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Low-temperature resistivity minimum in dilute Mn-doping $Na_{0.7}Co_{1-x}Mn_xO_2$: A Kondo-like oxide with strong disorder characteristics

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We present the results of low-temperature transport behavior and magnetic properties for dilute Mn-doped $Na_{0.7}Co_{1-x}Mn_xO_2$ system with $x=0$, 0.03, 0.07, 0.1. The results show that the properties are very sensitive to Mn doping at low temperatures. A unique resistivity minimum is found with a characteristic of metallic-semiconductor transition (<50 K) for all the doped samples. Combining with the resistivity data in applied field, it can be understood within the theory of Kondo scattering induced by magnetic impurities and electron-electron (e-e) interaction enhanced by disorder. The best fitting was made in the framework of the two scattering mechanisms in a wide temperature range of 2–100 K. The results prove that the layer $Na_{0.7}Co_{1-x}Mn_xO_2$, a kind of typical Kondo-like oxide like the dilute convention alloys, is a strong disorder system in which exists enhanced e-e interaction, which reflects a typical characteristic of strong correlation systems.

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I. INTRODUCTION

The layered transition-metal oxide $Na_{\gamma}CoO_2$ engendered much interest to physicists and material scientists due to its promising thermoelectric properties.[1–5] It is difficult to understand its anomalous large thermoelectric power and low electrical resistivity in combination with low thermal conductivity in the framework of conventional band picture, which makes it possible for technological applications. The subsequent discovery of superconductivity in the hydrated cobalt oxide $Na_{0.35}CoO_2 \cdot 1.3H_2O$ causes even greater excitement[6–8] and raises very interesting questions about the pairing mechanism related to cuprate superconductors.[9] Tremendous amount of experimental and theoretical researches have been conducted on this compound system focusing on the electronic properties and mechanisms of transport as well as superconductivity.[10–12] The Na_xCoO_2 family exhibits a rich variety of anomalous transport and magnetic properties, which suggests that both the strong $3d$ electron correlation and the spin state of the cobalt ion play an important role.[2,13] For $Na_{\gamma}CoO_2$ system, it was firstly reported by Fouassiar *et al.* and showed four different phases of the nonstoichiometric oxide: α-$Na_xCoO_2(0.9 \le x \le 1)$, α'-$Na_xCoO_2(x=0.75)$, β-$Na_xCoO_2(0.55 \le x \le 0.6)$ and γ-$Na_xCoO_2(0.55 \le x \le 0.74)$ depending on composition and reaction temperature.[14] All the structures of the different phases consist of planes of edge sharing CoO_6 octahedra alternating with layers of Na along the c axis according to several stacking patterns.[15–17] The two-dimensional crystal structure and electronic properties share much in common with high T_c cuprates superconductors, e.g., Na layers act as charge reservoirs that donate electrons and the CoO_2 layers act as conductor layers. On the other hand, in Na_xCoO_2, cobalts form triangular lattice resulting in geometrical frustration of antiferromagnetic (AFM) order,[18] while the square Cu lattice invites AFM order. The physical properties are determined by the amount of sodium and water in $Na_{\gamma}CoO_2 \cdot yH_2O$ via their influence on the Co valence state and the resulting distortions of the CoO6 octahedra. Recently, Foo *et al.* studies show that as Na content increases from 0.3 to 0.75 the material Na_xCoO_2 cross over from a Curie-Weiss metal to a paramagnetic (PM) metal, separated by a charge ordered insulator at $x=0.5$.[19] Much work has been done to dope Na_xCoO_2 on Na or Co site focusing on improving its thermoelectric performances.[4,5,20,21] In this paper, we present the results of electrical transport for Mn doping on the Co site. A low temperature resistivity minimum was found accompanied by a metallic-semiconductor transition below 50 K for all the Mn-doped samples. Magnetic measurements indicate the existence of a localized magnetic moment for all the doped samples. The external magnetic field was used in order to check the possibilities of magnetic impurity spin scattering and e-e interaction. The results are well fitted in the framework of Kondo scattering and the e-e interaction in a wide temperature range 2–100 K. The results prove that $Na_{\gamma}CoO_2$ is a kind of Kondo-like oxide as the conventional dilute alloy and $NaCo_{1-x}Mn_xO_2$ have strong disorder characteristic, in which a kind of enhanced e-e interaction exists. It is meaningful to understand the physical mechanisms for strongly correlated layer $Na_{\gamma}CoO_2$ system.

II. SAMPLES AND EXPERIMENTS

The experimental samples were prepared by solid-state reaction with a nominal composition $NaCo_{1-x}Mn_xO_2$ ($x=0, 0.03, 0.05, 0.10$). Stoichiometric amount of Na_2CO_3, Co_3O_4 and MnO_2 were mixed up and sintered repeatedly in air. Since Na tends to evaporate during calcinations,[3] the undoped sample with the starting composition of $Na_{\gamma}CoO_2$ is expected to change to $Na_{\gamma}CoO_2$ with $0.70 < \gamma < 0.75$. X-ray diffraction performed by using Rigaku 18 kWD/max-RB x-ray diffractometer with Cu-$K\alpha$ radiation. The diffraction

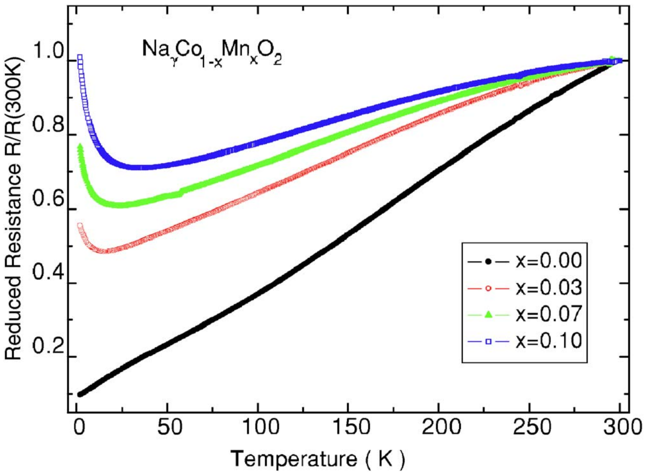

FIG. 1. (Color online) The reduced resistance as a function of temperature for $Na_{0.7}Co_{1-x}Mn_xO$ systems ($x=0,0.03,0.07,0.1$).

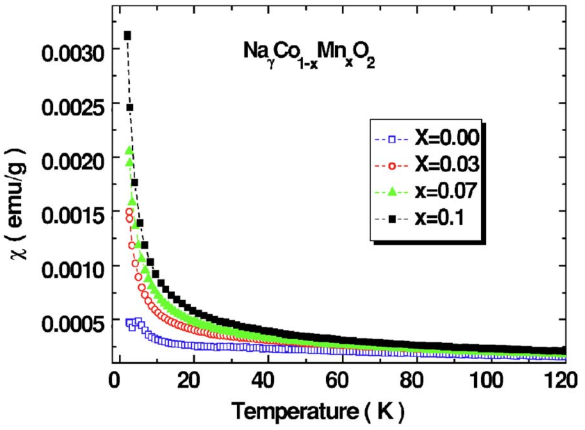

FIG. 2. (Color online) The results of the magnetic susceptibility for $Na_{0.7}Co_{1-x}Mn_xO_2$ systems ($x=0,0.03,0.07,0.1$).

data reveals that all the samples are single phase, which suggests that Mn has completely substituted for Co and all the peaks in the pattern can be indexed as the γ phase. Detailed Rietveld refinement shows a hexagonal layered structure with space group of $P6_3/mmc$. The Na concentration is determined to be 0.7 from a measurement of the lattice parameter of the c-axis, $c=10.94$ Å, as it was reported by Jansen *et al.*[22] The electrical transport using the four-probe method and magnetic measurements were carried out by physical property measurement system (PPMS-9, Quantum Design Inc.) in the temperature range of 2–300 K with the precision 20 nV for voltage, and 0.2 Oe for the magnetic field. All the results are well repeatable.

III. RESULTS AND DISCUSSION

Figure 1 shows the electrical resistivity as a function of temperature of 2.0–300 K for $NaCo_{1-x}Mn_xO_2$: $x=0$, 0.03, 0.05, 0.07, 0.1. For the sake of the comparison of all samples results in one figure, we introduced the arbitrary unit. It can be seen that, for the undoped sample ($x=0.0$), the resistivity shows an excellent metallic behavior in the temperature range we measured. In addition, it displays a T-linear variation below 100 K that is suggestive of a strong correlation behavior.[13] While for all the doped samples, the resistivity has a typical characteristic of metallic-semiconductor transition at low temperatures and shows a distinct resistivity minimum below 50 K which is strongly dependent on Mn content x. As the temperature decreases from the minimum, i.e., T_{min}, the resistivity begins an upturn. With increasing Mn doping levels, the upturn becomes steeper and T_{min} moves toward higher temperature. In temperature region above T_{min}, the resistivity for all the doped samples shows a metallic behavior and increases slightly in magnitude that can be attributed to the conventional impurity effect as Mn ion substitution. Above the minimum, all the curves retain almost the same slope. In fact, for undoped Na_xCoO_2 system with different Na content, such low temperature resistivity minimum was also found, which attributed the resistivity upturn to the spin-density wave opening a small gap at the Fermi surface and to a metamagnetic phase transition.[23,24] But in the present undoped $Na_{0.7}CoO_2$ sample, no resistivity minimum has been observed. This may be because the present undoped sample is γ phase while the samples in Refs. 23 and 24 are α phase. The transport behavior for $Na_{0.7}CoO_2$ sample of γ phase is believed to be completely different from the sample with α phase.[19] Obviously, the present resistivity minimum was resulted from the Mn doping. In particular, it is noticed that for the Cu-doped $NaCo_{1-x}Cu_xO_2$ system, no resistivity minimum was observed up to $x=0.1$.[21,25] This proves that the magnetic disturbance to the CoO_2 layers due to Mn doping plays an important role.[26]

In order to see these, the magnetic properties of samples were measured. Figure 2 shows the temperature dependence of magnetic susceptibility χ for Mn-doped $Na_{0.7}Co_{1-x}Mn_xO_2$ samples. It can be clearly seen that there are no typical magnetic transitions. In high temperature region, χ shows a weak dependence on doping and temperature. At lower temperatures, the undoped sample shows an anomalous change in χ similar to the result of Ref. 26, which was explained by spin glass such as cusp transition. For the doped samples, χ shows a drastic increase and increases in magnitude with increasing Mn content. These results indicate that the magnetic property of $Na_{0.7}CoO_2$ is extraordinary sensitive to the Mn doping at low temperatures, which can be interpreted by magnetic Mn^{3+} or Mn^{4+} substituting for nonmagnetic Co^{3+}.[27] In addition, all the doping samples follow a Curie-Weiss behavior: $\chi-\chi_0=C/(T+\theta)$ indicating the existence of localized moments with Curie constant $C=0.0051$, 0.0077, 0.0089 mol/g K, paramagnetic Curie-Weiss temperature $\theta=-2.15$, -1.12, -0.99 K for $x=0.03$, 0.07, 0.1 respectively. The effective moment of magnetic ions is enhanced with increasing Mn doping levels. As a result, the resistivity minimum connected with the existence of localized moments induced by the magnetic impurities Mn ions indicates a characteristic signature of Kondo scattering mechanism that can result in the low temperature resistivity upturn.

In many situations, low-temperature resistivity minimum is caused by Kondo effect, which was originally encountered in nonmagnetic systems with a slightly magnetic impurity as the alloys of Cu, Ag, Mg, Zn with Cr, Mn, and Fe as impurities and for very low temperature range.[28] Recently it was

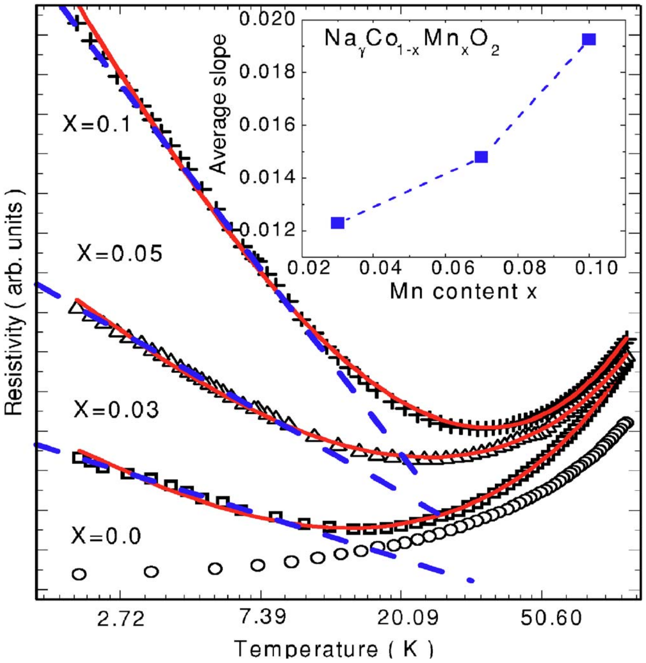

FIG. 3. (Color online) The electrical resistivity as a function of ln T for experimental samples in the temperature range of 2–100 K, which shows a good linear dependence on logarithmic temperature as the dashed lines. The insert gives the change of the slope by the dashed lines with different Mn content x in the low temperature region. The solid lines are the fitting using Eq. (1) in the whole range of 2–100 K.

also found in strong correlated manganites as well as ferromagnetism.[29,30] According to the Kondo theory, the relation between electrical resistivity and temperature can be expressed by the formula $\rho_k = \rho_0 + \rho_s \ln T$. Here, ρ_0 is the residual resistivity independent on temperature and field. The second term: $\rho_s \ln T$, is the contribution from the interaction between localized magnetic moments and the conductive electrons. The parameter ρ_s describes the strength of the spin scattering. In order to see the possible existence of Kondo scattering, we change the temperature axis from linear to natural logarithm scale in the temperature range 2–100 K. Figure 3 shows the resistivity $\rho(T)$ as a function of ln T for Na$_{0.7}$Co$_{1-x}$Mn$_x$O$_2$. It can be clearly seen a good linear dependence on the temperature ln T as fitting gives by dashed lines at low temperatures. In general, the slope of the curves below $T_{\min}$, which is written as $\bar{\rho}_s = |\rho_{2K} - \rho_{\min}| / |T_{2K} - T_{\min}|$ is a representation of average strength of the magnetic scattering and directly proportion to ρ_s. The insert of Fig. 3 points out that the magnitude of the $\bar{\rho}_s$ below $T_{\min}$ increases with increasing Mn content. Therefore, with the increase of Mn, the increase of the resistivity at low temperatures tends to be gradually enhanced, i.e., spin scattering is strengthened.

It must be noted that the discussion above is in a field-free situation. If the resistivity minimum is exclusively dominated by Kondo effect, as we know, the spin scattering of conductive electrons should be distinctively suppressed by an external magnetic field. This will result in flattening of the upturn and cause the $T_{\min}$ to move to the lower. In order to check the validity of the Kondo mechanism, an external magnetic field applied for the electrical resistivity measurement will be very necessary. Figure 4 are the results of resistivity as a function of temperature for the doped sample with $x=0.1$ in zero field and two external fields of 3.0 and 6.0 Tesla. It can be clearly seen that the external field has some suppression effect on the resistivity upturn. The insert of Fig. 4 shows the slope of the curves versus applied fields at low temperatures. It can be seen that the slope decreased with increasing field. But based on the present high external magnetic fields, this effect is not very evident comparing with conventional dilute alloys. The weak effect of the external field indicates that: (1) the low temperature resistivity minimum behavior is not very sensitive to applied fields; (2) the pure Kondo mechanism is insufficient to explain the resistivity minimum. So we expect other mechanisms probably exist working on the low temperature resistivity minimum in our doped samples.

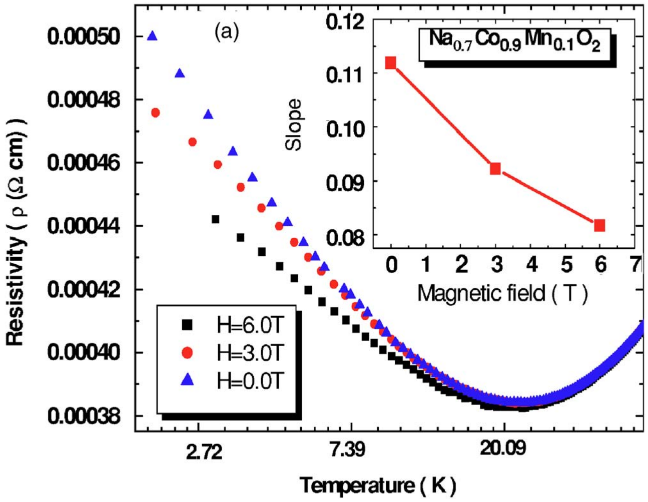

FIG. 4. (Color online) Resistivity vs. temperature at external magnetic field of 0, 3.0, and 6.0 Tesla for Na$_{0.7}$Co$_{0.9}$Mn$_{0.1}$O$_2$ sample. The inset shows the results of the change of curves slope with external magnetic field in the range of low temperature.

Generally, except for the Kondo mechanism, a low temperature resistivity minimum may also arise in disordered systems from quantum interference effect. This can lead to correction to the resistivity from two different sources, i.e., the e-e interaction and weak localization. Since Na$_\gamma$CoO$_2$ is a strongly correlated system, strong e-e interaction should not be neglected and it should play an important role in the electronic transport. Here, the present Na$_{0.7}$Co$_{1-x}$Mn$_x$O$_2$ may be a strong disorder system accompanied by an enhanced e-e interaction that cannot be easily turned by the external field. This is different from the layer perovskite manganites with a weak disorder characteristic.[29] In fact, electron-electron interaction has been successfully applied to understand the low temperature resistivity upturn and its increase with an applied field for many disordered alloys and compounds.[31–33] For our samples Na$_{0.7}$Co$_{1-x}$Mn$_x$($x=0.03, 0.07, 0.1$), in a strong magnetic field, the Kondo scattering will be suppressed whereas the e-e interaction will be enhanced. The inconspicuous suppression of resistivity upturn can be successfully interpreted if the response of the two scattering

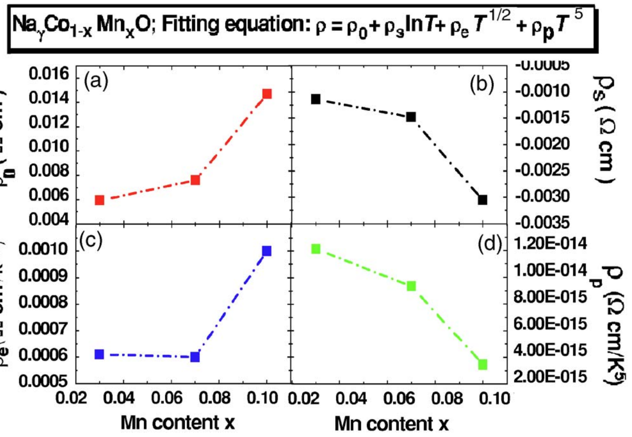

FIG. 5. (Color online) The dependence of the fitted parameters on Mn content x by Eq. (1) for Na$_{0.7}$Co$_{1-x}$Mn$_x$O$_2$ systems ($x=0,0.03,0.07,0.1$).

mechanisms to the external field is comparable. Recently, Li *et al.* have revealed an existence of giant e-e scattering in the Fermi-liquid state of Na$_\gamma$CoO$_2$.[34] As the present resistivity minimum at low temperatures is induced by the Mn impurity, e-e interaction together with Kondo scattering is expected to explain the resistivity minimum and its dependence on the external field. This is because that both of the mechanisms can result in the existence of a resistivity minimum or an upturn at low temperatures and their responses to the external field on the ρ-T curve tend to cancel each other.

Next, we further test our assumption of the coexistence of Kondo scattering and e-e interaction in our doped samples. In general, the resistivity can be represented as $\rho=\rho_{el}+\rho_{in}$, in which ρ_{el} and ρ_{in} are the contributions due to elastic (electron-impurity and Coulomb interaction) and inelastic (e.g., electron-phonon (e-p) interaction) processes.[35] According to the Mathiessen's rule, ρ_{el} can be expressed as $\rho_{el}=\rho_0+\rho_s \ln T+\rho_e T^{1/2}$ at low temperatures. The first term ρ_0 is the residual resistivity, the second one is corresponding to Kondo scattering and the last one describes the e-e interaction contribution to the resistance. Normally, the part ρ_{in} increases with increasing temperature obeying a power law $\rho_{in}=\rho_p T^p$, in which the coefficient ρ_p is independent on the applied magnetic field H. Considering the temperature range discussed here is far below Deby temperature,[36] ρ_{in} takes the form$\rho_{in}=\rho_p T^5$.[37,38] Therefore, the total resistivity is given as

$$\rho(T)=\rho_0+\rho_s \ln T+\rho_e T^{1/2}+\rho_p T^5. \tag{1}$$

To give a quantitative verification, we fitted the experimental data using Eq. (1) for all the doped samples in the range $2<T<100$ K. As shown by solid line in Fig. 3, the data is perfectly fitted in such a wide temperature range. In Eq. (1), the coefficients in every term (fitting parameters) are meaningful. They should describe the related intensity for various scatterings or interactions such as the residual resistivity, magnetic impurity/spin scattering, e-e interaction and e-p interaction. From the fitting results, we plotted the variation of fitting parameters with deferent Mn content as shown in Fig. 5. It can be clearly seen that the parameters are strongly dependent on Mn content. The residual resistivity ρ_0, increases with increasing doping levels, which can be attributed to the impurities effect induced by Mn substitution. It will increase the intensity of electron-impurity scattering and Coulomb interaction. The magnetic impurity or spin scattering ρ_s decreased, or increase in the absolute value with increasing Mn content x, which is also in an agreement with the inset of Fig. 3. The e-p interaction coefficient ρ_p decreased with increasing Mn content x. However, we noticed that the inelastic scattering contribution to the resistivity, i.e., the e-p interaction term decided by ρ_p was much smaller than the rest of interaction terms. In order to see these quantificationally, we calculated the values of various terms at a low temperature of 10 K listed in Table I. It can be seen that there is a difference of 10^7 in magnitude. Even if it is at 100 K, the difference is still about 10^4. Therefore for the present Na$_{0.7}$Co$_{1-x}$Mn$_x$O$_2$ system, the inelastic contribution to resistivity by the e-p interaction of $\rho_p T^5$ can be neglected in discussed temperature range. We therefore conclude that the low temperature resistivity minimum in the doped samples is dominated by the Kondo scattering and e-e interaction.

TABLE I. The comparison between the resistivity values for various terms in Eq. (1) at the low temperature of 10 K. (Units: Ω cm.)

x	ρ_0	$\rho_s \ln T$	$\rho_e T^{1/2}$	$\rho_p T^5$
0.03	5.94×10^{-3}	-2.62×10^{-3}	1.93×10^{-3}	12.1×10^{-10}
0.07	7.60×10^{-3}	-3.41×10^{-3}	1.90×10^{-3}	9.35×10^{-10}
0.10	14.7×10^{-3}	-7.02×10^{-3}	3.16×10^{-3}	3.44×10^{-10}

For the present Na$_{0.7}$Co$_{1-x}$Mn$_x$O$_2$ samples, it is a typical strong disorder system as proved by the inconspicuous suppression upon applied fields magnetic in resistivity and the best fitting. Generally, in the presence of strong disorder, the e-e interaction term takes the form[34]

$$\rho_e T^{1/2}=\rho_0^2(e^2/\hbar)(1/4\pi^2)(1.3/\sqrt{2})(4/3+3F_\sigma)/\sqrt{T/D}. \tag{2}$$

Here, the parameter D is the electron's diffusion coefficient and F_σ is the electron's screening parameter. D can be calculated from the Einstein relation

$$D=(1/2)e^2\rho_0 N(\varepsilon_F). \tag{3}$$

$N(\varepsilon_F)$ is the state density. F_σ is given by the following relation:

$$F_\sigma=[(32/3)F]\{[1+(1/2)F]^{3/2}-1-(3/4)F\}. \tag{4}$$

Here, F is the Coulomb potential averaged over the Fermi surface, which in the Thomas–Fermi approximation is given by

$$F=\ln[1+(2k_F/\kappa)^2]/(2k_F/\kappa)^2, \tag{5}$$

in which $K_F=mv_F/\hbar\sim0.61\times10^8$ cm^{-1} for the metallic compounds. $\kappa=[e^2N(\varepsilon_F)/\varepsilon_0]^{1/2}$ is the inverse screening length and ε_0 is the electrical field constant. By using the values of fitting ρ_e and the equations above, the state density can be calculated with a value of $N(\varepsilon_F)\sim4.81\times10^{43}$ J^{-1}/mol^{-1}, which is in fairly good agreement with the values of $N(\varepsilon_F)\sim8.8$ eV^{-1} on a per formula unit, i.e., 1.65

$\times 10^{43}$ J^{-1}/mol^{-1} reported in Ref. 39. For the doping samples, $N(\varepsilon_F)$ is about $1\sim 2$ magnitude larger than undoped samples i.e., $N(\varepsilon_F)\sim 2.50\times 10^{44}$ J^{-1}/mol^{-1}, 7.20×10^{43} J^{-1}/mol^{-1}, and 1.19×10^{45} J^{-1}/mol^{-1} for x=0.03, 0.07, and 0.1, respectively. It is known that strong e-e scattering can result in a change in the state density near the Fermi energy as suggested for the resistivity minimum.[40] In present doped samples the resistivity minimum may relate to the increase of the state density at Fermi level induced by Mn doping. As in other systems, near the metal-insulator transition the Coulomb interactions between carriers are enhanced by the diffusive nature of the transport proved in theory and experiments.[41] Here the enhancement would result from the finite probability of two carriers interacting more than once within a phase-breaking scattering time.[41] The scattering amplitudes interfere coherently, leading to an increased Coulomb coupling and a square-root singularity in the electronic state density at the Fermi energy. Here, the present experiments have demonstrated that such an e-e interaction plays an important role in the low temperature transport and is quantitatively consistent with the strong disorder picture.

When in an applied field, on the one hand, the spins of local moments tend to be ordered. This will reduce the interaction between conducting electrons and local moments, leading to a decrease in the spin scattering contributing to the resistivity. On the other hand, as to the e-e interaction enhanced by disorder, the resistivity and its upturn at low temperatures can be enhanced by the application of a magnetic field.[33] According to Lee *et al.*,[37] the e-e interaction contributing to the magnetoconductivity correction has been expressed by

$$\sigma_{ee}(H,T)-\sigma_{ee}(H,0)=-[e^2/(4\pi^2\hbar)]\sqrt{(k_BT)/(2\hbar D)}\,g_3(h), \tag{6}$$

in which $g_3(h)$ is a function of the argument $h=g\mu_B\mu_0H/(k_BT)$ and can be computed numerically and it always shows a positive sign.[33,42] Obviously, e-e interaction can result in a positive magnetoresistance, i.e., the resistivity increases in response to an applied field. As a result, with the field the low temperature resistivity minimum and its upturn contributed by the e-e interaction will be enhanced and this will compensate for the suppression of the Kondo scattering by the field.

IV. CONCLUSIONS

The electronic transport and susceptibility properties are studied for dilute Mn doped $\mathrm{Na_{0.7}Co_{1-x}Mn_x}$ system with x=0, 0.03, 0.07, 0.1. The experiment results show that electrical and magnetic properties at low temperatures are very sensitive to Mn doping while the doping effects are not so obvious at higher temperatures. A temperature resistivity minimum is found accompanied by a metallic-semiconductor transition below 50 K for all Mn-doped samples. The weak dependence of resistivity on external field proves that the present $\mathrm{Na_{0.7}Co_{1-x}Mn_xO_2}$ is a strong disorder system. The resistivity results are well fitted in the framework of Kondo scattering and e-e interaction in a wide temperature range of 2–100 K. We argue that the explanations of the resistivity upturn observed may rely on coexistence of the Kondo-like scattering induced by magnetic impurities and e-e interaction enhanced by disorder. It is meaningful to understand the physical mechanisms of strong correlated layer $\mathrm{Na_yCoO_2}$ system.

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