

Occurrence of superconductivity in Ca- and Sr-doped $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$

H. L. Tsay and Y. C. Chen

Department of Electrical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China

F. L. Juang, W. M. Wang, and H. D. Yang

Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China

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Polycrystalline samples of $(\text{Pr}_{1-x}\text{M}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ ($\text{M}=\text{Ca}$ and Sr ; $0 \leq x \leq 0.3$; $\delta \sim 0.1$) with tetragonal perovskitelike structure were synthesized and investigated by powder x-ray-diffraction, electrical-resistivity, magnetic-susceptibility, and specific-heat measurements. Superconductivity can be achieved by partially substituting Ca or Sr for Pr in semiconducting $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$. The T_c (midpoint) is about 17 K with $x=0.1$ for both Ca- and Sr-doped systems. The observation of the magnetic shielding effect with powder samples confirms the bulk-nature superconductivity. In addition, the reduced effective magnetic moment μ_{eff} ($\mu_B/\text{Pr mol}$) derived from the Curie-Weiss-like magnetic susceptibility of $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ is found to increase with Ca or Sr doping, while the linear term coefficient γ ($\text{mJ}/\text{Pr mol K}^2$) of specific heat is almost independent of the doping. These results are discussed in conjunction with hole-filling and hybridization effects for the quenching of superconductivity in $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ and compared with those in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

The absence of superconductivity and anomalous magnetic properties of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have received much attention since this compound was first synthesized. $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ forms the same orthorhombic structure as that of high- T_c $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y-123), but it is curiously not superconducting.¹ In order to shed light on the basic mechanism of oxide high- T_c superconductivity, the $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system has become one of the most studied subtopics in the field of high-temperature superconductivity for the past several years. Plenty of experiments and interpretation which focused on the depression of T_c in $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ have been conducted and proposed.²⁻⁴ Nevertheless, there are still unsolved questions to date. On the other hand, Neumeier *et al.*⁵ have demonstrated the variation of T_c in the $(\text{Y}_{1-x-y}\text{Ca}_y\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system, suggesting that the hole-filling and pair-breaking mechanisms dominate separately in the suppression of superconductivity in Pr-doped 123 system. In our earlier studies,⁶ the single-phase bulk samples $(\text{Pr}_{1-x}\text{Ca}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($x \leq 0.3$) are all semiconducting. At higher doping level ($x \sim 0.5$), where the bulk sample is multiphase and metastable, thin films of nearly single phase can be obtained and become superconducting.^{7,8} In those papers, the doping of the same valent-state cation Sr fails to make $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconducting. The reason for the difference between Ca and Sr doping is not yet clear.

Recently, the Sr-based 123 structure has been stabilized by partially substituting the Mo-O for Cu-O chains.⁹ Subsequently, single-phase $\text{RSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ ($\text{R}=\text{rare earths}$) have been successfully synthesized and found to have a T_c around 30 K, except $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$, which is as a semiconductor as $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$.¹⁰ In our preliminary studies on the $(\text{Y}_{1-x}\text{Pr}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ ($0 \leq x \leq 1$; $\delta \sim 0.1$) system,^{11,12} the critical concentration $x_{\text{cr}} \sim 0.85$ required to suppress the T_c to zero is larger than

$x_{\text{cr}} \sim 0.55$ in $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$; the normal state resistivity ($\rho_{100\text{ K}}$) of $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ is about three orders of magnitude smaller than that of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$; and no indication of magnetic ordering transition was observed in $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ by specific-heat measurement down to 0.6 K in contrast to the antiferromagnetic transition at 17 K in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. These provide another chance to study the occurrence of superconductivity in Ca- and Sr-doped Pr-based 123 cuprates. In this paper, we present the electrical, magnetic, and thermal results for Ca- and Sr-doped $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ and compare these results with those in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

All polycrystalline samples $(\text{Pr}_{1-x}\text{M}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ ($\text{M}=\text{Ca}$ or Sr and $x=0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3$) were prepared by the solid-state-reaction method under identical condition. Sample preparation and characterization were described elsewhere.¹² Electrical-resistivity measurements were performed by the standard four-probe method. Magnetic susceptibility was measured by using a superconducting quantum interference device (SQUID) magnetometer. Low-temperature specific heat was measured with a ³He thermal relaxation calorimeter and the heat-pulse technique¹³ was used. The samples were attached to a sapphire chip (addenda), which has two separated silicon films deposited on it to serve as the heater and thermometer, respectively. The Si-film thermometer was calibrated against a precalibrated germanium thermometer. The chip was then connected to a constant-temperature copper block with a weak thermal link, thermal conductance κ of which was measured at each temperature by applying a small power $P=\kappa(T_{\text{sample}}-T_{\text{block}})$ to the chip. When the power was turned off, the sample temperature relaxed exponentially to the block temperature with a time constant $\tau=C/\kappa$. Thus the total heat capacity C was obtained.

Figure 1 shows room-temperature powder x-ray-diffraction patterns for $(\text{Pr}_{1-x}\text{M}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ with

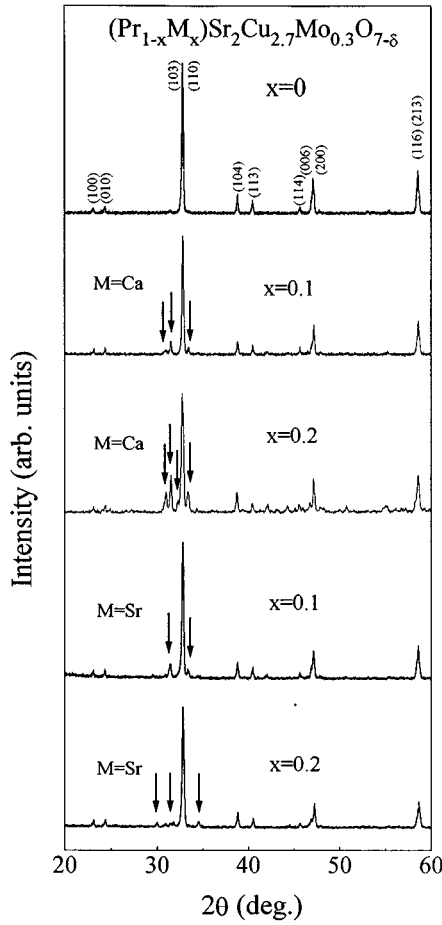


FIG. 1. Room-temperature powder x-ray-diffraction patterns for $(\text{Pr}_{1-x}\text{M}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ with $M=\text{Ca}$ and Sr ; $x=0, 0.1$, and 0.2 . Miller indices are indicated using space group $P4/mmm$. Impurity peaks are pointed by arrows.

$M=\text{Ca}$ and Sr ; $x=0, 0.1$, and 0.2 . In contrast to the Ca-doped sample, in which the impurities prevail as $x>0.1$, the Sr-doped samples retain the structure even at $x=0.2$. Little variation of lattice parameter a for $P4/mmm$ phase in the Ca-doping case suggests that most of doped Ca atoms substitute for Pr atoms in the tetragonal 123 structure. Moreover, the increase in lattice constants a and c in the Sr-doping system is consistent with the fact that the excess Sr atoms substitute for Pr atoms.

Electrical resistivity as a function of temperature for $(\text{Pr}_{1-x}\text{M}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ for $M=\text{Ca}$ and Sr with $x=0, 0.1$ and 0.2 is shown in Fig. 2. T_c (midpoint= 17 and 21 K with $x=0.1$ and 0.2 for $M=\text{Ca}$ and Sr , respectively). The absence of superconductivity in the sample $\text{Pr}(\text{Sr}_{0.9}\text{Ca}_{0.1})_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ (not shown) may rule out the possibility that the superconductivity in $(\text{Pr}_{1-x}\text{Ca}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ is caused by Ca substitution for Sr. The low temperature χ - T curve in the inset demonstrates the bulk superconductivity for $(\text{Pr}_{0.9}\text{Ca}_{0.1})\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$. This is different from that in $(\text{Pr}_{1-x}\text{Ca}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system, where the superconductivity can be achieved only in the thin films but not in the bulk samples.^{7,8} It is worth mentioning that the superconductivity of $(\text{Pr}_{1-x}\text{Ca}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ can only be observed in orthorhombic films but not in

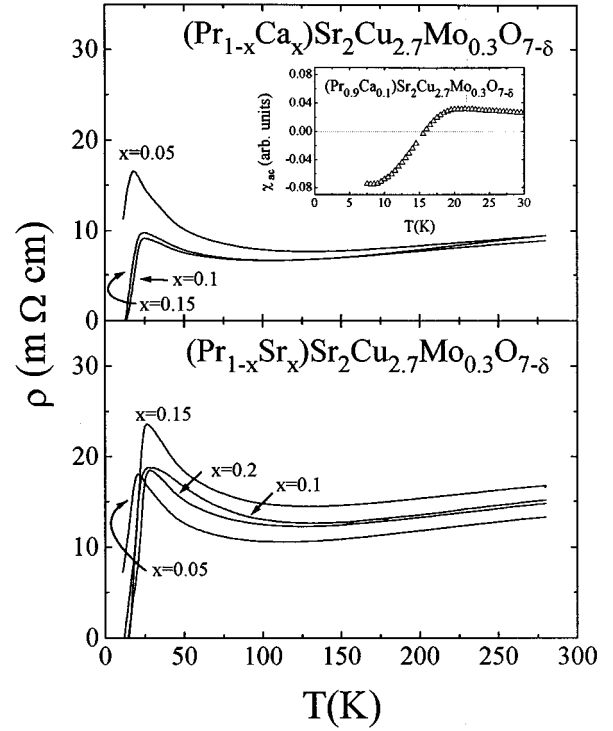


FIG. 2. Electrical resistivities as a function of temperature for $(\text{Pr}_{1-x}\text{M}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ with $M=\text{Ca}$ (upper) and Sr (lower). Inset shows the low-temperature ac susceptibility for $(\text{Pr}_{0.9}\text{Ca}_{0.1})\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$.

the tetragonal ones.⁸ However, the superconducting $(\text{Pr}_{1-x}\text{Ca}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ and $(\text{Pr}_{1-x}\text{Sr}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ bulk samples investigated here are all tetragonal. The observation of superconductivity in both Ca and Sr doping on $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ is in contrast to that in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, where a semiconducting behavior was observed in Sr-doped film.⁸ The difference between Ca- and Sr-doped $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been argued⁸ to be consistent with the ionic size dependence of T_c observed in the $(\text{R}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ systems,^{14,15} and it implies that the hybridization between Pr and CuO_2 plane is important in the quenching of superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. However, this ionic-size effect cannot successfully explain why the T_c in the different size Ca- and Sr-doped $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ is about the same with the same doping level. Furthermore, the superconductivity in $(\text{Pr}_{1-x}\text{M}_x)\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ ($M=\text{Ca}$ and Sr) is observed at much lower doping level with $x\sim 0.1$ than that in $(\text{Pr}_{1-x}\text{Ca}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $x\sim 0.5$. Therefore, if the valence of Pr ions in both systems is the same, the hole-filling picture cannot be applied to these cases either. Nevertheless, the T_c (~ 17 K) of $(\text{Pr}_{0.9}\text{Ca}_{0.1})\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ is much higher than $T_c\sim 0$ K of $(\text{Pr}_{0.9}\text{Y}_{0.1})\text{Sr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$. This illustrates that the divalent Ca must do something different from the trivalent Y in the occurrence of superconductivity. Most recently, Blackstead and Dow¹⁶ proposed that the Ba-site Pr suppresses superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ based on the mixing of Pr and Ba using the criterion of ionic size effect. However, the ionic size of Sr^{2+} is closer to Pr^{3+} than Ba^{2+} is, thus Sr may get more mixing with Pr. Therefore $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ would have been more insulating than $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Nevertheless, the room-

TABLE I. Lattice parameters, superconducting transition temperature T_c (midpoint), effective magnetic moment μ_{eff} , and linear term coefficient γ of specific heat for $RSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$.

R	a (Å)	c (Å)	T_c (K)	μ_{eff} ($\mu_B/\text{Pr mol}$)	γ (mJ/Pr mol K ²)
Pr	3.858(2)	11.616(10)		3.05	212
Pr _{0.9} Ca _{0.1}	3.857(1)	11.624(9)	17	3.52	227
Pr _{0.9} Sr _{0.1}	3.863(1)	11.624(10)	17	3.52	221

temperature resistivity of the former is about three orders of magnitude smaller than that of the latter. This fact appears to be inconsistent with their proposal. In particular, superconductivity can be achieved with lower Ca doping in $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ than in $PrBa_2Cu_3O_{7-\delta}$. Thus it is difficult to claim that the suppression of T_c is induced by Ba/Sr-site Pr in these Pr-based compounds. An alternative explanation is to consider the hybridization which takes place between Pr and CuO_2 planes.^{17,18} Under this picture, hybridization will localize the mobile holes and eventually destroy superconductivity. The strength of this hybridization in $PrBa_2Cu_3O_{7-\delta}$ can be argued to be weakened by substituting Sr for Ba which will result in an increase in Pr-O(3) bond length.¹⁹ Therefore, the hybridization in the Sr-based 123 is weaker than that in the Ba-based 123. This weakening in hybridization can be regarded as a reason why less Ca or Sr doping is needed to delocalize the trapped holes and restore the superconductivity in the $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ case (see Table I).

Figure 3 shows the inverse magnetic susceptibility as a function of temperature for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$, $(Pr_{0.9}Ca_{0.1})Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$, and $(Pr_{0.9}Sr_{0.1})Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. The effective magnetic moment μ_{eff} for the Pr ions derived from the Curie-Weiss susceptibility is 3.05, 3.52, and 3.52 $\mu_B/\text{Pr mol}$, respectively. The shortness in the μ_{eff} for Pr ions with respect to that for free Pr^{3+} ions (3.58 μ_B) has been argued to be the indication of the electronic interaction between Pr and CuO_2 planes. This electronic interaction results in a crystalline field effect (CFE) and a reduction of effective magnetic moment.²⁰ The electronic interaction (hybridization) between Pr and CuO_2 planes in the Sr-based system is further weakened by Ca and

Sr doping. Therefore, the increase of the μ_{eff} for Pr ions can be ascribed to the weakening of CFE. However, it should be noted that value for μ_{eff} ($\mu_B/\text{Pr mol}$) is basically kept constant through $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ series²¹ even in the superconducting samples. In the Ca- or Sr-doping cases shown here, these doped divalent ions will weaken the interaction between Pr and CuO_2 planes. It seems that the weakening of this interaction will resume the effective moment of Pr^{3+} ions. However, this viewpoint needs more data and analyses.

Figure 4 shows the low-temperature specific heat for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$, $(Pr_{0.9}Ca_{0.1})Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $(Pr_{0.9}Sr_{0.1})Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. The data are fitted to the equation $C = A/T^2 + \gamma T + BT^3$ in the temperature range of 0.6–2.5 K, where the first term is the contribution from a nuclear Schottky anomaly and the third term is the sum of the lattice and three-dimensional magnetic contributions. The fitting values for linear term coefficient γ are 212, 227, and 221 mJ/Pr mol K² for the above three compounds, respectively. Even though the γ value depends on the various fitting procedures or fitting ranges by different groups,^{2,12,22} the large value of γ has been commonly recognized. This little dependence of γ value on Ca and Sr doping is similar to that observed in $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$.²² It is emphasized that the heavy-fermion-like γ value for these Pr-based cuprates does not depend on whether samples are superconducting or insulating. This implies that the large γ value may not be

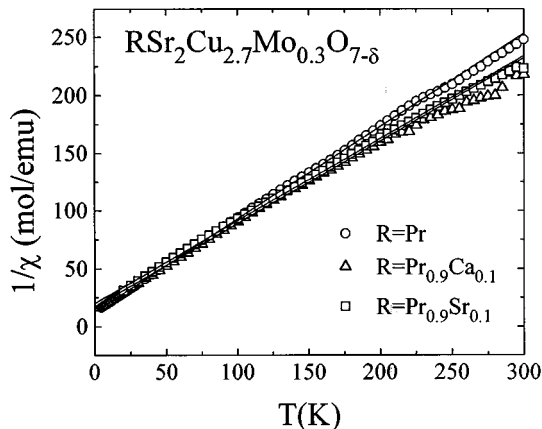


FIG. 3. Inverse magnetic susceptibility as a function of temperature for $(Pr_{1-x}M_x)Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ with $M = \text{Ca}$ and Sr ; $x = 0$ and 0.1 in the temperature range of 30–300 K.

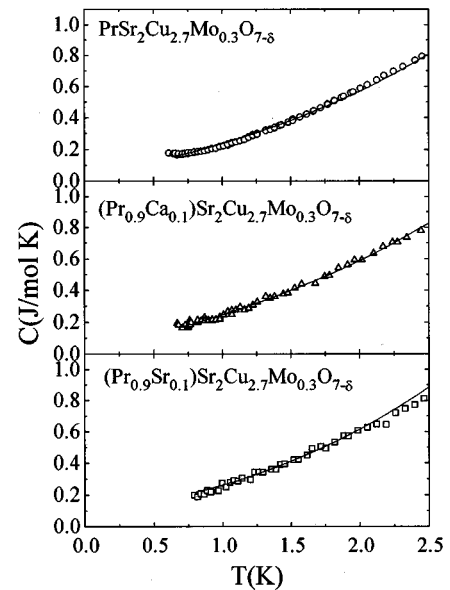


FIG. 4. Low-temperature specific heat for $PrSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$, $(Pr_{0.9}Ca_{0.1})Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$ and $(Pr_{0.9}Sr_{0.1})Sr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}$. Lines are fits to the equation $C = A/T^2 + \gamma T + BT^3$.

closely related to the suppression of superconductivity in these Pr-based cuprates. The origin of large γ value in these Pr-based compounds needs further clarification.

In summary, superconductivity can be achieved in 10 at.% Ca- or Sr-doped $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$ bulk samples, which is in contrast to what was observed in Ca-doped $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film, where it needs 50 at.% Ca doping to make sample superconducting. The μ_{eff} for Pr ions is found to increase with Ca or Sr doping. These results can be ex-

plained in the framework of hybridization between Pr and CuO_2 planes. The doping of Ca or Sr will further weaken the weak hybridization in $\text{PrSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7-\delta}$, delocalize the trapped holes, and consequently restore the superconductivity.

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