Magnetotransport and magnetism in single-crystal $PrBa_2Cu_3O_{7-\delta}$

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The $PrBa_2Cu_3O_{7-\delta}$ (Pr 123) system is known to exhibit antiferromagnetic ordering of the Cu spins in the Cu-O planes and chains, in addition to the observed antiferromagnetism due to the ordering of the Pr ions. The antiferromagnetism of the Cu-O planes is generally associated with the insulating nature of transport in Pr 123 and electrical conduction is believed to result through ''hopping'' transport between disordered Cu-O chain segments. However, the possible effects of magnetic ordering in the Cu-O chains on transport properties have not been discussed. If the Cu-O chains play a dominant role in the electrical transport (as suggested by many of the popular theories), then the magnetic ordering of the chains should also be seen in the transport properties. We present magnetization and magnetotransport measurements on single crystal Pr 123 samples which suggest that the magnetism associated with the Cu-O chains does indeed mediate transport in this system. These results confirm that the chains play a significant role in the transport properties and underscore the need for further study of the interplay between magnetism and transport in Pr 123. [S0163-1829(96)01742-0]

I. INTRODUCTION

$PrBa_2Cu_3O_{7-\delta}$ is unique among the ''123'' cuprates in that it is nonmetallic and does not exhibit a superconducting transition. The insulating nature of Pr 123, together with its ideal lattice match to the superconducting 123 materials suggest this material as a good candidate for a barrier layer in tunnel junctions. Such junctions have been fabricated and, in some cases, have resulted in the observation of an anomalously long proximity effect.[1,2] Recently, Cucolo *et al.*[3] have reported the successful growth of planar $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta'}/YBa_2Cu_3O_{7-\delta}$ junctions in which evidence for S-I-S quasiparticle tunneling is observed. These observations are difficult to reconcile with experiments suggesting that variable range hopping (VRH) transport dominates in the $PrBa_2Cu_3O_{7-\delta}$ system. Understanding transport in Pr 123 is crucial if real applications are to be achieved. In this paper we present magnetotransport measurements which show that the magnetism associated with the Cu-O chains affects the transport properties of this system. The implication of our results for variable range hopping between disordered Cu-O chain segments as a dominant mechanism of conduction in this system are discussed.

II. THEORY

Several models have been proposed which incorporate mechanisms such as magnetic pair breaking,[4] hole filling,[5–7] and hole localization[8] to explain the lack of superconductivity and/or the nonmetallic behavior of Pr 123. Each of these explanations places certain restrictions on the allowed valency of the Pr ion. At present, none of these theories can be simultaneously reconciled with the experimental results obtained from inelastic neutron scattering,[9] Mössbauer,[10] and x-ray-diffraction[11] measurements which have provided conflicting evidence concerning the valency of the Pr ion. However, many of the theories agree that hybridization of Pr $4f$ orbitals with Cu-O valence band states is the underlying source of the anomalous behavior observed in Pr 123.

Maple *et al.*[12] were among the first to suggest that hybridization of Pr $4f$ orbitals with valence band states was the source of the nonmetallic behavior and the absence of superconductivity in Pr 123. Experimental evidence for the hybridization of Pr $4f$ orbitals with Cu-O valence band states includes the observations of an anomalous pressure dependence of T_c in mixed $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds,[13] the small (as compared to the free ion value of Pr^{3+}) effective moment obtained from susceptibility measurements[5] and the complex line shapes of resonant-photoemission[14] and inelastic neutron scattering measurements.[8] In addition, band structure calculations[4] have shown the Pr $4f$ levels to be near in energy to that of the Cu-O valence band levels. Fehrenbacher and Rice[15] have developed a theory based on hybridization of localized states which accounts for the semiconducting behavior of this material. Liechtenstein and Mazin[16] noted that this model failed to explain the results of doping studies[17,18] indicating that the suppression of T_c with Pr concentration levels is dependent on the host rare earth. In their interpretation of the Fehrenbacher and Rice model, Liechtenstein and Mazin describe the hybridized state as a dispersive band, rather than a well localized phenomena. Both models assume delocalized states among Cu-O chain segments with the insulating nature of Pr 123 being attributed to oxygen disorder.

Hybridization of rare earth impurity $4f$ orbitals with conduction band levels in metals is known to be the source of interactions which produce anomalous magnetotransport properties[19] and which can induce antiferromagnetism in both the carrier spins and the magnetic ions.[20,21] Self-consistent, spin-polarized band-structure calculations suggest that the hybridization of the Pr $4f$ orbitals in Pr 123 introduces excess spin into the Cu-O planes.[4] Recent NMR stud-

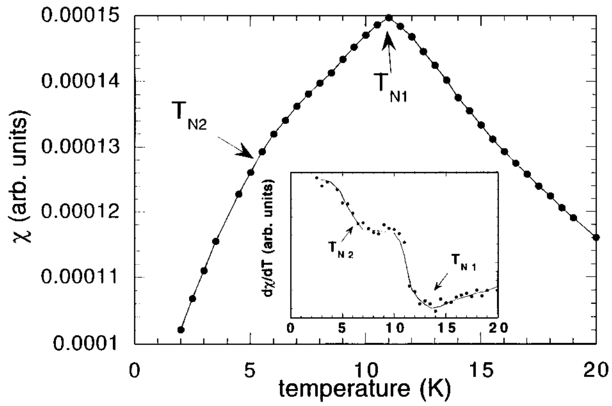

FIG. 1. Temperature dependence of the magnetic susceptibility for a single crystal sample of $PrBa_2Cu_3O_{7-\delta}$ (sample one) in an applied field of 2 T showing the antiferromagnetism associated with the Pr ions (T_{N1}) and Cu-O chains (T_{N2}). The solid line is a guide to the eye. The inset shows the data plotted as $d\chi/dT$ versus temperature.

ies have provided evidence for a Pr induced ferromagnetic coupling between the Cu-O planes.[22] Based on these results, we consider antiferromagnetic interactions mediated by the Cu-O planes a possible source of the ordering observed in the Pr ions at anomalously high temperatures between 12–17 K.[7,23–25] The Cu spins in the Cu-O planes in highly oxygenated Pr 123 are also antiferromagnetic with a Néel temperature near 300 K.[26] This is reminiscent of the oxygen deficient superconducting 123 materials which exhibit antiferromagnetism in the Cu-O planes at temperatures considerably higher than 300 K. A third magnetic transition has also been observed near 5 K by Kebede *et al.*[7] in both their specific heat and susceptibility measurements. There is considerable experimental evidence which suggests that this low temperature transition is related to the ordering of the Cu-O chain spins.[27,28] If the 5 K transition is indeed due to antiferromagnetism in the Cu-O chains then (assuming chain segments are an integral part of electrical conduction in this system) it should also be seen in the magnetotransport properties.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In order to further understand the relationship between transport and magnetism in the Pr 123 system, we have measured the magnetoresistance and magnetization of single crystal samples. The Pr 123 single crystals reported on here were grown using a self-decanting flux method.[29] Magnetotransport measurements were made in a 13 T superconducting magnet with the field applied parallel to the crystals' c axes and the current applied along the a-b planes. A hall sensor mounted on the sample holder was used to orient the crystals in field. Magnetization measurements were performed in a dc superconducting quantum interference device susceptometer manufactured by Quantum Design.

Pr 123 has proven to be a complex magnetic system. Figure 1 shows the magnetic susceptibility as well as $d\chi/dT$ for a single crystal Pr 123 sample (sample one) at low temperatures. The data clearly show evidence of two magnetic transitions. These results are in excellent agreement with measurements we have obtained on polycrystalline samples and with those of by Kebede *et al.*[7] also on polycrystalline samples. The onset of the higher temperature transition occurs at approximately 13 K and is consistent with the antiferromagnetic ordering of the Pr ions observed in elastic neutron diffraction,[24] specific heat,[7] and susceptibility[24,25] measurements. The onset of the lower temperature transition occurs at approximately 6 K and is attributed to antiferromagnetic ordering of Cu spins in the Cu-O chains. Rosov *et al.*[28] have studied this transition in oxygen deficient single crystal samples and have shown that the onset of antiferromagnetism in the Pr 123 Cu-O chains is strongly dependent on oxygen content. Their results indicate that the Néel temperature of the Cu-O chains decreases with increasing oxygen content. This would account for the suppression of the Néel temperature observed in our samples as opposed to the >80 K transition observed in Rosov *et al.*'s results, since our samples are estimated (based on x-ray-diffraction studies) to have an oxygen content $7\text{-}\delta=6.8$–6.9. The reason for stronger antiferromagnetism in the Cu-O chains with increasing disorder is unclear, however, one explanation is that the disordered segments are more easily coupled to the antiferromagnetic Cu-O planes.

If Cu-O chain segments play a major role in the transport properties of this system, as suggested by Rice and Fehrenbacher[15] and Liechtenstein and Mazin[16], then magnetic ordering in the Cu-O chains must certainly be observed in transport measurements. In particular, one would expect to see a significant change in the temperature dependence of both the resistivity and the magnetoresistance near the Néel temperature of the Cu-O chains. Since the Cu-O planes are presumed to be antiferromagnetic insulators, then if the chain segments consist of delocalized states a dominant contribution to the resistivity is expected to occur at the ''ends'' of the disordered chain segments where the current must pass through the insulating Cu-O planes. It is due to these regions that one might expect to see variable range hopping behavior between disjointed chain segments, with antiferromagnetic fluctuations contributing to the conductivity at temperatures slightly above the Néel temperature of the Cu-O chains. In this picture, we expect that the antiferromagnetic ordering of the Cu-O chain segments makes it energetically less favorable for a charge carrier to ''hop'' to a nearby segment, thereby increasing the hopping distance. We would, therefore, expect that the antiferromagnetism of the Cu-O chains would adversely affect electrical transport.

The resistivity of Pr 123 is typically analyzed in terms of variable range hopping[30,31] which predicts a temperature dependence of the form $R=R_0\exp(T_0/T)^p$. The parameter p determines the dimensionality of the system with $p=1/4$ for three-dimensional (3D) hopping and $p=1/3$ for 2D hopping. It should be emphasized that the resistivity data reported in the literature is characterized by wide variability in the determined p values. This, together with the uncertainty concerning the nature of transport in the chains, leads us to conclude that the exact nature of electrical conduction in this system is undetermined, with no decisive evidence to support *exclusively* VRH (either 2D or 3D) and/or activated transport, rather than a composite of insulating and metallic behavior. However, in order to present our data in a way consistent with previously published results we analyze the

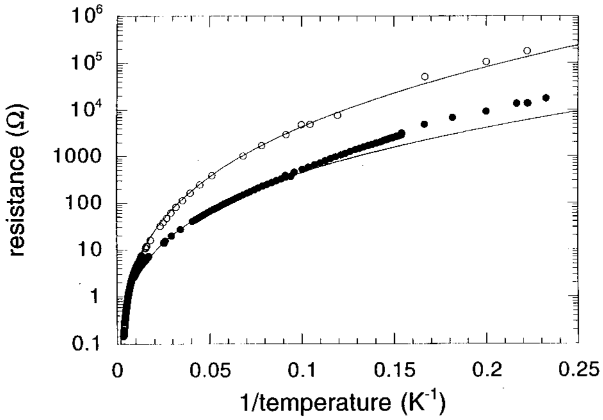

FIG. 2. Resistance versus temperature for single crystal samples (samples 1 and 2) of $PrBa_2Cu_3O_{7-\delta}$. The solid lines represent fits of the 3D VRH expression data above the ordering temperature of the Cu-O chains.

temperature dependence of our resistivity measurements in terms of 3D VRH and simply note that we were able to obtain equally good fits using 2D VRH and activated expressions. Figure 2 shows the resistance versus temperature data for two single crystal samples (samples 1 and 2). The solid lines in the figure represent the fit of a 3D VRH expression to the data above 15 K (where the effects of the antiferromagnetic fluctuations are presumed to be negligible). In both samples, the low temperature data fall above the fitted curve which suggests that the antiferromagnetism associated with the Cu-O chains adversely affects transport in this system. Again, similar results were obtained when we tried to fit the expressions for 2D VRH and semiconducting behavior to the data. It is interesting to note that the effect is somewhat suppressed in sample 2. This sample also obtained a resistivity that was an order of magnitude larger than sample 1. A larger effect was also seen in a third sample which exhibited a resistivity comparable to sample 1. The high resistivity, the observation of a slightly increased Néel temperature (compared to sample 1) and sample 2's history (which included a high temperature anneal in air) are all evidence of an increased oxygen deficiency. Since the disorder associated with the Cu-O chains is presumably the source of the insulating character of Pr 123, it is perhaps not surprising that the effects on the transport properties of the antiferromagnetic transition are less pronounced in an oxygen reduced sample where the chains are less effective in ''shorting'' the current.

Figure 3 plots the magnetic field dependence of the magnetoresistance data for sample one at $T=6$ and 4.5 K, above and below the low temperature magnetic ordering transition, respectively. The field was applied parallel to the crystal's c axis. The solid lines represent fits of an H^2 field dependence over the range of data to which a satisfactory fit could be obtained. The results indicate that at low temperatures (below the ordering temperature of the Cu-O chains) the magnetoresistance increases quadratically at low fields but then increases more slowly above 6 or 7 T. Above the magnetic ordering temperature, an H^2 dependence is observed up to the highest field applied (10 T). This results in a ''peak'' in the temperature dependence of the magnetoresistance as shown in Fig. 4 for both samples 1 and 2. Comparison of the

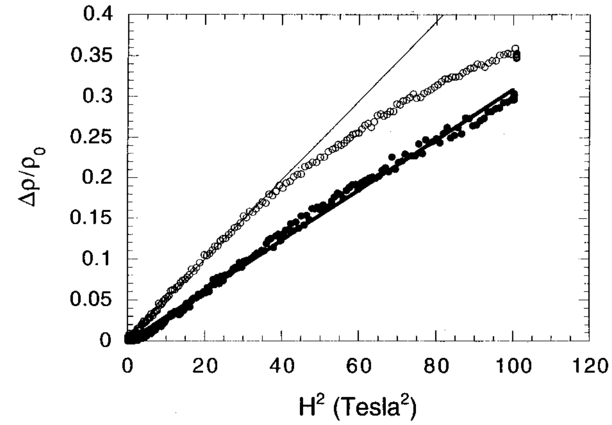

FIG. 3. Magnetoresistance of a single crystal sample of $PrBa_2Cu_3O_{7-\delta}$ (sample 1) at $T=6$ K (filled circles) and $T=4.5$ K (open circles) above and below the ordering temperature of the Cu-O chains. The solid lines represent fits of an H^2 field dependence to the data over a range to which a satisfactory fit could be obtained.

data obtained from the two samples reveals that the effect is slightly suppressed in sample 2 as might be expected due to the increased oxygen deficiency of this crystal. These results are consistent with those of Lee *et al.*[32] and Iwasaki *et al.*[33] who have observed large positive H^2 dependent magnetoresistances in $PrBa_2Cu_3O_{7-\delta}$ thin film samples. Lee *et al.* interpret their results as evidence for a coexistence of metallic and nonmetallic hopping conduction in the Pr 123 system.

The magnetoresistance of thin film samples of $PrBa_2Cu_3O_{7-\delta}$ has also been measured by van Ancum *et al.*[34] who interpret their results in terms of VRH which predicts a ''crossover'' from low field behavior $[\rho(H)/\rho(0) \propto \exp(H^2)]$ to high field behavior $[\rho(H)/\rho(0) \propto \exp(H^{0.5})]$ at a critical field $H_c(T)$. For comparison, we show the results obtained from applying van Ancum *et al.*'s analysis to our data in Fig. 5. Although we obtain similar trends as van Ancum *et al.* (i.e., a crossover from ''low-field'' to ''high-field'' behavior), in order to get a reasonable

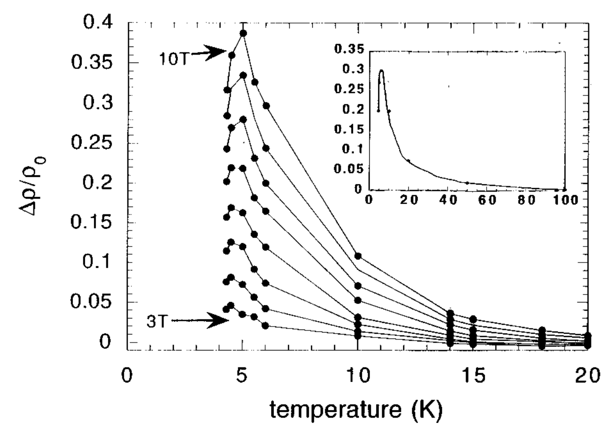

FIG. 4. Magnetoresistance versus temperature plot of sample one for various applied fields. The inset shows the data obtained from sample two in an applied field of 10 T. The field was applied parallel to the crystals' c axes.

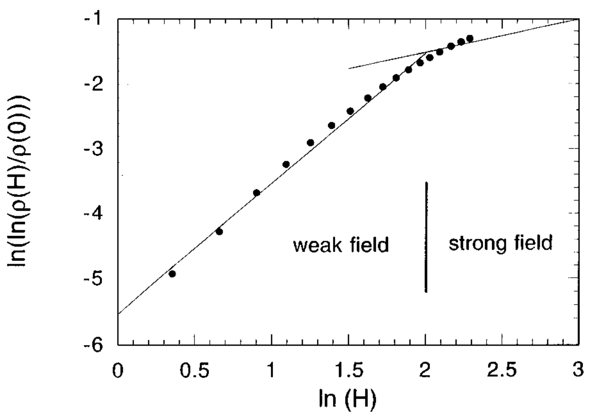

FIG. 5. Results obtained from the fits of VRH expressions for magnetoresistance at $T=4.3$ K. The predicted expressions are $\rho(H)/\rho(0)\propto\exp(H^2)$ for low fields while for high fields $\rho(H)/\rho(0)\propto\exp(H^{0.5})$.

fit to the expected high field behavior we must define a critical field $H_c\sim7.4$ T which is inconsistent with the 4.5 T value predicted at 4.3 K from van Ancum *et al.*'s results. This inconsistency may be attributable to differences in sample quality or perhaps even to a difference in dimensionality; they assume 2D VRH for their samples based on a calculation of a hopping distance along the c axis, $r_z>100$ nm, which is greater than the thickness of their films.[35] In their report, van Ancum *et al.* do not comment on whether they were able to obtain a satisfactory fit using an H^2 field dependence. However, the fact that we obtain excellent fits using an H^2 dependence (above the Néel temperature of the Cu-O chains) together with the various independent observations of H^2 behavior questions whether a strict VRH picture is appropriate in describing transport in Pr 123.

The coincidence of the 5 K magnetic transition with features in the magnetotransport data clearly indicates that the Cu-O chains play a crucial role in the transport properties of the Pr 123 system. The zero-field resistivity results are not inconsistent with models which describe transport in this system in terms of hopping between localized states on disordered chain segments. However, this picture presents a puzzle when one considers that *both* the application of a magnetic field as well as the antiferromagnetic ordering of the Cu-O chains adversely affect the conductivity, suggesting that antiferromagnetic fluctuations play a role in the hopping mechanism. The observation of positive H^2 dependent magnetoresistance adds a further complication. If, as suggested by Lee *et al.*, the observed H^2 dependence is due to classical orbital magnetoresistance observed in metallic and some semiconducting systems, then our results are more easily understood. The coincidence of a peak in the magnetoresistance with the antiferromagnetic ordering of the Cu-O chains suggests a fundamental change in the band structure of the system, perhaps due to the doubling of the unit cell, which is associated with the onset of high field saturation magnetoresistance.

IV. CONCLUSION

In summary, we have shown that the antiferromagnetic transition seen near 5 K in Pr 123 is coincident with a peak in magnetoresistance and a deviation from 3D VRH in the temperature dependent resistivity. These results support theories which argue that the Cu-O chains play a crucial role in the transport properties of this system. While there have been several studies which have investigated the antiferromagnetism in the Cu-O planes and the Pr ions, we are aware of only Rosov *et al.*'s[28] study of the low temperature antiferromagnetism in the Cu-O chains as a function of oxygen content. This work focused primarily on oxygen deficient samples in which the Cu-O chains ordered at much higher temperatures and did not explore the effects of the magnetism on transport properties. Our results underscore the need for a more thorough study over a wide range of oxygen contents in order to determine the exact nature of the interplay between magnetism and transport in this system.

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[35] The hopping distance, r, is a function of the radius of the localized wave function a_H. Van Ancum *et al.* reference a value of $a_H=8.5$ nm as determined by Kabasawa *et al.* (Ref. 30) for the calculation of r. This value is inconsistent with the prediction of Mott's criterion ($N^{1/3}a_H=0.26$ at a metal/insulator transition) for this material. As Kabasawa *et al.* point out, for the 2D case $N^{1/2}a_H\sim 0.85$ based on the density of states estimated from the relation $N_F=k_BT_0/C\alpha^2$, (N of the order of N_F) where C is a constant and T_0 and α ($a_H=1/\alpha$) are determined from I-V measurements. Clearly, this result is inconsistent with the observed insulating nature of $PrBa_2Cu_3O_{7-\delta}$. For the 3D case, if we use the density of Cu-O chain states as estimated by Matsuda *et al.* (Ref. 6), then we obtain $N^{1/3}a_H\sim 7$.