

Kondo effect in underdoped n -type superconductorsTsuyoshi Sekitani,¹ Michio Naito,² and Noboru Miura¹¹*Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan*²*NTT Basic Research Laboratories, Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan*

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We present high-field magnetotransport properties of high-quality single-crystalline thin films of heavily underdoped nonsuperconducting $(\text{La,Ce})_2\text{CuO}_4$, $(\text{Pr,Ce})_2\text{CuO}_4$, and $(\text{Nd,Ce})_2\text{CuO}_4$. All three materials show identical behavior. They are metallic at high temperatures and show an insulating “upturn” at low temperatures. The insulating upturn has a $\log T$ dependence, but saturates toward the lowest temperatures. Notably, the insulating upturn tends to be suppressed by applying magnetic fields. This negative magnetoresistance has a $\log B$ dependence, and its anisotropy shows a nonsimple behavior. We discuss these findings from the viewpoints of Kondo scattering and also two-dimensional weak localization, and demonstrate Kondo scattering as a more plausible explanation. The Kondo scatters are identified as Cu^{2+} spins in the CuO_2 planes.

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It has been claimed that the normal state of high- T_c cuprate superconductors is “anomalous.” Especially, there has been considerable controversy as to whether the normal ground state is metallic or insulating. To clarify this issue, the transport properties of the low-temperature normal state have been investigated on various cuprates by suppressing superconductivity with high magnetic fields. Boebinger, Ando *et al.* performed extensive studies on hole-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) and $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+y}$, and observed unusual insulating behavior, which they claimed to be a generic normal-state property of under-doped cuprates.¹⁻⁴ Recently, Fournier *et al.* investigated the normal state of electron-doped $(\text{Pr,Ce})_2\text{CuO}_4$ (PCCO) in detail, and pointed out many similarities to hole-doped LSCO in spite of the “apparent” electron-hole doping asymmetry as frequently mentioned.^{5,6} These results seem to indicate that cuprates, regardless of being the hole or electron doped, commonly show an “insulator-metal” crossover as a function of the doping level. In the underdoped regime, the resistivity shows an insulating “upturn” ($d\rho/dT < 0$) at low temperatures, which has a $\log T$ dependence in many cases. There has been much speculation with respect to its origin, but a clear explanation has not yet been reached. In order to unveil the nature of this $\log T$ insulating upturn, we have performed systematic magnetotransport experiments on electron-doped $(\text{Nd,Ce})_2\text{CuO}_4$ (NCCO), PCCO, and $(\text{La,Ce})_2\text{CuO}_4$ (LCCO) using pulsed magnetic fields up to 50 T.^{7,8} In this

paper, we present the results for heavily underdoped nonsuperconducting specimens. The purpose of using nonsuperconducting samples is to avoid the influence of superconductivity and thereby to observe the normal-state transport down to zero magnetic field. Our results strongly indicate that the origin of the low-temperature “insulating” behavior is the Kondo scattering by magnetic moments of Cu^{2+} .

Magnetotransport experiments were performed on high-quality c -axis oriented NCCO, PCCO, and LCCO films at temperatures from 1.5 K to 300 K. The films were grown by MBE on either SrTiO_3 (001) or KTaO_3 (001) substrates. The thickness of the films was $\sim 1000\text{\AA}$. All of the films, for which we show the results in this paper, are heavily underdoped and nonsuperconducting. In order to show the quality of our films, the T_c and resistivity values for our typical optimum doped films as well as the heavily underdoped films used for this study are summarized in Table I. The requirements to prepare such high quality of films are stringent cation stoichiometry adjustment and careful removal of apical oxygen without phase decomposition. The details of our film growth were described in Refs. 9–11.

High magnetic fields up to 50 T were produced by a pulse magnet, which was energized by a capacitor bank of 900 kJ (5 kV or 10 kV). The resistivity was measured by the standard four-probe method with electrodes formed by Ag or Au evaporation. A dc current of the order of $1\sim 10\ \mu\text{A}$ was supplied in plane.

TABLE I. Important parameters for $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{Ln}=\text{Nd,Pr,L a}$) films with heavily underdoping and optimally doping, Ce content x , the superconducting temperature T_c , the Kondo temperature T_K , the Kondo magnetic field B_K , the resistivity minimum temperature T_{min} , the residual resistivity ρ_0 , the unitarity-limit resistivity ρ_u , and the resistivity at 300 K $\rho_{R.T.}$.

Sample	x	T_c (K)	T_K (K)	B_K (T)	T_{min} (K)	$\rho_0(\mu\Omega\ \text{cm})$	$\rho_u(\mu\Omega\ \text{cm})$	$\rho_{R.T.}(\mu\Omega\ \text{cm})$
$\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$	0.045		15.7	23.4	103	198	720	750
	0.090	30				25		250
$\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$	0.098		18.7	27.8	59	110	159	327
	0.135	25				15		200
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	0.086		17.9	26.6	73	300	570	763
	0.145	24				15		150

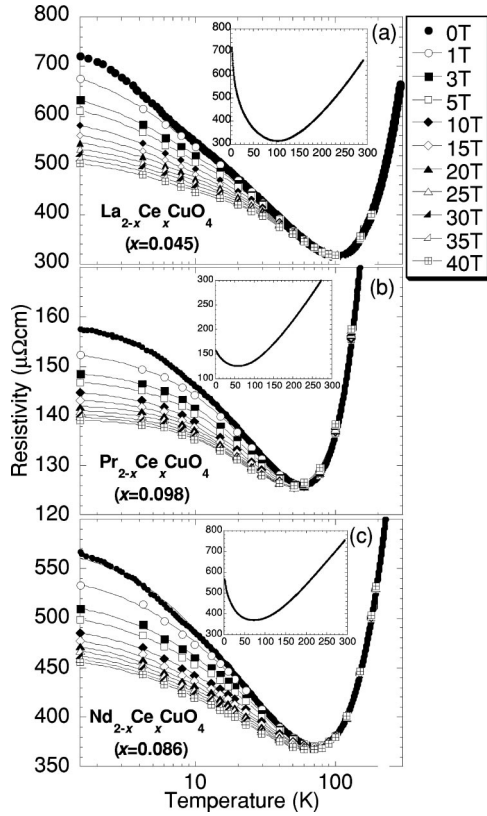


FIG. 1. In-plane resistivities in magnetic fields as a function of $\log T$ for $(\text{La,Ce})_2\text{CuO}_4$ (a), $(\text{Pr,Ce})_2\text{CuO}_4$ (b), and $(\text{Nd,Ce})_2\text{CuO}_4$ films (c). The insets show the linear-scale replots of the zero-field data.

The in-plane resistivities in different magnetic fields applied parallel to the c axis are shown in Fig. 1. The insets show the linear-scale replots of the zero-field data. The behaviors for all NCCO, PCCO, and LCCO films are similar to one another. The resistivity shows metallic behavior ($d\rho/dT > 0$) with a T^2 dependence down to the resistivity-minimum temperature (T_{min}). Below T_{min} , the resistivity increases as the temperature is lowered (we call this behavior as an “upturn” in this paper). This insulating upturn has a $\log T$ dependence, but saturates toward the lowest temperatures. Furthermore, the upturn tends to be suppressed by applying magnetic fields. Similar results have recently been reported for nonsuperconducting PCCO films by Fournier *et al.*⁶

Figure 2 shows the in-plane resistivity as a function of magnetic field B at various temperatures. Here the field is applied parallel to the c axis. The data are plotted against $\log B$ in order to see the field dependence of the negative magnetoresistance. It was confirmed that there is no heating effect due to eddy currents in our experiments since the data recorded from both up- and down-sweeps of the pulsed magnetic field nearly coincide. The behaviors for all NCCO, PCCO, and LCCO are again almost identical. Negative magnetoresistance appears at temperatures below the resistivity minimum (T_{min}) and becomes more prominent with decreasing temperature. It has a $\log B$ dependence, but saturates toward $B=0$ T. In hole-doped cuprates such as LSCO, nega-

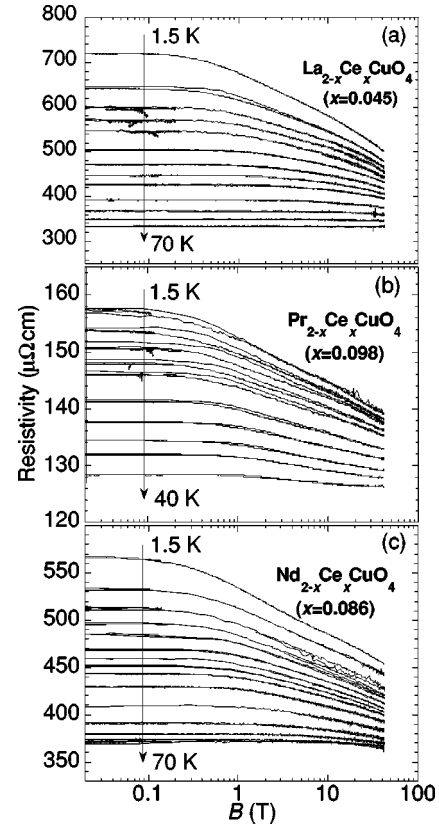


FIG. 2. Magnetoresistance curves as a function of $\log B$ at different temperatures for $(\text{La,Ce})_2\text{CuO}_4$ (a), $(\text{Pr,Ce})_2\text{CuO}_4$ (b), and $(\text{Nd,Ce})_2\text{CuO}_4$ films (c).

tive magnetoresistance in in-plane transport have been reported by other groups.^{1,12} Especially, Preyer *et al.* observed isotropic negative magnetoresistance in high-quality single crystal of LSCO.¹²

In order to demonstrate the anisotropy of the negative magnetoresistance, Fig. 3 shows the magnetoresistance curves against $\log B$ for different field directions. The angle dependences of the magnetoresistance are depicted in Fig. 4. The angle θ in this figure is defined with respect to the c axis. The curves, except for $\theta=90^\circ$, almost fall into the same line, indicating weak anisotropy. For $\theta=90^\circ$, however, the curve deviates from this trend line. The dissimilar behavior for $\theta=90^\circ$, where B is parallel to the layer, is not well understood, however, at least in some part may be related to the complicated magnetic structure in the charge reservoir blocks (Ln_2O_2 layers), since different behavior is observed for different Ln.

The two main features, the $\log T$ -dependent insulating upturn and the $\log B$ -dependent negative magnetoresistance, which have been observed in the present experiment, can be explained either by localization or by Kondo scattering. The former possibility has been pointed out by several authors.^{5,6,13,14} Calculations based on two-dimensional (2D) weak localization predict, for simplest cases, a $\log T$ -dependent divergence of resistivity toward $T=0$ K and a $\log B$ -dependent negative magnetoresistance. However, this possibility may be ruled out because the anisotropy of the negative magnetoresistance does not follow a cosine depen-

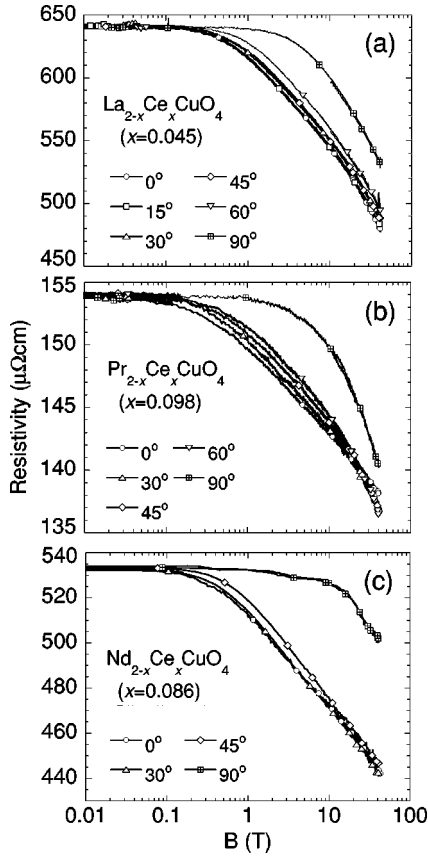


FIG. 3. Anisotropy of magnetoresistance at 4.2 K. The angle (θ) of the magnetic-field direction is defined with respect to the c axis.

dence. Moreover, in 2D weak localization, the coefficient (α) for $\log T$ -dependent conductivity and also for $\log B$ -dependent magnetoconductivity per sheet should be material-independent universal values. However, we found that the observed α value depends on the doping level and also on the material. Figure 5 shows such an example, which shows the doping dependence of the coefficient for NCCO.^{7,8} The coefficient α changes significantly from 0.9 to 14.6 as x varies from 0.086 (heavily underdoped) to 0.146 (optimum).

The weak anisotropy of the observed negative magnetoresistance suggests that the observed phenomena should be

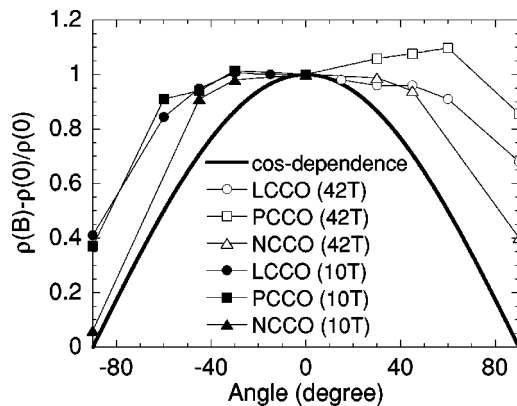


FIG. 4. Comparison between the angular dependence of negative magnetoresistance at 4.2 K and a cosine dependence.

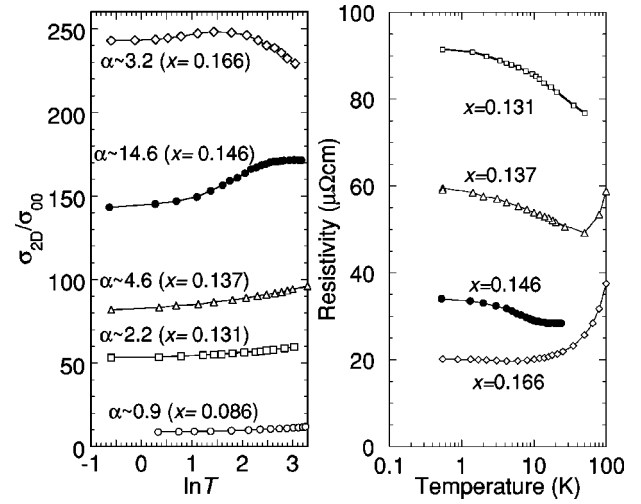


FIG. 5. Doping dependence of upturn in NCCO films [$x = 0.086$ (under-doping) to 0.166 (over-doping)] by suppressing the superconductivity with high magnetic fields at low temperatures [right], and the normalized values of the coefficient (α) of $\log T$ [$\sigma_{2D} = d/\rho$, $\sigma_{00} = (e^2/\pi h)$, $\sigma_{2D}/\sigma_{00} = \alpha \ln T$] (left).

spin related in origin. Hence, next we discuss our experimental results on the basis of the Kondo scattering. The Kondo effect, which arises from the exchange interaction between itinerant conduction electrons and localized spin impurities, leads to anomalous temperature dependences in various physical parameters due to the Fermi-surface effect. The anomalous behaviors, in essence, originate from singlet formation between a conduction electron and a localized spin below the Kondo crossover temperature T_K . With regard to the resistivity, a third-order Born approximation for the spin

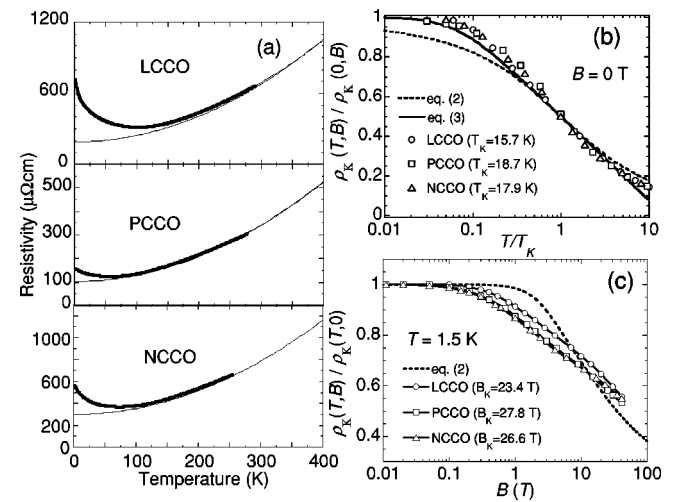


FIG. 6. Fitting procedure to obtain ρ_K by subtracting $\rho_0 + \rho_i$ from the experimental resistivity (a), and resultant $\rho_K(T, B=0 T)$ (b) and $\rho_K(T=1.5 K, B)$ (c). The T and B dependences of ρ_K are compared with the theoretical predictions from single-impurity Kondo scattering: the dashed lines represent the KMHZ or the generalized Hamann formula [Eq. (2)] and the solid line represents the empirical formula [Eq. (3)] with $T_K = 15.7 K$, 18.7 K, and 17.9 K for LCCO, PCCO, and NCCO, respectively.

inversion scattering gives rise to a log T -dependent upturn. This log T -dependent resistivity does not diverge toward 0 K, but has a finite maximum value (unitarity-limit scattering) at $T=0$ K, which differs from the behavior predicted by 2D weak localization. High magnetic fields act to suppress the spin inversion (or, equivalently, to dissociate Kondo singlets) and thereby give negative magnetoresistance, which is isotropic in ideal cases. The negative magnetoresistance has a log B dependence in the intermediate field region, and saturates both toward $B=0$ T and toward $B>B_K$ (B_K : Kondo crossover field). This simplest Kondo description can be applied to Al and noble metals (Cu, Ag, and Au) containing 3d magnetic impurities such as Mn and Fe, and also to some rare-earth compounds containing 4f magnetic impurities. One typical material for the latter category is (La,Ce)B₆, for which extensive magnetotransport data are available.¹⁵ The magnetotransport properties observed here for (Ln,Ce)₂CuO₄ qualitatively agree with the above Kondo predictions, and furthermore look very similar to those for (La,Ce)B₆. In the simplest Kondo systems, negative magnetoresistance should be isotropic. In actual cases, however, weak but finite anisotropy has been reported for anisotropic

materials.^{16–19} The anisotropic negative magnetoresistance has been understood as an anisotropic g value due to the crystalline electrical field. A similar explanation may also be applied to our cases.

We give some quantitative discussions below. First, we compare the experimental temperature and magnetic-field dependences with theoretical predictions for the Kondo resistivity. To extract the Kondo resistivity $\rho_K(T,B)$, we assume that the resistivity can be decomposed into three parts,

$$\rho(T,B) = \rho_0 + \rho_i(T) + \rho_K(T,B), \quad (1)$$

where ρ_0 represents temperature-independent impurity scattering and ρ_i represents a high-temperature T^2 component (empirical, the origin of this T^2 dependence is not known). Here we neglect conventional orbital (positive) magnetoresistance that might give a slight B dependence to ρ_0 and to ρ_i . With a standard fitting procedure for subtracting ρ_0 and ρ_i as shown in Fig. 6(a), we can get $\rho_K(T,B=0)$ in Fig. 6(b) and $\rho_K(T=1.5\text{ K},B)$ in Fig. 6(c). The approximate theoretical expression (the so-called ‘‘KMHZ’’ or the generalized ‘‘Hamann’’ formula²⁰) for the Kondo resistivity $\rho_K(T,B)$ is given as

$$\rho_K(T,B) = \frac{\rho_u}{2} \left\{ 1 - \frac{f(T,B)}{\sqrt{f^2(T,B) + \pi^2 \left[S(S+1) + \frac{1}{4} \tanh^2 \frac{\beta g \mu_B B}{2} \right]}} \right\}, \quad (2)$$

$$f(T,B) = \ln \frac{T}{T_K} + \text{Re} \psi \left[\frac{1}{2} + \frac{\beta g \mu_B B}{2\pi i} \right] - \psi \left[\frac{1}{2} \right],$$

where ρ_u represents the unitarity-limit resistivity and $\psi(z)$ denotes the digamma function [$\psi(z)$ has a logarithmic dependence in the asymptotic limit of $z \rightarrow \infty$].^{21,22} This formula is based on the Suhl-Nagaoka theory for the Kondo effect.^{23–25} In Fig. 6(b), the zero-field data are compared with the prediction (dashed line) by Eq. (2) with $T_K=15.7$ K, 18.7 K, and 17.9 K for LCCO, PCCO, and NCCO, respectively. The agreement is fair for $T/T_K \geq 1$. However, the experimental data deviates from Eq. (2) for $T/T_K < 1$. This discrepancy may be due to inapplicability of Eq. (2) to $T/T_K \ll 1$. For $T/T_K \ll 1$, most of the existing data for $\rho_K(T,B=0)$ for typical Kondo materials can be better described by the ‘‘empirical’’ formula,^{26,27} which is given as

$$\rho_K(T) = \frac{\rho_u}{2} \left\{ 1 - \frac{\ln[(T^2 + \theta^2)/T_K^2]^{1/2}}{\pi[S(S+1)]^{1/2}} \right\}, \quad (3)$$

where $\ln(\theta/T_K) = -\pi[S(S+1)]^{1/2}$, namely, $\theta = 0.066T_K$ for $S = 1/2$.²⁵ Our experimental data for $T/T_K \leq 1$ is also in good agreement with this ‘‘empirical’’ formula, which is indicated by a solid line in Fig. 6(b). In spite of this good agreement for the temperature dependence, the magnetic-field depen-

dence $\rho_K(T=1.5\text{ K},B)$ does not agree with Eq. (2) as is shown in Fig. 6(c). This discrepancy might be ascribed to the approximation of the KMHZ formula.^{21,22} The Kondo crossover temperature T_K and the Kondo crossover field B_K as determined by $k_B T_K = S g_{\text{eff}} \mu_B B_K$ with $S = 1/2$ and $g_{\text{eff}} = 2$ are summarized in Table I.

Finally, we discuss the origin of the Kondo scatterer. Nd³⁺ has a paramagnetic spin moment, and Pr³⁺ can also have a paramagnetic spin moment at high magnetic fields although the ground state is nonmagnetic. Therefore, the interaction between conduction electrons and spin moments of Nd³⁺ or Pr³⁺ might be a candidate for the Kondo scattering. Actually, Maiser *et al.* pointed out the possible interaction between conduction electrons and spin moments of Nd³⁺ ions at very low temperatures.²⁸ However, an essentially similar behavior is also observed in LCCO, where La³⁺ should not have a spin moment. So we can exclude the possibility of Nd³⁺ or Pr³⁺ spins as the Kondo scatterer. Therefore, we explore the other possibility, i.e., Cu²⁺ local spins in the CuO₂ plane. Regarding the magnetism in the CuO₂ planes for electron-doped (Ln,Ce)₂CuO₄, there have been many studies in the past, although the results have not been

well converging. One early study by μ SR for NCCO indicated that antiferromagnetism persists up to $x \sim 0.14$, above which superconductivity suddenly sets in.²⁹ However, it is now well established that interstitial apical oxygen tends to stabilize antiferromagnetic correlation, and may modify the intrinsic magnetism in the T' compounds. Therefore, different "recipes" to remove apical oxygen may give different sample properties. This can be noticed by the facts that there exist very large sample dependence in the resistivity upturn and also the residual resistivity value reported in the past. The intrinsic magnetic phase diagram for electron-doped $(\text{Ln,Ce})_2\text{CuO}_4$ cannot be reached without complete removal of interstitial apical oxygen. According to the "old" magnetic phase diagram mentioned above,²⁹ Cu^{2+} should be antiferromagnetically ordered at low temperatures in all of the films studied here. If this *were* the case, the single-impurity Kondo scattering approximation would not work. As an experimental fact, however, our experimental results can be well described by simple single-impurity Kondo theories.

This fact may bring the "old" magnetic phase diagram into doubt. We suggest that a very small number of Cu^{2+} Kondo impurities are induced by residual apical oxygen.

Our magnetotransport experiments on heavily underdoped nonsuperconducting $(\text{La,Ce})_2\text{CuO}_4$, $(\text{Pr,Ce})_2\text{CuO}_4$, and $(\text{Nd,Ce})_2\text{CuO}_4$ thin films have shown that the anomalous low-temperature transport common in these compounds is most likely governed by the Kondo scattering by Cu^{2+} spins in the CuO_2 planes. A similar conclusion has been reached in hole-doped cuprates from the recent defect-controlled transport experiments by Rullier-Albenque *et al.*³⁰ Our results may lead to a better understanding of the doping-induced "insulator-metal" crossover in cuprates.

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