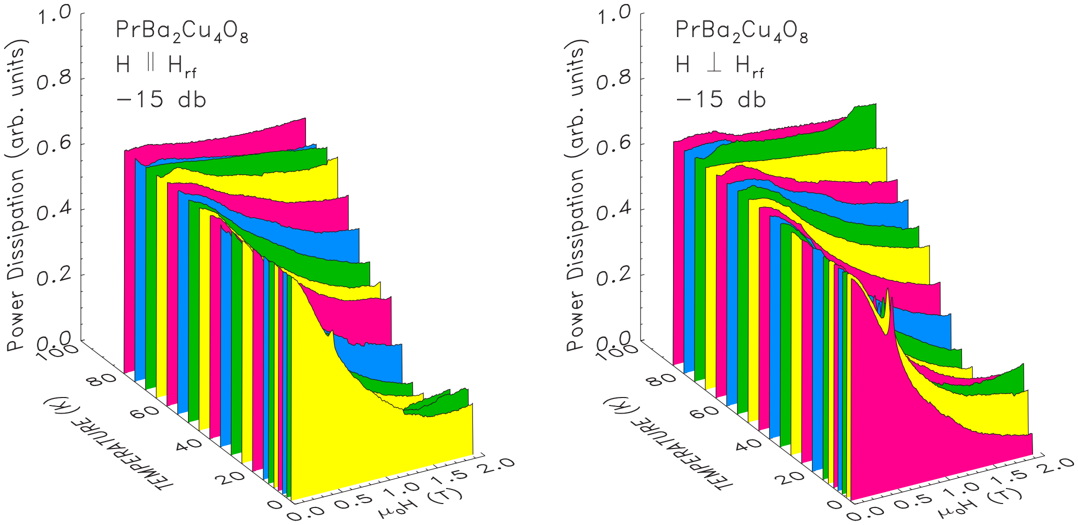

FIG. 5. (Color online) Temperature dependence of the AFMR signal on an arbitrary (but consistent) scale as a function of applied field, H for both resonance (right panel) and nonresonance configurations (left panel). The AFMR signal vanishes for temperatures of ~80 K, establishing the ordering temperature. In the resonance configuration, $H \perp H_{rf}$, the Cu ESR is identified at low temperatures; otherwise, the spectra for the two configurations are similar.

with the unique double chain layers characteristic of this structure. As far as we know, this is the only example of a cuprate material which does not exhibit a superconducting-insulator transition but instead exhibits a metal-insulator transition.

The question remains as to why this material fails to exhibit superconductivity. Perhaps the more focused question to answer is why there seems to be no charge transfer to the cuprate planes.

V. CONCLUSIONS

The neutron diffraction studies of Li *et al.*[66] did identify order in the Pr sublattice of Pr124 but failed to identify cuprate-plane magnetic order. Their magnetization data contained a feature near 200 K, which was interpreted as possibly being due to Cu order. The NMR results of Fujiyama *et al.*[33] demonstrate the presence of ordered cuprate planes, at a temperature much higher than found in these measurements. This difference may be attributable to the differing preparation procedures and resultant $\mathrm{Pr_{Ba}}$ defect contents.

Pr124 exists in a form which is metallic at low temperatures without becoming superconducting, a result apparently unique among the cuprates. While it is not possible for us to determine if the Cu ESR signal arises exclusively either from $\mathrm{BaCuO_2}$ or in part from isolated chain-layer defects, the variation of the c-axis parameter is consistent with variable $\mathrm{Pr_{Ba}}$ defect content. The Ba-site defects, $\mathrm{Pr_{Ba}}$, result in a contraction of the c axis. Because the rejected Ba is essentially insoluble on Pr sites, an impurity phase must form. $\mathrm{BaCuO_2}$ was identified by x-ray diffraction as an impurity phase and exhibits the appropriate Cu ESR.

Despite the lack of superconductivity, Bäckström *et al.*[67] recently identified the appearance of a pseudogap near 160 K, associated with a change in the Ba-phonon width, possibly due to cuprate-plane preformed pairs. The issue of what causes the existence of the pseudogap is a continuing source of controversy. Shibauchi *et al.*,[68] in a widely cited paper, attribute the pseudogap to the development of a state which competes with the superconducting state. Recently, a similar claim was made by Tanaka *et al.*[69] However, Valla *et al.*,[70] argue for a different conclusion, one featuring preformed pairs. The general issue remains unresolved. Since in Pr124 the planes do not even conduct (they are magnetically ordered), any preformed pairs must be formed in (or near) the BaO layer, where they were detected. The question as to how magnetic pair-breaking defects usually result in insulators, but do not do so in Pr124, may have a simple answer. We speculate that preformed pairs, broken by magnetic scattering, result in quasiparticles which are localized charge carriers. The *double chain layer* of the Ln124 materials may provide a sort of isolation barrier to pair breaking, due to the short c-axis coherence length. The point is that $\mathrm{Pr_{Ba}}$ on *one side* of the double chain layer may be incapable of breaking pairs on *both sides* of the chain layers, in the neighboring BaO layers. Thus, the one-dimensional chain conductivity will be only partially disrupted, yielding a metal, not a superconductor. These results are consistent with a view that chain layers alone do not superconduct. In turn, the superconductivity of Pr123 cannot be solely attributed to the chain layers. This means that Pr on the Pr site has no negative impact on the superconductivity of Pr123, but Pr on the Ba site does.

Proposals

We propose that, following the results of Usagawa *et al.*,[15] it may be possible to grow superconducting films of Pr124 on single crystal (110) oriented substrates of Y124 with pulsed laser deposition. Another technique which may be effective is epitaxial growth via MBE.

Finally, if Mazin's view as to the origin of superconductivity[71] in Pr123 were correct, Pr124 would be a superconductor and Pr123 would always superconduct. The superconductivity of Pr123 has often led to the speculation that Ba substitutes for Pr (Ba_{Pr}), a proposal which has no experimental support; there is no evidence even for La and Ba to site exchange[40,41,72] in La123.

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