Superconductivity and magnetism in $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$

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Polycrystalline samples of $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ ($0 \le x \le 1$) with tetragonal perovskite-like structure were synthesized and investigated by powder x-ray-diffraction, electrical-resistivity, magnetic-susceptibility, and specific-heat measurements. It is found that the T_c decreases monotonically with Pr concentration x from $T_c \sim 33$ K for $x=0$ to $T_c \sim 12$ K for $x=0.7$. The critical concentration x_{cr} required to suppress the T_c to zero is estimated to be around 0.85. Even though the $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ exhibits a semiconducting behavior, the normal-state resistivity at $T \ge 100$ K remains nearly the same order of magnitude as that of superconducting $YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. An effective magnetic moment $\mu_{eff} \sim 3\mu_B$ is obtained from the simple Curie-Weiss law and a huge linear term coefficient of specific heat $\gamma \sim 440$ mJ/mol K^2 is determined for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. No magnetic transition is observed for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ down to 0.6 K. However, a superconducting transition with $T_c \sim 17$ K is seen by partially substituting Ca for Pr in $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. The similarities and differences in superconductivity and magnetism between $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ are compared and discussed.

I. INTRODUCTION

It is widely known that all but three rare-earth ions, Ce, Pm, and Tb, can substitute Y forming an $RBa_2Cu_3O_{7-\delta}$ (1237) structure with T_c near 90 K (Ref. 1) except for $PrBa_2Cu_3O_{7-\delta}$, which is a semiconductor.[2] Meanwhile, an antiferromagnetic order in $PrBa_2Cu_3O_{7-\delta}$ was observed below $T_N = 17$ K by magnetic-susceptibility and heat-capacity measurements.[3,4] This magnetic-ordering temperature 17 K of $PrBa_2Cu_3O_{7-\delta}$ is about 2 orders of magnitude higher than expected if one scales the T_N for $GdBa_2Cu_3O_{7-\delta}$ ($T_N = 2.2$ K) assuming either purely dipolar interactions or Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange. The absence of superconductivity and the unusual magnetic order for $PrBa_2Cu_3O_{7-\delta}$ have been a puzzle since this compound was first synthesized. In order to shed light on the basic mechanisms of oxide high-T_c superconductivity, therefore, the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system has become one of the most studied subtopics in the field of high-T_c superconductivity. Plenty of experiments and interpretations focused on the depression of T_c with increasing x in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and the magnetic coupling interactions for high T_N in $PrBa_2Cu_3O_{7-\delta}$ have been conducted and proposed.[5-7] Nevertheless, to date there are still many unsolved questions to be further clarified.

On the other hand, despite the chemical similarity between Sr and Ba, however, the tetragonal Sr-based 1237 structure can be stabilized only by substituting Mo-O, Fe-O, or Ga-O partially or completely for the Cu-O chain.[8] This is because the shortening of the Sr-O bond will ensure a greater tolerance to the length of other planar Sr-O bonds, and thus will enhance the lattice match among constituent elements and the affinity of the deplacement O(1) atoms to their surroundings.[9] Recently, single-phase $RSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ has been successfully synthesized, in which R represents all rare-earth elements except Ce and Lu.[10] These compounds were reported to have a T_c centering around 30 K, except for La, Pr, and Nd which are not superconducting.[9] Thus, this provides another chance to examine the effect of Pr on T_c and the unusual magnetic ordering in the YPr-1237 system. In this paper, we present structural, electrical, magnetic, and specific-heat results for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$, and compare with those for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

II. EXPERIMENTAL METHODS

All polycrystalline samples $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ ($0 \le x \le 1$) and $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ ($0 \le x \le 0.15$) were prepared by the solid-state-reaction method under identical conditions. High-purity powders of Y_2O_3, Pr_6O_{11}, $SrCO_3$, $CaCO_3$, CuO, and MoO_3 were mixed in appropriate proportions. The mixed powder was compacted and fired for 3 h at 1020 °C in an oxygen atmosphere. It was then slowly cooled to room temperature at flowing oxygen. The above process was repeated twice. The oxygen content is considered to be in the range 6.9–7.0 using this heat treatment for samples.[9] The structural analysis was carried out by powder x-ray diffraction using Cu $K\alpha$ radiation. Lattice parameters were calculated from the diffraction peak positions by the method of least squares. Electrical resistivity $\rho(T)$ measurements were performed on rectangular specimens cut from sintered pellets employing the standard four-probe method with silver paint contacts attached to electrical leads. The magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) over the temperature range 5–300 K at a field of 5 kOe. The specific heat of pieces ($\sim$2 mg) cut from the samples was measured in the range 0.6–40 K with a ^{3}He relaxation calorimeter using the heat pulse technique.[11] The samples were attached to a sappire chip, which has two separated silicon films deposited on it to serve as the heater and the thermometer. The Si-film thermometer was calibrated against a calibrated germanium thermometer. For each point of the specific-heat measurements, a small heat power was introduced to the chip and the thermal relaxation was measured and analyzed to obtain the specific heat of the samples.

III. RESULTS AND DISCUSSION

X-ray-diffraction patterns (not shown) reveal that all samples $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ ($0 \le x \le 1$) display a tetragonal symmetry, instead of the orthothombic structure of Ba-based 1237. This suggests that Mo is doped into Cu(1) sites. Calculated results listed in Table I and plotted in Fig. 1 show that lattice parameters increase linearly with the Pr concentration. This indicates that the Pr substitutes for Y readily. Temperature dependence of normalized resistivity for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ with various x is shown in Fig. 2. At $x=0$, the ρ-T curve and T_c (midpoint) $\sim$33 K are consistent with those reported previously.[9] For low x ($x \le 0.2$), the resistivity shows a metalliclike behavior; however, it begins to develop a broad maximum just above T_c for $x \ge 0.3$. The upturn of resistivity observed at higher x ($x \ge 0.3$) in this system is similar to that observed in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. It is found that the T_c decreases monotonically with Pr concentration x from $T_c \sim 33$ K for $x=0$ to $T_c \sim 12$ K for $x=0.7$. The critical concentration x_{cr} required to suppress the T_c to zero is estimated to be around 0.85. These digital values of T_c versus x are also listed in Table I. The Abrikosov and Gor'kov[12] (AG) pair-breaking theory predicts that the reduced transition temperature $T_c(x)/T_c(0)$ is a universal function of reduced concentration x/x_{cr}:

$$\ln[T_c(x)/T_c(0)] = \psi(1.2) - \psi[\tfrac{1}{2} + 0.14xT_c(0)/x_{cr}T_c(x)] ,$$

where ψ is the digamma function. Curve (1) of Fig. 3 shows the AG fit of $T_c(x)/T_c(0)$ versus x for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ using $x_{cr}=0.85$. Obviously, curve (1) is far below the data points. A plausible conclusion for the failure of curve (1) to fit the data is that the AG pair-breaking theory simply does not agree with the data. It is noted that the disagreement can be improved just by assuming $T_c'(0) \sim 1.2T_c(0)$ as seen in curve (2). The physical meaning of $T_c'(0)$ here is similar to that of $T_{c0}(0)$, the maximum obtainable value of $T_c(0)$ described in Ref. 13 or that of $T_c'(0)$, the linearly extrapolated $T_c(x)$ as $x \to 0$ described in Ref. 14. This suggests that our sample $YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ may be in the over-hole-doping state as same as $YBa_2Cu_3O_{7-\delta}$. This also reveals complicated mechanisms on the depression of T_c at the low Pr doping level $x \le 0.2$. On the other hand, the AG pair-breaking theory does not predict that a metal-insulator (MI) transition will accompany the suppression of superconductivity with the introduction of magnetic impurities. The fact that a MI transition is observed in this and other 1237 systems indicates a reduction in the mobile hole carrier density with Pr substitution. Therefore, a mechanism other than AG theory on the suppression of T_c in $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ should be considered and taken into account. For comparison, the T_c versus x (curve 3) for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (reproduced from Fig. 55 of Ref. 5) is also included in Fig. 3. It is clear that the suppression

TABLE I. Lattice parameters a and c, superconducting transition temperature T_c (midpoint), and electrical resistivity at 100 K ($\rho_{100\,K}$) for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_7$ with $x=0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.

$Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_7$	a (Å)	c (Å)	T_c (K)	$\rho_{100\,K}$ (mΩ cm)
$x=0$	3.810(2)	11.538(5)	33.2	4
$x=0.1$	3.814(1)	11.534(4)	33.1	
$x=0.2$	3.818(1)	11.545(4)	31.6	9
$x=0.3$	3.826(1)	11.547(5)	29.7	
$x=0.4$	3.830(1)	11.555(5)	25.9	11
$x=0.5$	3.835(1)	11.575(4)	22.2	
$x=0.6$	3.840(1)	11.580(4)	17.3	11
$x=0.7$	3.844(1)	11.591(5)	12.2	
$x=0.8$	3.850(1)	11.606(4)	<10	6
$x=0.9$	3.853(1)	11.613(4)		
$x=1$	3.858(2)	11.616(10)		15

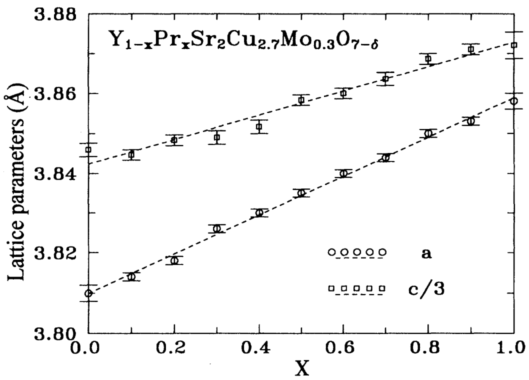

FIG. 1. Lattice parameters a and c as a function of Pr concentration x $(0 \le x \le 1)$ for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. Dashed lines are guides to the eye.

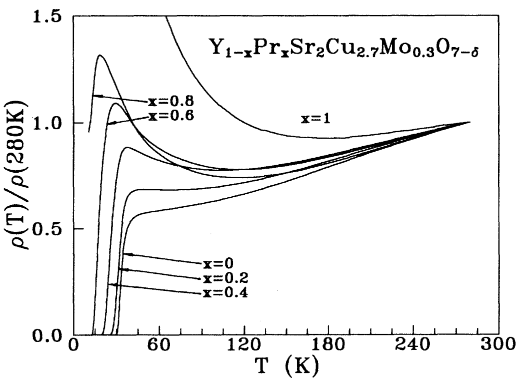

FIG. 2. Normalized electrical resistivity as a function of temperature for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ with $x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.

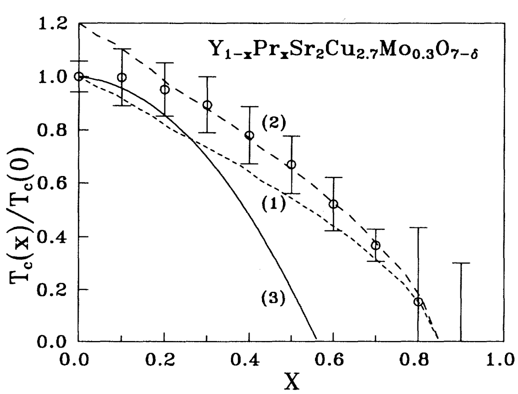

FIG. 3. $T_c(x)/T_c(0)$ as a function of x for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. Curves (1) and (2) are fit to the AG theory with different $T_c'(0)$. Curve (3) is the T_c vs x for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ reproduced from the Fig. 55 of Ref. 5. See text for more detail.

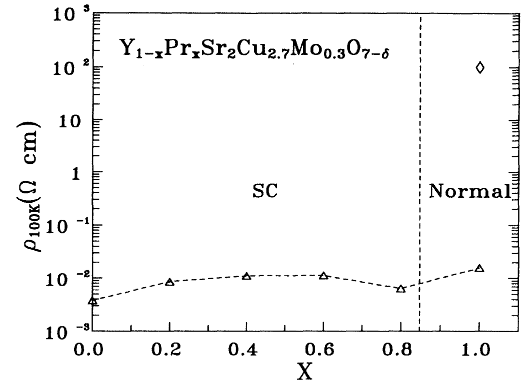

FIG. 4. The resistivity at 100 K ($\rho_{100\ K}$) as a function of x for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. The $\rho_{100\ K}$ for $PrBa_2Cu_3O_{7-\delta}$ is marked by $\Diamond$ for comparison.

of T_c with x is much weaker in the former than that in the latter. Figure 4 shows the normal-state resistivity at 100 K ($\rho_{100\ K}$) as a function of x for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. The $\rho_{100\ K}$ keeps nearly the same order of magnitude through the whole range of x. In addition, the value of $\rho_{100\ K}$ for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is about 4 orders of magnitude smaller than that for $PrBa_2Cu_3O_{7-\delta}$.[15,16] From these results, it is clear that Pr substitution has less effect on both T_c and resistivity in the $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ system than in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. This correlation of T_c and resistivity is consistent with the hole-filling–localization model.

The normal paramagnetic behavior of magnetic susceptibility and the inverse magnetic susceptibility as a function of temperature for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is shown in Fig. 5. A best fit to Curie-Weiss law

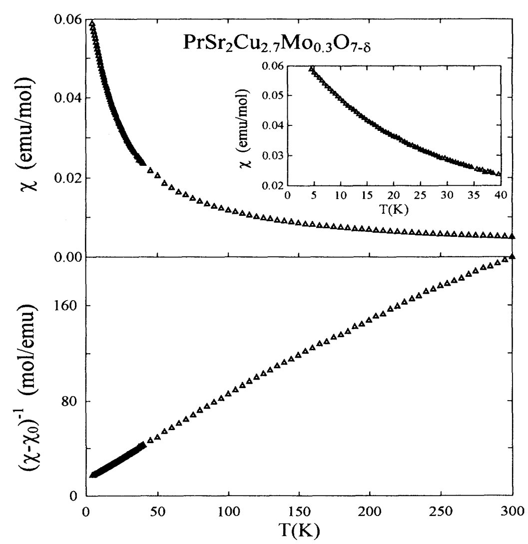

FIG. 5. Magnetic susceptibility and inverse magnetic susceptibility for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ in the temperature range 5–300 K. The inset shows the low-temperature (5–40 K) magnetic susceptibility.

$\chi=\chi_0+C/(T\sim\Theta)$ in the range $20\leq T\leq 300$ K yields the sum of temperature-independent terms $\chi_0=2.03\times10^{-5}$ emu/g, the paramagnetic Curie-Weiss temperature $\Theta=-11$ K, and the effective magnetic moment $\mu_{\rm eff}=3.05\mu_B$. The derived value of $\mu_{\rm eff}$ is close to that for $PrBa_2Cu_3O_{7-\delta}$ and falls between the free-ion values expected for $Pr^{3+}(3.58\mu_B)$ and $Pr^{4+}(2.54\mu_B)$. However, it is well known that Curie-Weiss moments can be reduced from expected free-ion values by the presence of crystal-field effects. Soderholm and Goodman[17] also argued that this type of analysis for the determination of a valence state is too simple for these complicated materials. Besides, Soderholm *et al.*[18] and Hilscher *et al.*[19] have shown that the experimental magnetic-susceptibility[18,19] and specific-heat[19] data for $PrBa_2Cu_3O_{7-\delta}$ can be interpreted consistently in terms of standard crystal-field (CF) theory of Pr^{3+} based on the CF parameters extracted from the neutron-diffraction data.[20] The low-temperature magnetic susceptibility of $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ shown in the inset of Fig. 5 shows no indication of magnetic anomaly down to 5 K in contrast to a slope change observed at 17 K in magnetic susceptibility of $PrBa_2Cu_3O_{7-\delta}$.[3,21] In our previous studies,[21,22] the antiferromagnetic transition temperature T_N in $PrBa_2Cu_3O_{7-\delta}$ is depressed as the transition metal and Ca substitute partially for Cu(1) and Ba, respectively, such as in the $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ and $Pr(Ba_{1-x}Ca_x)_2Cu_3O_{7-\delta}$ systems. Thus no observation of magnetic ordering transition for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ in this temperature region is expected.

Low-temperature ($0.6\leq T\leq 40$ K) specific heat C and C/T for $YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ are shown in Fig. 6. The superconducting transition at $T_c\sim 33$ K for polycrystalline $YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ cannot be discerned within our calorimeter resolution. No anomaly is observed in $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ indicating no magnetic-ordering transition down to 0.6 K in contrast to a clear anomaly at $T_N\sim 17$ K for $PrBa_2Cu_3O_{7-\delta}$.[3,4] This is consistent with the magnetic susceptibility result as mentioned above. The Pr-related magnetic contributions to specific heat ΔC in $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is calculated by

$$\Delta C=C(PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}) - C(YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta})\ ,$$

where the lattice contribution to specific heat for these two compounds is assumed to be identical. Figure 7 shows the ΔC and the $\Delta C/T$ as functions of temperature for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ in the range $0.6\leq T\leq 20$ K. The features of these two curves are quite similar to those observed in $Y_{0.4}Pr_{0.6}Ba_2Cu_3O_{7-\delta}$.[4,23] Ghamaty *et al.*[23] gave a good description for those data with a combination of nuclear Schottky anomaly, linear term, and Kondo anomaly contributions. This suggests that the magnetic coupling strength in $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is much weaker than that in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ at $x=1$ and may be about the same level as that at $x=0.4-0.6$. This also means that $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ may be just in the ambiguous region for the superconductivity in competition with magnetic order. The analysis for a linear term coefficient of specific heat γ in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ has been discussed by many groups.[3,4,23,24] Generally, the low-temperature specific heat C can be combined with magnetic, electronic, and lattice contributions. In the $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ case, the magnetic part may include several terms, such as nuclear Schottky anomaly, linear term, Kondo anomaly, and/or magnetic ordering contributions as described for $Y_{0.4}Pr_{0.6}Ba_2Cu_3O_{7-\delta}$.[23] Nevertheless, to limit and simplify the preliminary analysis, the linear term coefficient or specific heat γ was just calculated by the usual procedure of extrapolating

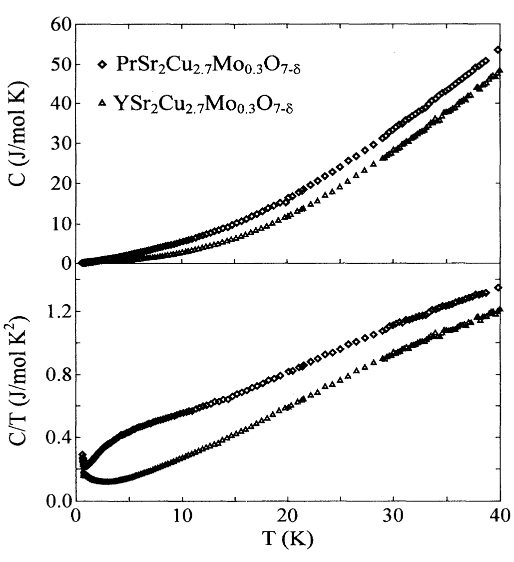

FIG. 6. Low-temperature ($T\leq 40$ K) specific-heat C and C/T for $YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$.

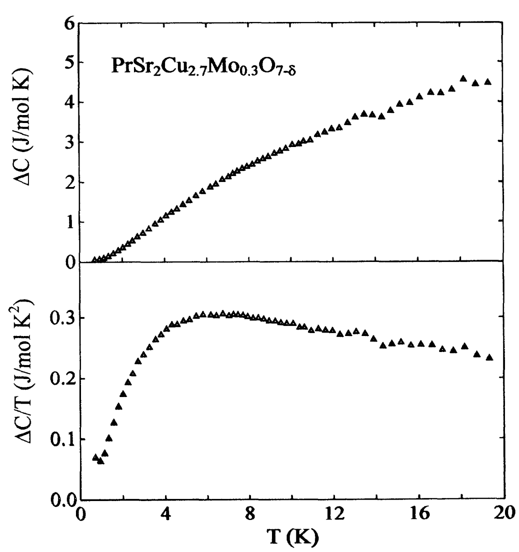

FIG. 7. Pr-related magnetic contributions to specific heat, $\Delta C=C(PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta})-C(YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta})$ and $\Delta C/T$ as a function of temperature in the range of 0.6 $K\leq T\leq 20$ K.

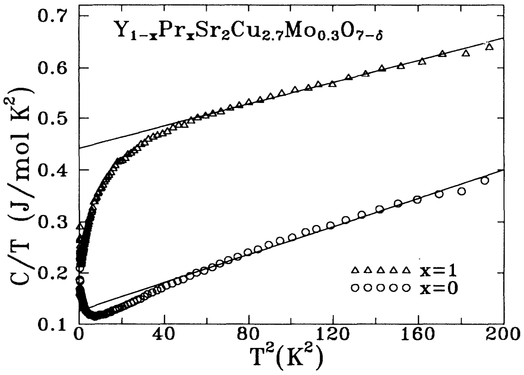

FIG. 8. C/T vs T^2 curves for $YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. Lines are the best linear fit in the range $6 \leq T \leq 14$ K.

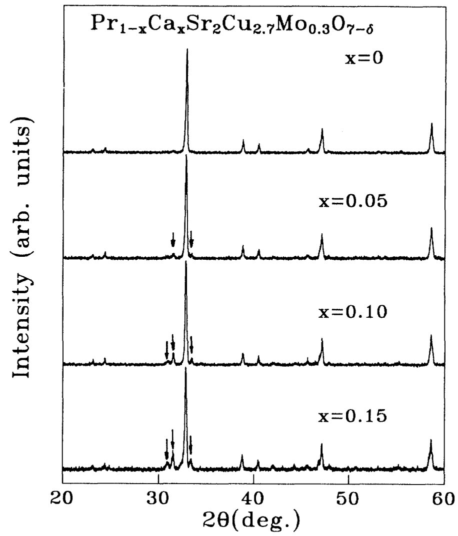

FIG. 9. Room-temperature powder x-ray-diffraction patterns for $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ with $x=0$, 0.05, 0.1, and 0.15. Impurity peaks are indicated by arrows.

the nearly linear C/T value to $T=0$. C/T versus T^2 for $YSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ in the range $6 \leq T \leq 14$ K is shown in Fig. 8. Huge values of $\gamma \sim 120$ and 440 mJ/mol K^2 were obtained for these two compounds, respectively, indicative of a characteristic of heavy-fermion-like behavior. These γ values are larger than those from corresponding $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system[3,4,23,24] but are comparable to those when Cu is replaced by Fe.[4] It has been pointed out that this γ value can be substantially reduced by considering magnetic contributions.[24]

Because the $\rho_{100\,K}$ for $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ keeps nearly the same order of magnitude through the whole range of x and the $\rho_{100\,K}$ of $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is much smaller than that of $PrBa_2Cu_3O_{7-\delta}$, it suggests that the $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ may be in the vicinity of the borderline of metal-insulator transition. Also, the magnetic coupling strength in $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is about the same as in $Y_{0.4}Pr_{0.6}Ba_2Cu_3O_{7-\delta}$ suggesting that the ground state of $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is close to a competitive region of superconductivity and magnetic order. In order to elucidate these points, the $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ system was synthesized and studied. X-ray-diffraction patterns for $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ $(0 \leq x \leq 0.15)$ is shown in Fig. 9. It is found that the Sr-based-1237 structure basically persists but with visible impurity peaks indicated by arrows. Clearly, the solid-solution limit in $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is smaller than that in $Pr_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, in which x can exceed 0.3. This indicates that the Sr-based 1237 fits better the larger cation in the rare-earth sites than the Ba-based 1237 does. This is consistent with the fact that $LaSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $LuBa_2Cu_3O_{7-\delta}$ are stable, but $LuSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $LaBa_2Cu_3O_{7-\delta}$ are difficult to synthesize.[10,25] The resistivity as a function of temperature for $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ with various x is shown in Fig. 10. A superconducting transition is observed as $x \geq 0.05$ and reach a maximum T_c at $x \sim 0.1$. The resistivity and magnetic shielding effect with an expanded temperature scale for $Pr_{0.9}Ca_{0.1}Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ is shown in the inset of Fig. 10. The onset of superconductivity occurs at ~ 22 K and reaches the zero resistance at 14 K. This demonstrates a bulk nature of superconductivity in the bulk Ca-doped Pr-1237 samples. Norton *et al.*[26,27] have reported superconductivity with $T_c \sim 40$ K in $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ thin film but not in the bulk target. In fact, why the superconductivity only seen in the $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ thin film but not in the bulk sample is not yet clear. Norton *et al.*[26,27] also concluded that their result is consistent with the view that the hole

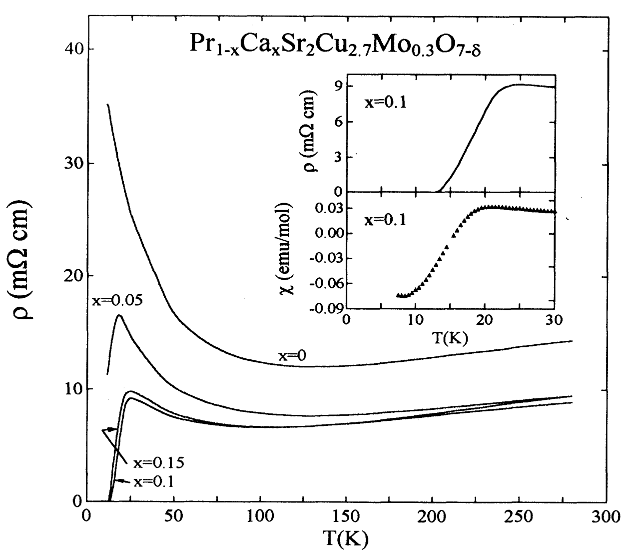

FIG. 10. Electrical resistivity as a function of temperature for $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ with $x=0$. 0.05, 0.1, and 0.15. The inset shows the low-temperature ($T \leq 30$ K) resistivity and magnetic shielding effect for $Pr_{0.9}Ca_{0.1}Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$.

localization, due to hybridization of Pr $4f$ electronic levels with the O $2p$ orbitals, contributes substantially to the suppression of superconductivity by Pr in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and this suppression can be partially compensated by appropriate hole doping with Ca. It is believed that the similar argument would be applicable to the $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ system. The occurrence of superconductivity in the $Pr_{0.9}Ca_{0.1}Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ bulk sample can be attributed to a much weaker hybridization in $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ than in $PrBa_2Cu_3O_{7-\delta}$. It is emphasized that the T_c for $Pr_{0.9}Ca_{0.1}Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ ($T_c\sim17$ K) and $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ ($T_c\sim40$ K) are much higher than that for $Pr_{0.9}Y_{0.1}Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ ($T_c\sim0$ K) and $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_{7-\delta}$ ($T_c\sim0$ K), respectively. This illustrates that the divalent Ca must do something different from the trivalent Y in the occurrence of superconductivity. Even though the hybridization of Pr $4f$ electrons with the CuO_2 valence band could lead to a magnetic pair-breaking effect,[16,28] the hole localization or filling mechanism should play a more important role in the suppression of superconductivity in the Pr-doped 1237 systems.

It is interesting to study the correlation among the absence of superconductivity, anomalously high T_N, reduced effective magnetic moment $\mu_{\rm eff}$, and huge linear term coefficient of specific heat γ in these Pr-based cuprates. These parameters for four selected Pr-based compounds including $PrBa_2Cu_3O_7$, Pr_2CuO_4, $PrBa_2Cu_2NbO_8$, and $PrSr_2Cr_{2.7}Mo_{0.3}O_7$ are listed in Table II for comparisons. Where the Pr_2CuO_4 formed T'-type structure consists of only the square-planar CuO_4 arrangement with no apical oxygen atoms and the $PrBa_2Cu_2NbO_8$ has a similar structure to $PrBa_2Cu_3O_7$ but with NbO_2 planes replacing the CuO chains. There are several features which can be pointed out from this table.

(1) All four Pr-based compounds before doping are semiconductors even though some of its isostructural compounds are superconducting at high temperatures. In fact, the Pr_2CuO_4 seems to have very different structural and physical properties from the other three compounds. For example no indication of any magnetic ordering transition, $\mu_{\rm eff}\sim3.51\mu_B$ close to $3.58\mu_B$ an expected value for a free Pr^{3+} ion, and a metal-like γ value suggest that the ground state of Pr_2CuO_4 is clearly nonmagnetic.[29] Whereas the anomalous properties for the other three compounds may be attributed to the unique magnetic and electronic characteristic of Pr ions.

(2) Superconductivity is not observed with or without doping if the compound exhibits a high T_N (~10 K), such as bulk $PrBa_2Cu_3O_7$ and $PrBa_2Cu_2NbO_8$. However, superconductivity can be achieved by an appropriate doping if the compound exhibits low T_N(~0 K), such as Pr_2CuO_4 and $PrSr_2Cu_{2.7}Mo_{0.3}O_7$. Thus the magnetic coupling mechanism between Pr-Pr interactions may be a key factor for the suppression of T_c in these Pr-based cuprates.

(3) The high T_N and a reduced $\mu_{\rm eff}$ accompanied with a small γ for $PrBa_2Cu_2NbO_8$ are interesting. If the reduction of $\mu_{\rm eff}$ for Pr ion were ascribed to a large crystal-field effect (CFE) and the strong magnetic correlations (high T_N) of the Pr magnetic moments were caused by an enhanced hybridization of Pr $4f$ electrons with holes in the CuO_2 planes, the large CFE seems to act independently of this strong hybridization in these materials. In other words, the reduction of $\mu_{\rm eff}$ resulted from the large CFE may not be so relevant to the suppression of T_c. This is also evidenced by that a superconductivity was observed in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$,[33] $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$, and $Pr_{1-x}Ca_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ systems with a reduced $\mu_{\rm eff}$ even in superconducting samples.

(4) It is difficult to relate the huge γ to other parameters from the information listed in Table II. In fact, the origin of the huge γ for some Pr-based compounds is not yet clear. The change in γ value does not depend on whether samples are superconducting or insulating in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (Ref. 24). This suggests that the huge γ is not closely responsible for the suppression of T_c. In addition, a high T_N(~12 K) with a small γ in $PrBa_2Cu_2NbO_8$ and a low T_N (~0 K) with a huge γ in $PrSr_2Cu_{2.7}Mo_{0.3}O_7$ also suggest that the huge γ is not primarily due to the strong coupling between Pr ions.

The observation for the rare-earth ionic-radius effect on the suppression of T_c (Refs. 14, 15, and 34) and of T_N (Ref. 35) in the $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system strongly suggests that the hybridization of Pr $4f$ electrons with the holes in the CuO_2 planes must play an important role in these anomalous physical properties. Moreover, the hybridization of Pr $4f$ electrons with holes in Cu-O_2 planes has been proposed by Torrance and Metzger[36] as a mechanism that causes a localization of the conducting

TABLE II. Antiferromagnetic transition temperature T_N, effective magnetic moment $\mu_{\rm eff}$, linear term coefficient of specific heat γ, and superconducting transition temperature T_c(midpoint) for some selected Pr-based compounds.

Compound	T_N (K)	$\mu_{\rm eff}$ (μ_B)	γ (mJ/mol K^2)	T_c (K)	Ref.
$PrBa_2Cu_3O_7$	17	2.97	300	Not observed	4
$Pr_{0.9}Ca_{0.1}Ba_2Cu_3O_7$				Not observed	22
Pr_2CuO_4	Not observed	3.51	1.5	Not observed	29
$Pr_{1.85}Ce_{0.15}CuO_4$				17	30
$PrBa_2Cu_2NbO_8$	12	2.86	3.1	Not observed	31
$Pr_{0.9}Ca_{0.1}Ba_2Cu_2NbO_8$				Not observed	32
$PrS_2Cu_{2.7}Mo_{0.3}O_7$	Not observed	3.05	440	Not observed	This work
$Pr_{0.9}Ca_{0.1}Sr_2Cu_{2.7}Mo_{0.3}O_7$				17	This work

holes in the Cu-O_2 planes. The enhanced hybridization can yield both the unexpected high magnetic ordering temperature and the suppression of superconductivity.[37]

IV. CONCLUSION

The suppression of T_c in $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ has been studied and compared to that in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. The x dependence of T_c cannot be simply described by the AG pair-breaking model, though the disagreement can be improved with the use of the optimal $T_c(0)$. The large value of x_{cr} and the low normal-state resistivity indicate that the localization of the conduction holes induced by Pr substitution is rather weaker in $Y_{1-x}Pr_xSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ than in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. This correlation of T_c and resistivity is consistent with the hole-filling–localization model. The observations of a reduced μ_{eff} and a huge γ are similar in both systems. In contrast to a $T_N \sim 17$ K seen in $PrBa_2Cu_3O_{7-\delta}$, no indication of any magnetic ordering transition down to 0.6 K is observed in $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. In addition, a superconducting transition with $T_c \sim 17$ K is observed resistively and inductively in $Pr_{0.9}Ca_{0.1}Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. Basically these results are discussed and explained within a framework that a strong magnetic correlation (high T_N) of the Pr magnetic moments is caused or mediated by an enhanced hybridization of Pr $4f$ electrons with holes in the CuO_2 planes. As a consequence, this is thought to be the primary origin for the suppression of T_c in these Pr-based cuprates.

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