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Electrical and magnetic properties of superconducting-insulating Pr-doped $GdBa_2Cu_3O_{7-y}$

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An extensive study of magnetic, electrical transport, and structural properties of the normal and superconducting states of $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$ (GdPr-123) are presented. Ceramic compounds have been synthesized by the solid-state reaction technique, and characterized by x-ray-diffraction, scanning-electron-microscopy, thermogravimetric, and differential-thermal analyses. The superconducting transition temperature is reduced with increasing Pr content x in a nonlinear manner, in contrast to Abrikosov-Gor'kov pair-breaking theory. Magnetic susceptibility measurements show that the nominal Pr valence is 3.86+, independently of x. A metal-insulator transition is observed at $x_{\mathrm{cr}} \approx 0.45$, similar to that in the oxygen-deficient $RBa_2Cu_3O_{7-y}$ (R-123) system. Based on this resemblance, we suggest that both Pr doping and oxygen deficiency act through the same mechanism. Hence, the environment surrounding the CuO_2 layers is important to high-T_c superconductivity (HTSC). In this sense, HTSC cannot completely be a two-dimentional feature. A chain-plane-correlation effect is plausible. [S0163-1829(97)05634-8]

Among the high-T_c superconductors studies so far, $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ (RPr-123) systems, in which R is Y or rare earth, seem to be the most puzzeling in view of the following two facts.

(1) In $RBa_2Cu_3O_{7-y}$ (R-123) compounds with R being a paramagnetic ion, magnetic ordering occurs in the low temperature region [e.g., around 2K in Gd-123 (Ref. 1)] and is seemingly independent of the superconducting electrons. In binary intermetallics, even small amounts of magnetic impurity could cause a marked depression of T_c.[2] In R-123 compounds (R being a paramagnetic rare-earth ion, e.g., Gd) superconductivity dominates the magnetic interactions. Since the presence of these ions preserves superconductivity, it can be concluded that the interaction between the R element and conduction electrons is very weak, and hence, the conventional pair-breaking mechanism[3] will not be effective in this case.

(2) Pr is the only rare earth ion which can form the magnetic insulator $PrBa_2Cu_3O_{7-y}$ (Pr-123) (Refs. 4 and 5) having an isomorphic crystal structure with $YBa_2Cu_3O_{7-y}$ (Y-123). The origin of this behavior in Pr-123 and RPr-123 is of fundamental interest, since any reasonable explanation of the mechanism responsible for high-temperature superconductivity (HTSC) should also explain why Pr-123 is not a superconductor.

Several models have been proposed for describing the anomalous behavior of RPr-123 compounds of which the most important are (1) hole filling, considering the Pr valence to be close to 4+ or a mixed valence for Pr ions[6] and (2) magnetic pair breaking, assuming Pr is in the trivalent state and acts as a strong magnetic pair breaker.[7] This mechanism, however, cannot explain why starting from $x \approx x_{\mathrm{cr}}$ the system becomes insulating. Also, it was established that the substitution of Pr by Ca both in RPr-123 (Ref. 8) and in pure Pr-123 (Ref. 9) induces the transition back to high-T_c superconducting state, which seems incompatible with this model. (3) Another model is strong hybridization of Pr $4f$ and Cu $3d$–O $2p$ orbitals, the well-defined model combining the features of both above models.[10] It is believed that the larger radial extent of the Pr ion leads to a significant hybridization of the Pr $4f$ electrons with the CuO_2 valence band.

The metal-insulator transition (MIT) is a common feature of all doped high-T_c superconductors. In R-123, both oxygen depletion[11] and Pr doping could cause a MIT.[4] In the insulating state at low carrier concentrations[12] and in the normal states of $YBa_2Cu_{-x}Li_xO_{6.5+y-x/2}$ and $Bi_2Sr_2CaCu_{2-x}Li_xO_{8+y-x/2}$,[13] a variable-range hopping (VRH) conduction mechanism has been reported. A different temperature dependence of hopping conductivity, i.e., $Ln\sigma \sim T^{-1/2}$, would have arisen by Coulomb interaction between the localized electrons.[14] Thermoelectric power measurements have indicated the possibility that correlated electrons play a role in the superconduтivity mechanism.[15] On the basis of the quantum percolation theory, we interpret the normal-state electrical properties of insulating and metallic samples by VRH and Coulomb gap (CG) mechanisms, respectively.

Fourteen polycrystalline GdPr-123 samples with different x's were prepared by the standard solid-state reaction technique.[16] The samples were characterized by scanning-electron-microscopy (SEM), x-ray-diffraction (XRD), thermogravimetric-analysis (TGA), and differential-thermal (DT) techniques. The magnetization and Meissner effect measurements were made on a VSM PAR 155. The standard dc four-probe technique was used to measure resistivity of the samples in the temperature range 10–300 K using a closed-cycle refrigerator.

XRD analysis of the powder before and after sintering of all samples indicates that for the small amounts of x, 123 phase structure with $Pmmm$ orthorhombic symmetry dominates. With increasing x, before sintering, transient secondary phases $BaCuO_2$ and $PrBaO_3$ with the main peaks at $2\theta \approx 29.3°$ and $28.9°$, respectively (Fig. 1), are dominant, but after sintering the proportion of these phases reduces to less than 1%. The lattice constant ratios a/b and c/b, and the cell volume V, obtained by Reitveld analysis, are listed in Table I. It is evident that replacement of Gd by Pr yields an isotropic expansion of the orthorhombic lattice. Increasing the cell

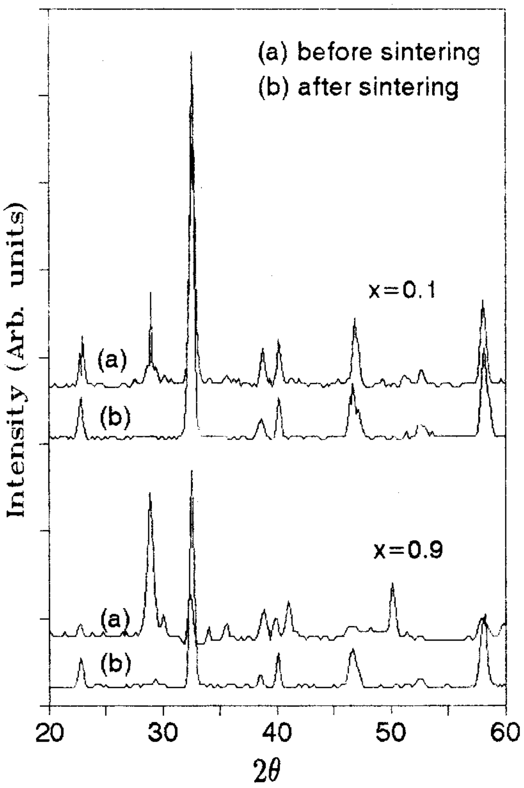

FIG. 1. XRD patterns.

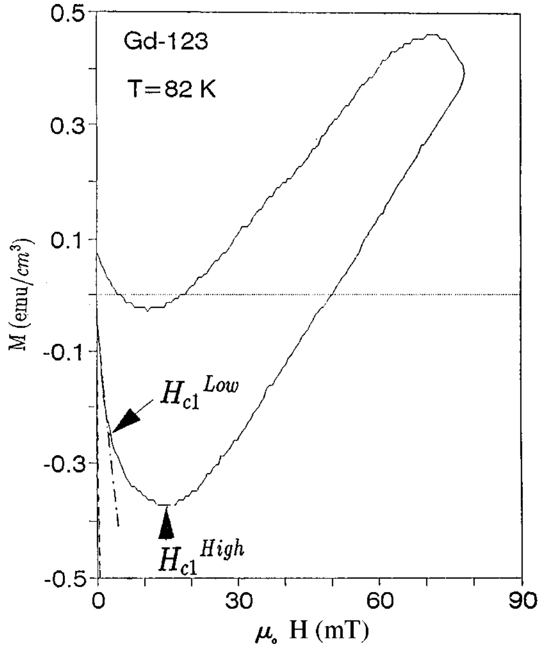

FIG. 2. Magnetic hysteresis loop.

volume by x, prevents the complete substitution of Gd^{3+} by Pr^{4+}, since the ionic radii are 0.938 Å for Gd^{3+}, and 1.013 and 0.9 Å for Pr^{3+} and Pr^{4+}, respectively. SEM analysis reveals no significant effect on the microstructure by substituting of Gd by Pr. From TGA and DT analyses it appears that the oxygen content, listed in Table I, is essentially independent of Pr concentration and that y is in the range 0.03–0.18 for all x's in this system.

Superconducting-state magnetization $M(\mu_0 H)$ for Gd-123 is shown at $T=82$ K in Fig. 2. For reference, the perfect diamagnetism due to the Meissner effect is shown by a straight line. The lower critical fields are determined from the $M(\mu_0 H)$ curve as the magnetic fields at which the magnetic flux begins to penetrate the superconducting intergrain ($H_{c1}^{\rm low}\approx 4.5$ mT) and intragrain ($H_{c1}^{\rm high}\approx 15$ mT) regions. In a weak magnetic field the diamagnetism of the supercurrent is dominant. With increasing magnetic field the magnetization of Gd ions increases gradually and the total magnetization will also increase positively. Consequently, it results in the coexistence of superconductivity with the magnetism of Gd^{3+}. Using Bean's model,[17] one can make a rough estimate of the critical current, $J_c^{\rm mag}\approx 4\times 10^2$ A/cm^2 at 82 K, which is higher than the $J_c^{\rm res}$, obtained from resistivity measurements. This is reasonable, since $J_c^{\rm mag}$ and $J_c^{\rm res}$ are related to the intragrain and intergrain superconducting behaviors, respectively.

The $\chi(T)$ data well obey the Curie-Weiss law $\chi=\chi_0+C/(T-\theta)$. On the basis of this equation, the fitting parameters are obtained and listed in Table I. For Gd-123 sample, we find $\mu_{\rm eff}=7.38\mu_B$ which is in good agreement with the Hund's-rule ground-state result $7.98\mu_B$ for the Gd^{3+} free ion. Figure 3 shows the typical $\chi^{-1}(T)$ for different samples. Assuming the weak interaction of Gd and Pr moments, we can write the observed χ for a GdPr-123 sample with definite x as

TABLE I. The lattice parameters, oxygen content, χ_0 and C for different x.

x	a/b	c/b	V (Å^3)	7-y	χ_0 (emu/mole)	C (K emu/mole)
0	0.9877	2.9923	175.587	6.92	2.4×10^{-5}	6.81
0.05	0.9882	2.9951	175.844	6.86	4.8×10^{-5}	6.52
0.1	0.9852	2.9872	175.373	6.97	9.1×10^{-5}	6.24
0.15	0.9864	2.9892	175.586	6.94	9.5×10^{-4}	5.9
0.25	0.9859	2.9895	176.325	6.83	-5.1×10^{-5}	5.3
0.3	0.9869	2.9892	175.541	6.97	-2.5×10^{-5}	5.04
0.35	0.9859	2.9877	175.812	6.93	3.2×10^{-5}	4.75
0.45	0.9854	2.9849	176.098	6.92	3.2×10^{-5}	4.15
0.6	0.9862	2.9885	176.174	6.87	1.7×10^{-4}	3.36
0.7	0.987	2.9893	176.629	6.82	2.6×10^{-5}	2.71
1	0.987	2.9847	176.902	6.85	-2.2×10^{-5}	1.08

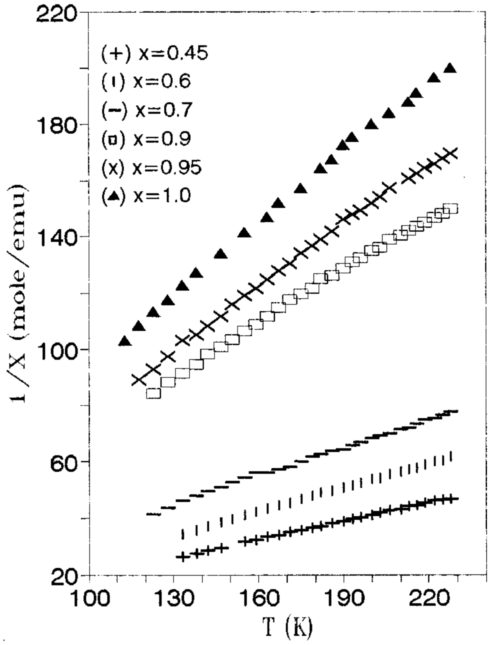

FIG. 3. Inverse magnetic susceptibility versus temperature.

$$\chi(T)=\frac{(1-x)C(\mathrm{Gd}^{3+})+xC(\mathrm{Pr}^{V})}{T-\theta}.$$

Thus, for each sample, using the obtained Curie constant per Pr ion, we calculated μ_{eff} per Pr ion. It is evident that $\mu_{\mathrm{eff}}/\mathrm{Pr}$ ion for different samples are distributed around the mean value of $2.69\mu_B$ which is close to $2.54\mu_B$ for the free Pr^{4+} ion. Using the theoretical results $\mu_{\mathrm{eff}}(\mathrm{Pr}^{3+})=3.58\mu_B$ and $\mu_{\mathrm{eff}}(\mathrm{Pr}^{4+})=2.54\mu_B$ and the weight relation $2.69\mu_B=(4-V)\mu(\mathrm{Pr}^{3+})+(V-3)\mu(\mathrm{Pr}^{4+})$, the formal valence of Pr is obtained to be 3.86+, which agrees with previous reports.[6,18]

Is it possible to reconcile the apparent high fraction of Pr^{4+} found by magnetic measurements with the relatively low fraction found by spectroscopy? The extensive hybridization of $4f$ with $5d$ electrons observed by high-energy spectrocopy[19] indicates that the concepts of valence and valence determination from magnetic susceptibility through a simple effective moment calculation and from spectroscopic measurements are not comparable. So the discrepancy of the results on the Pr valence is due to the differing nature of the involved experiments. Inelastic neutron scattering (INS) on a series of YPr-123 polycrystalline samples[20] was found to consist of broad, low-intensity peaks that are difficult to interpret. Unfortunately, the features in INS spectrum of Pr-123 are rather broad, presumably owing to the admixture of the localized $4f$ and the conduction electrons, making it difficult to determine the Pr-crystalline electric-field (CEF) energy-level scheme directly.[21] INS measurements of Pr-123 with respect to CEF splitting were reported by other groups.[22] Although the spectra differ from group to group, they all agree in the conclusion that the widths of the excited lines are broader in the Pr system compared to other rare-earth systems, a result which requires an explanation. We must note that more recent experimental[23] and theoretical[24] investigations have pointed out, through quantitative analyses, the significance of the decrease in the mobile hole concentration in the CuO_2 planes due to the Pr doping and have suggested the possibility that the Pr valence is intermediated between 3+ and 4+.

The electrical resistivity measurements show that the normal states of $x<0.45$ samples are metallic and at $T<T_c$, become superconductors. T_c decreases with increasing x and ultimately the samples with $x\geqslant 0.45$ show a semicoducting behavior and are no longer superconductors.[4] The metal-insulator transition occurring in this system is similar to that in the oxygen-deficient R-123 system.[11,25] The resemblance of $\rho(T)$ for both systems allows one to conclude that Pr doping reduces carrier concentration, either by hole filling or by hole localization, in a qualitatively similar way with oxygen depletion. The results of electrical resistivity measurements of the GdPr-123 samples also reveal the considerably larger influence of the Pr substitution on T_c and $\rho(T)$ dependence than in the corresponding Y-based system.[7,10]

The resistivity of each sample possesses a T_{min} at which $\rho(T)$ has a minimum. When T_{min} is quite high, $\rho(T)$ only shows a semiconducting behavior in the temperature range of measurements (10–300 K), and when T_{min} is very low, $\rho(T)$ only shows a metallic behavior. Fitting the experimental data for different samples with the hopping conduction relation,[14] $\rho=\rho_0(T/T_0)^{2p}\exp(T_0/T)^p$, in which $p=\frac{1}{4}$ and $p=\frac{1}{2}$ in VRH and CG regimes, respectively, we find that with decreasing x, there is a crossover from the VRH to CG regime. The $\rho(T)$ of $x<0.35$ samples could be fitted better with this equation in the CG regime. The monotonous behavior of T_0 and the gradual change of ρ from metallic to semiconducting as a function of x suggest that E_F is in the localized states region, in the semiconducting samples. Hence, the insulator-to-metal transition observed by increasing Gd content is a consequence of correlations and charge transfer through the long localization lengths rather than of crossing the mobility edge. Another feature of these observations is that in Gd-rich samples, where the CG regime dominates, the density of states (DOS) at E_F is zero. However, in the Pr-rich samples where the VRH regime dominates, the DOS at E_F is nonzero but is in the localized state region.[26] The important question is why Pr substitution for R in R-123 would create such disorder, which, as a result, forces E_F to move into the region of localized states, whereas other rare-earth ions do not lower T_c. Presumably, since Pr has a tolerance of being in different oxidation states, such a disorder is due to the Pr valence fluctuations in the RPr-123 or even in Pr-123 materials.

Decreasing T_c with increasing x shows that the Pr content, carrier concentration, and T_c are closely related to each other. To investigate the existence of such a strong correlation between T_c and the formal valence of Cu-O, we use the susceptibility results of the samples which show that Pr^{3+} and Pr^{4+} coexist in the series of GdPr-123, and the following equation, to estimate the value of holes per cell for Cu-O band. Supposing the mean valence of Pr to be 3.86+, and that the valence of the Cu ion is partially 2+ and 3+, we have according to the charge balance equation

$$(1-x)\mathrm{Gd}^{3+}+0.86x\mathrm{Pr}^{4+}+0.14x\mathrm{Pr}^{3+}+2\mathrm{Ba}^{2+}$$
$$+(7-y)\mathrm{O}^{2-}+(3-\delta)\mathrm{Cu}^{2+}+\delta\mathrm{Cu}^{3+}=0,$$

where δ is the value of holes per cell for GdPr-123. The values of δ obtained by this equation as well as T_c/T_{c0} for

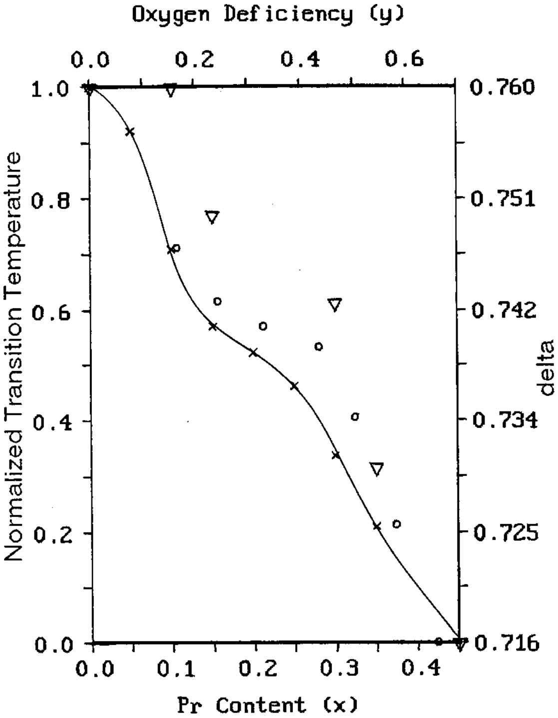

FIG. 4. (×) $T_c/T_{c0}(x)$ of the GdPr-123 system (left-hand y axes), (○) $T_c/T_{c0}(y)$ of the Y-123 system from Ref. 11 (left-hand y axes), and (▽) $\delta(x)$ of the GdPr-123 system (right-hand y axes). The solid line is a guide to the eye.

various x's are shown in Fig. 4. Here $\delta(x)$ follows the $T_c(x)$ curve within the limits of accuracy of determining the oxygen content of the samples. This figure also reveals that the $T_c(x)$ curve strongly deviates from the prediction of Abrikosov-Gor'kov (AG) theory. This is not surprising or unreasonable, since AG theory is based on the magnetic pair breaking of the phonon-mediated Cooper pairs. The formation of Cooper pairs as such in HTSC is highly questionable and has not yet been resolved experimentally or theoretically.

Consistent with the reports on the other Pr-doped R-123 systems,[4,6,27] the $T_c(x)$ curve consists of a flat region for T_c at $x \approx 0-0.05$. There is another flat region for T_c at $x \approx 0.15-0.25$, which is consistent with previous reports on this system.[4,28] The data points from Ref. 11 for an oxygen-depleted system of Y-123 are also plotted in Fig. 4 as a function of y for comparison. The close agreement between our results and those of the deoxygenated system indicates clearly a strong correlation between Pr substitution and deoxygenation in the R-123 system.

As a final noteworthy fact, it should be noted that partial substitution of Pr for R in R-123 suppresses superconductivity and leads to the establishment of antiferromagnetic (AF) order[29] in the same layer which was responsible for superconductivity. Regardless of whether the large overlap of the Pr $4f$ electrons with those of neighboring CuO_2, which, on the one hand, enhances the Pr-Pr exchange and, on the other hand, is effective in destroying superconductivity in the CuO_2 planes, leads to AF ordering in these planes, or another mechanism is responsible for this behavior, it can be concluded that the environment surrounding the CuO_2 layers is very important to superconductivity in these copper oxides. This environment provides the proper source or sink of the charge carriers. Therefore, in this sense, HTSC cannot be a completely two-dimensional feature. As a matter of fact, there are many items of evidence, such as the resemblance of $T_c(y)$ and $T_c(x)$, which lead to the concept of the chain-plane-correlation (CPC) effect as an explanation for HTSC in GdPr-123 system.

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