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Magnetic ordering and transport properties of $PrBa_2Cu_4O_8$

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We present studies of the thermal, magnetic, and electrical transport properties of polycrystalline $PrBa_2Cu_4O_8$ prepared at ambient oxygen pressure. Measurements of the low-temperature specific heat $C(T)$ and magnetic susceptibility $\chi(T)$ show similar results as in $PrBa_2Cu_3O_7$. An anomaly observed at 17 K in $C(T)$ and $d\chi/dT$ may be due to the antiferromagnetic ordering of the Pr sublattice. The upper limit of the entropy associated with the magnetic ordering is estimated to be 6.6 J/mol K. The free magnetic moment from a simple Curie-Weiss fit is $3.11\mu_B$. These similarities in magnetic properties of $PrBa_2Cu_3O_7$ and $PrBa_2Cu_4O_8$ suggest that the magnetic coupling mechanism might be mainly associated with the CuO_2 planes. The resistivity $\rho(T)$ is nearly metallic from 1.5 to 300 K. Comparisons of samples prepared by different methods suggest that the anomaly in resistivity around 200 K may be extrinsic. The behavior of $\rho(T)$ is rather puzzling and cannot be explained simply by a dimensional crossover of charge transport arising from the double CuO chains. Other similarities and differences of the mentioned physical properties between $PrBa_2Cu_4O_8$ and $PrBa_2Cu_3O_7$ are stressed as well. [S0163-1829(97)01845-6]

I. INTRODUCTION

Since the discovery of high-temperature superconductors, Pr substitution in $YBa_2Cu_3O_7$ (Y123) has stimulated much interest. The absence of superconductivity, the insulating electrical behavior, the anomalously high Néel temperature T_N, and the large linear term γ of the specific heat in $PrBa_2Cu_3O_7$ (Pr123) all remain unsolved issues.[1] Furthermore, whether these unusual properties are related to each other still lacks general agreement.[2] In a very recent paper,[3] the metallic resistivity and 80 K superconductivity of a Pr123 single crystal was reported. These results contradict other reports on Pr123 single crystals[4] and are certainly controversial. To try to solve these puzzles, $PrBa_2Cu_4O_8$ (Pr124) has been one of the most desirable compounds. Since the structure of Pr124 is very similar to that of Pr123 except the double CuO chain instead of a single CuO chain, comparative studies of Pr123 and Pr124 could be very informative. Nevertheless, the synthesis of Pr124 has been known to be rather difficult, and only a few successful syntheses of relative pure Pr124 by the O_2-HIP (hot isostatic pressing) method were reported.[5,6] Very recently, we have successfully synthesized Pr124 at ambient oxygen pressure.[7] Judging from electrical resistivity $\rho(T)$ and other properties, the sample quality is comparable to that by HIP.[6–9]

In this paper, we report the studies of low-temperature specific heat C and the magnetic susceptibility χ of Pr124 prepared at ambient oxygen pressure. The electrical resistivity $\rho(T)$ is also discussed. Experimental data show that both C and χ of Pr124 are very similar to those of Pr123. An unambiguous anomaly in C and χ occurs at 17 K, possibly due to the antiferromagnetic ordering of Pr as in Pr123. The analyses of data reveal a picture of mixed valent Pr consistent with a recent theory of hybridization.[10,11] However, $\rho(T)$ of Pr124 shows metallic behavior at low temperatures, which is different from the insulating $\rho(T)$ of Pr123. Although this metallic behavior could be from charge transport of the double CuO chains,[9] it is argued that a complete understanding of $\rho(T)$ is still unavailable.

II. EXPERIMENTS

Very recently, we have successfully synthesized polycrystalline Pr124 at ambient oxygen pressure by the nitric pyrolysis method, and the details were described in Ref. 7. The powder x-ray-diffraction pattern in Fig. 1 shows a nearly single ''124'' phase with lattice constants $a = 3.879$ Å, $b = 3.902$ Å, and $c = 27.28$ Å. The inset of Fig. 1 is the low-angle diffraction patterns of Pr124 and Pr123. The indexed peak (002) in $PrBa_2Cu_4O_8$ corresponds to (001) in $PrBa_2Cu_3O_7$ due to the doubling of lattices in the c-axis direction. Because of the minor structural difference, the former should appear at around 6.5° while the latter is at 7.5°. Indeed, the inset of Fig. 1 shows the expected patterns. It is therefore plausible that the main phase in our sample is

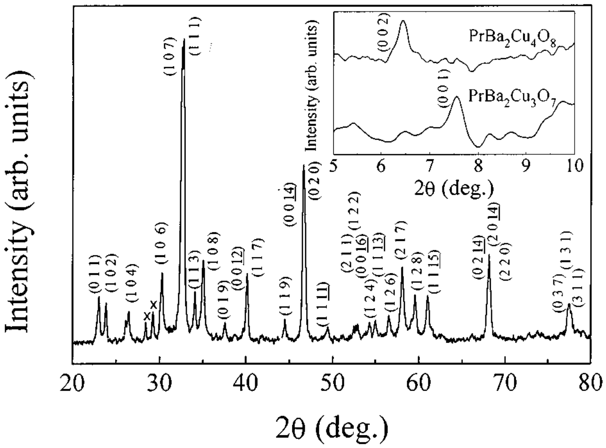

FIG. 1. X-ray-diffraction patterns of $PrBa_2Cu_4O_8$. The symbol × indicates peaks associated with impurity $BaCuO_2$. Inset: low-angle x-ray-diffraction patterns of $PrBa_2Cu_4O_8$ and $PrBa_2Cu_3O_7$. The index (002) in $PrBa_2Cu_4O_8$ corresponds to (001) in $PrBa_2Cu_3O_7$ due to the doubling of lattices in the c-axis direction.

''124'' and the amount of Pr123 negligible. Thermogravimetric analyses also reveal a thermal stability distinct from that of Pr123.[7] $\rho(T)$ was measured by the standard four-probe method from 1.5 to 300 K. $C(T)$ was measured from 0.5 to 40 K with a ^{3}He thermal relaxation calorimeter using the heat-pulse technique at zero external magnetic field.[12] $\chi(T)$ measurements were performed from 4.2 to 400 K with a magnetically shielded Quantum Design $MPMS_2$ superconducting quantum interference device (SQUID) magnetometer at the magnetic field $B_a = 1$ kOe.

III. RESULTS AND DISCUSSIONS

A. Magnetic ordering of Pr at 17 K

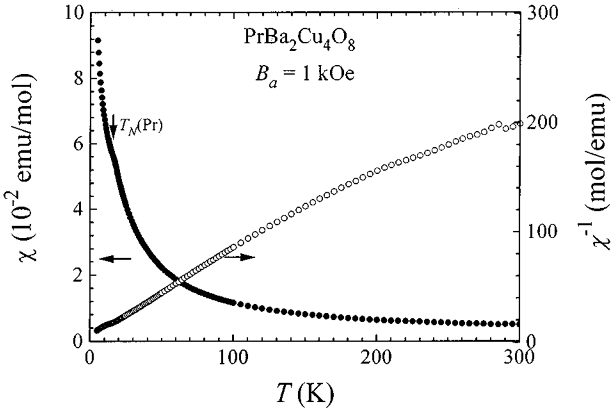

FIG. 3. $\chi(T)$ and $\chi^{-1}(T)$ of $PrBa_2Cu_4O_8$. The arrow indicates T_N of Pr.

$C(T)$ of Pr124 was measured from 0.5 to 40 K, as shown in Fig. 2. A clear peak was observed near 17 K as in the case of Pr123, where this anomaly is generally considered to be the antiferromagnetic ordering of Pr sublattices.[13–16] Figure 3 shows $\chi(T)$ from 4.2 to 300 K along with $\chi^{-1}(T)$. The marked 17 K anomaly shows up readily in Fig. 4, where χ^{-1} and $d\chi/dT$ at low temperatures are plotted. The magnetic origin of the peak in $C(T)$ is thus verified. Preliminary data from neutron elastic scattering also indicate a three-dimensional antiferromagnetic ordering of Pr happening below 17 K.[17] The neutron-scattering peaks are broader than what was seen in Pr123, and this broadening is attributed to the twice longer lattice parameter c in the ''124'' phase.[17]

The anomaly observed in $\chi(T)$ is in contrast with what was reported in Ref. 5, where no sign of magnetic ordering was observed at 17 K. However, in addition to $\chi(T)$, both $C(T)$ and neutron scattering are consistent with a picture of 17 K magnetic ordering of Pr sublattices in our samples. Since the magnetic ordering happens at almost the same temperature either in Pr124 or Pr123 regardless of the difference in chains, it is very suggestive that the magnetic coupling mechanism is mainly associated with the CuO_2 planes. There is another weaker anomaly in $C(T)$ near 3–4 K (see the inset of Fig. 2) with unknown origin, similar to what was observed in Refs. 13 and 14 for Pr123. This anomaly occurred at almost the same temperature in several Pr124 samples prepared by different methods.[7] Measurements of χ at 1 kOe

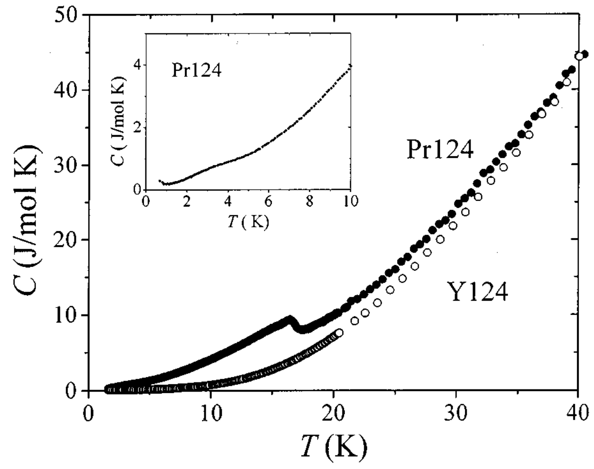

FIG. 2. Molar specific heat $C(T)$ of Pr124 and Y124. Inset: $C(T)$ from 0.5 to 10 K.

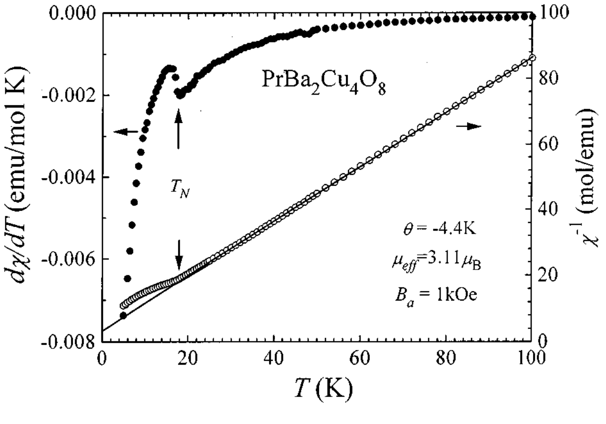

FIG. 4. χ^{-1} and $d\chi/dT$ vs T of $PrBa_2Cu_4O_8$ below 100 K. The anomaly due to the antiferromagnetic ordering of Pr is clearly indicated. A Curie-Weiss fit $\chi(T) = C/(T-\theta)$ is presented as the straight line.

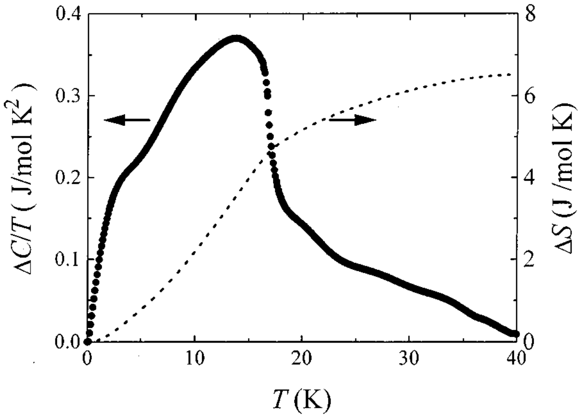

FIG. 5. Entropy change ΔS (the right-hand side) calculated from $\Delta C/T$ (the left-hand side) between Pr124 and Y124.

showed no corresponding signal of the 3.5 K anomaly. However, one has to be cautioned that, for a weak ferromagnetic ordering with such a low transition temperature, the 1 kOe magnetic field might mask it. Whether this lower-temperature anomaly is intrinsic remains to be clarified.

B. Entropy associated with Pr ordering

It has been proposed that the entropy associated with the antiferromagnetic ordering may yield important information about the valance of Pr.[14,15] The entropy ΔS associated with the magnetic ordering of Pr can be estimated by the integration of $\Delta C/T$ between Pr124 and $YBa_2Cu_4O_8$ (Y124) with respect to T.[18] For this purpose, we have also measured $C(T)$ of Y124 synthesized by the same method, as shown in Fig. 2. The result of the integration up to 40 K is presented in Fig. 5 and shows that $\Delta S = 6.6$ J/mol K. As seen from Fig. 5, certain amount of ΔS is contributed from the 3.5 K anomaly, although the main contribution no doubt comes from the well-known 17 K peak. Therefore, ΔS from Fig. 5 may be considered to be the maximum possible Pr contribution. The obtained value of ΔS lies between R ln 2 and R ln 3, which correspond to the entropy change associated with the magnetic ordering of $Pr^{4+}(^2F_{2/5})$ and $Pr^{3+}(^3H_4)$, respectively.

The Curie-Weiss fit $\chi(T) = C/(T-\theta)$ to the magnetic susceptibility data in Fig. 4 gives an effective moment $\mu_{\text{eff}} = 3.11\mu_B$ for Pr and $\theta = -4.4$ K. The negative θ is consistent with an indication of antiferromagnetism. Extending the fitting-temperature range to higher temperatures tends to give a more negative θ, which in general agrees with an antiferromagnetic ordering at 17 K, while μ_{eff} remains basically unchanged. It is noted that the value of μ_{eff} lies between the free-ion values of Pr^{4+} ($2.54\mu_B$) and Pr^{3+} ($3.58\mu_B$). ΔS in Pr123 was reported to be 5 J/mol K in Ref. 14 and $\geqslant 9$ J/mol K in Ref. 15. The Curie-Weiss fit of $\chi(T)$ gives the values of $(2.5-2.8)\mu_B$ in Pr123.[1] Owing to these similarities, any model which fits to explain $C(T)$ and $\chi(T)$ in Pr123 may be applicable to Pr124, too. Naively, these results of $C(T)$ and $\chi(T)$ for Pr124 are in favor of the recent theory of the transfer of the holes in CuO_2 planes from the Cu-O $pd\sigma$ band into a hybridization state.[10,11] However, as in Pr123, interpretation of $\chi(T)$ data might be complicated by the crystal-field effect.[19]

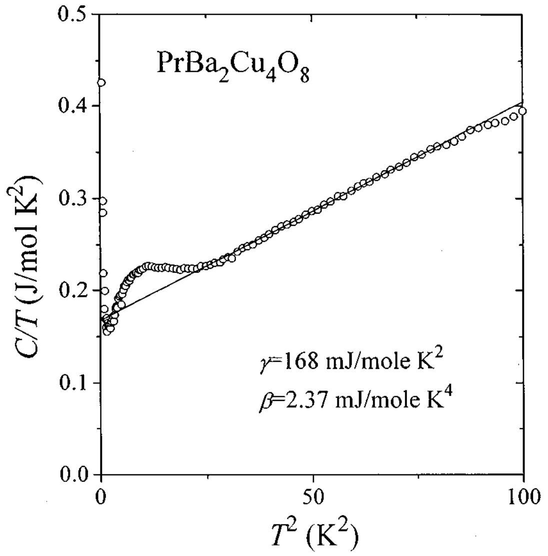

FIG. 6. C/T vs T^2 for $PrBa_2Cu_4O_8$. The solid line is the fit of $C = \gamma T + \beta T^3$ from 5 to 10 K.

C. Linear term γ in the low-temperature specific heat

One of the most notable properties of Pr123 is the ‘‘heavy-fermion-like’’ linear term γ in the low-temperature specific heat $C(T)$.[20] Whether this large γ is from carrier localization or a magnetic origin is still under debate. For Pr124, a plot of $C(T)$ vs T^2 reveals a straight line between 5 and 10 K, as shown in Fig. 6. Within this temperature range, $C/T \approx \gamma + \beta T^2$ with $\gamma = 168$ mJ/mol K^2 and $\beta = 2.37$ mJ/mol K^3. Both parameters are close to those in Pr123 obtained from the same temperature range.[13,14] Analysis of the lower-temperature range is complicated by the 3.5 K anomaly.

The $C(T)$ data of Pr124 and Y124 merge when T approaches 40 K. This kind of entropy removal extending to about $2T_N$ was observed in certain cases of magnetic ordering,[21] though short-range order or spin fluctuations might further strengthen it. It is worth noting that this mergence of $C(T)$ is in contrast with the nearly constant $\Delta C/T$ above T_N between Pr123 and Y123 in several reports.[15,22] Previously this constant $\Delta C/T$ was interpreted as the manifestation of the large γ in Pr123. Since $\Delta C/T$ between Pr124 and Y124 becomes very small at high temperatures, this may suggest that at least part of the observed large γ in Pr124 is due to the residual entropy of the 17 K magnetic ordering. Furthermore, suppose that the large observed γ in both Pr123 and Pr124 is due to the magnetic ordering, similar γ values in both compounds would again emphasize the identical 17 K ordering. The independence of T_N and γ on the transport properties in Pr123 and Pr124 suggests that the superficial correlation between magnetic and transport properties in Pr123 may deserve rethinking.[2] On the other hand, if this large γ is mainly due to the carrier localization, it would be interesting to understand why both Pr123 and Pr124 have a

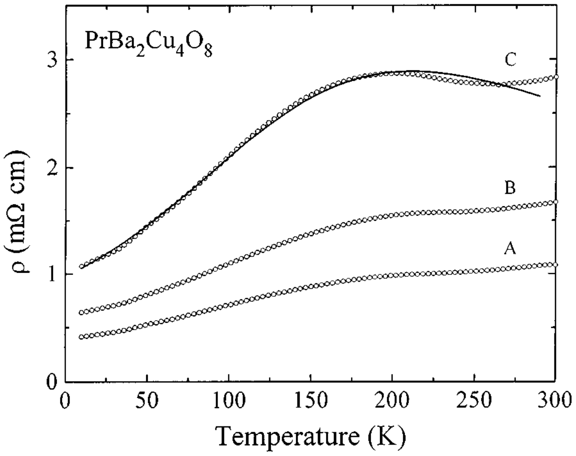

FIG. 7. $\rho(T)$ of three $PrBa_2Cu_4O_8$ samples prepared by different methods. Samples A and B were prepared by the nitric pyrolysis method. Sample C was prepared by the oxalate coprecipitation method. The open circles are the experimental results, and the solid lines represents the fit of a 1D-2D crossover of charge transport arising from the double CuO chains (see text).

similarly huge γ, but with so much different transport properties, which will be discussed in the following section.

D. $\rho(T)$ of Pr124

Unlike the rather ''expected'' behavior of $C(T)$ and $\chi(T)$, the transport properties in Pr124 are certainly distinct from those of Pr123. Figure 7 shows $\rho(T)$ of three Pr124 samples prepared by different methods. Samples A and B were prepared by nitric pyrolysis method. Sample C was prepared by oxalate coprecipitation method.[7] Among them, sample A represents one of the best samples in the literature judged from $\rho(T)$.[5–9] One could ask, while so similar in structure, specific heat, and magnetic properties, why is $\rho(T)$ of Pr124 so much different from that of Pr123 and, in particular, is metallic at low temperatures? In addition, what is the origin of the shoulder in $\rho(T)$ of Pr124?

One of the aspects in Fig. 7 is that the lower ρ is, the less pronounced the shoulder around 200 K. $d\rho/dT$ is even positive through the whole temperature range in sample A. Therefore, this anomaly in $\rho(T)$ might be at least partially extrinsic. $\chi(T)$ in Fig. 3 shows a slight change in the slope around 200 K. Whether this is related to the shoulder in $\rho(T)$ remains to be clarified. If this is true, the origin of this anomaly certainly deserves further investigation.

The low-temperature metallic $\rho(T)$ is even more interesting. Below 50 K, $\rho(T)$ is roughly with a $T^{1.5}$ dependence, agreeing with what was reported in Ref. 9. It was further proposed that this low-temperature charge transport arises from the double CuO chains and can be explained in terms of the one-dimensional to two-dimensional (1D-2D) crossover around 100 K, inferred from the Hall coefficient and the thermal power of Pr124.[9] To the best of our knowledge, there is still no elaborate theoretical formulism for this 1D-2D crossover. However, to examine this proposal, an empirical fit of the parallel combination $\rho^{-1}=(R_{\mathrm{LT}}e^{kT/t})^{-1}+R_{123}^{-1}$ may be helpful. Here R_{LT} is obtained from the fit of $\rho(T)$ of Pr124 below 50 K and is supposed to represent the 2D metallic behavior of the double CuO chains at low temperatures. The term $e^{kT/t}$ is added to tune the 1D-2D crossover. The parameter t is basically the interchain hopping energy, and t/k should be about the crossover temperature (~ 100 K according to Ref. 9). R_{123} is the resistivity of Pr123 which was determined experimentally from a Pr123 sample. The result of the fit for sample C is shown in Fig. 7. Though giving a qualitative description of $\rho(T)$ at low temperatures, this fit starts to deviate from the data at high temperatures. Also, the fit results in a very large $t/k \approx 500$ K. Furthermore, the same fit fails to describe $\rho(T)$ of samples A and B. The main reason is the metallic behavior near 300 K for samples A and B. It should be noted that this positive slope in $\rho(T)$ at high temperatures becomes more obvious when the sample quality is improved, as shown in Fig. 7.

If conductivity of Pr124 is attributed to the double CuO chains, that $\rho(T)$ is metallic at low temperatures and shows no indication of localization in charge transport is certainly unusual. It is generally believed that all the states are localized in either a one- or two-dimensional system no matter how weak the disorder.[23] As T approaches zero, the strong localization leads to an exponential increase in $\rho(T)$, while the weak localization leads to an logarithmic increase.[24] Neither was observed in Pr124. In the two-dimensional case, recent theoretical work suggests that there is an universal sheet resistance of the order of $h/4e^2 = 6.5$ kΩ which separates insulating and superconducting behavior at low temperatures.[25,26] Experimental work on disorder superconducting thin films and several cuprate systems seems to imply the existence of a superconductor-insulator transition.[27,28] Assuming a two-dimensional charge transport for Pr124 at low temperatures, the sheet resistance is only about 3 kΩ at 10 K. Therefore it might not be insulating. However, no definite evidence of superconductivity has been observed in Pr124 yet. Recent work in silicon suggests a true metal-insulator transition due to the carrier concentration in the two-dimensional system.[29] The dimensionality of the transport properties of Pr124 and related problems may require more work to settle.

Previous full potential linearized augmented plane wave (FLAPW) calculations revealed similar chain bands in both Y123 and Y124.[30] Therefore, it is also puzzling that the charge transport of the double CuO chain in Pr124 would differ so much from that of the single CuO chain in Pr123. This difference might be due to the less fragile double chains or different values of t. Certainly, band structure calculations of Pr124 concentrated on the dispersion of the a- or c-axis direction are desirable.

As mentioned before, there is a weak anomaly in $C(T)$ near 3.5 K. In addition, a feature of resistivity drop ($\sim 50\%$) was found to occur in the same temperature range, which was current and magnetic-field dependent. Preliminary data of χ_{ac} measurements at $B_a = 1$ Oe and $f = 1000$ Hz also showed some weak features between 3.5 and 4 K. Whether this is due to superconductivity or a magnetic origin needs to be clarified by further work.

IV. CONCLUSION

We have measured various physical properties of Pr124 prepared at ambient oxygen pressure. It is found that both

$C(T)$ and $\chi(T)$ are very similar to those in Pr123, regardless of the structural difference in the chains. All the magnetic related data, such as an antiferromagnetic ordering of Pr near 17 K, ΔS of the magnetic ordering estimated from $C(T)$ measurements of Pr124 and Y124, and the Curie-Weiss fit of $\chi(T)$, give similar results as in Pr123. Therefore, the T_c suppression theory proposed by Fehrenbacher and Rice and further detailed by Liechtenstein and Mazin seems to apply to Pr124, too. On the other hand, the 1D-2D crossover cannot fully explain the behavior of $\rho(T)$ of Pr124. More work is needed to explain the differences in the transport properties between Pr124 and Pr123.

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