Magnetic and Transport Properties in $CoSr_2Y_{1-x}Ca_xCu_2O_7$ ($x=0$~$0.4$)

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Magnetic and transport properties of $CoSr_2Y_{1-x}Ca_xCu_2O_7$ system have been investigated. A broad maximum in M(T) curve, indicative of low-dimensional antiferromagnetic ordering originated from $CoO_{1+\delta}$ layers, is observed in Ca-free sample. With increasing Ca doping level up to 0.2, the (M,T) curve remains almost unchanged, while resistivity is reduced by three orders. Higher Ca doping level leads to a drastic change of magnetic properties. In comparison with the samples with $x=0.0~0.2$, the temperature corresponding to the maximum of M(T) is much lowered for the sample $x=0.3$. The sample $x=0.4$ shows a small kink instead of a broad maximum and a weak ferromagnetic feature. The electrical transport behavior is found to be closely related to magnetic properties for the sample $x=0.2$, 0.25, 0.3, 0.4. It suggests that $CoO_{1+\delta}$ layers are involved in charge transport in addition to conducting $CuO_2$ planes to interpret the correlation between magnetism and charge transport. X-ray photoelectron spectroscopy studies give an additional evidence of the transfer of the holes into the $CoO_{1+\delta}$ charge reservoir.

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INTRODUCTION

Charge transport and high temperature superconductivity (HTSC) is believed to reside in the $CuO_2$ planes of all known HTSC cuprates, except that $CoO_{1+\delta}$ chains have been reported to participate in the b-axis transport of $YBa_2Cu_3O_{7-\delta}$. In $YBa_2Cu_3O_{7-\delta}$ (also denoted as $CuYBa_2Cu_3O_{7-\delta}$, $Cu1212$) there are two different $Cu$ sites, namely $Cu$(2) and $Cu$(1). $Cu$(2) resides in superconducting $CuO_2$ planes and $Cu$(1) in $CoO_{1+\delta}$ chains. Any breach of integral $CuO_2$ stacks, even at macroscopic level, affects superconductivity drastically. The $CoO_{1+\delta}$ chain acts as charge reservoir and provides the mobile carriers to superconducting $CuO_2$ planes.

Some attempts have been performed successfully for complete replacement of $CoO_{1+\delta}$ by other metal elements. $MSr_2YCu_2O_{7-\delta}$ (M=Nd, Tb, Ho, Er, Tm, Dy, Eu etc.) have attracted extensive attention in the past. Some of them have been made superconducting, such as Nb1212, Hg1212, Ru1212, Ti1212, Ga1212 and Fe1212, and some other, like Ta1212, remains nonsuperconducting. Another example, Co1212, kept nonsuperconducting since it was synthesized firstly in 1989, until very recently, Morita et al. made it superconducting (SC) by annealing Ca-doped Co1212 in ultra-high O$_2$ pressure (5GPa). However, the reason why the system is not SC before ultra-high pressure treatment and it becomes SC after ultra-high pressure treatment, still remains unknown.

Up to now, the research for Co1212 has been focused on its structure and magnetic properties. The structure of Co1212 is derived from $CuBa_2YCu_2O_7$ (Cu1212), by completely substituting divalent Cu(1) in $CoO_{1+\delta}$ charge reservoir of Cu1212 with trivalent Co ion. In Cu1212 the charge-reservoir $Cu$ atom with surrounding oxygen atoms forms a square $CoO_4$ polyhedron. However, the $CoO_4$ tetrahedral coordination polyhedron has been reported in Co1212. Ga1212 and Al-1212 have also been reported to have the tetrahedral polyhedron. Such $CoO_4$ tetrahedra forms a zigzag chain running diagonally relative to the perovskite base. A regular alternation of two zigzag chains, which are mirror images of each other, forms an orthorhombic superstructure. Unlike $CuO_4$ square chains in Cu1212, which is very easy to lose or obtain oxygen, the $CoO_4$ tetrahedral chains in Co1212 are reported to be a rigid configuration in terms of oxygen content. In Co1212, all of the Co ions reside on the Cu(1) sites. With Y$^{3+}$ substituted by Cu$^{2+}$, however, Co and Cu will intermixed partly. The M(T) curve of Co1212 exhibits a broad maximum, indicative of a low-dimensional magnetic ordering, which was thought to originating from Co$^{3+}$ spin. With no doubt, studies on the function of $CoO_4$ tetrahedra certainly give very useful information to settle the forenamed question. To our knowledge, no report has been reported on the transport properties of $CoSr_2Y_{1-x}Ca_xCu_2O_{7-\delta}$. In the present report, we investigated the magnetic and electrical properties on Ca substituted Co1212 from Ca content 0.0 to 0.4. It is found that with increasing Ca doping level, electrical transport properties become related to magnetic structure closely. Magnetic properties and their correlation

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with charge transport suggest that slightly partial holes induced by Ca doping reside on the CoO$_{1+\delta}$ layers and these holes influence the magnetic and charge transport properties dramatically. In addition, these holes cause CoO$_{1+\delta}$ to participate in bulk electrical transport. X-ray photoelectron spectroscopy (XPS) studies indicate that for high Ca doping level the valence of Co increases compared to the low doping level and thus confirm that holes enter into the charge reservoir.

**EXPERIMENT**

A series of samples with compound of Co$_x$Sr$_{2}$Y$_{1-x}$Ca$_x$CuO$_{7+\delta}$(x=0.0~0.4) were synthesized through a solid-state reaction route. Co$_2$O$_3$, SrCO$_3$, Y$_2$O$_3$, CaCO$_3$, and CuO, as the starting materials, were mixed in nominal composition and heated for 24 h at 950 °C and another 24 h at 1000 °C with intermediate grinding. Finally, the products were pelletized and sintered at 1010 °C for 24 h. The phase purity was checked for each sample with powder X-ray diffraction (XRD). Magnetization measurements were performed on each sample with a SQUID magnetometer in field cooling mode. For the sample $x=0.25$ and $x=0.4$, additional ZFC (zero field cooling) magnetization were performed. Resistance measurements were performed using AC four-probe method with AC bridge resistance bridge system (Linear Research Inc.; LR-700P). All samples for magnetization and resistance measurements have been annealed under 195 atm and ambient pressure oxygen atmosphere shows almost the same behavior in charge transport and magnetism. These results further confirm that the oxygen content in Co1212 cannot change easily. The XPS spectra were collected with an ESCALAB MK II electron spectrometer using Mg Kα radiation as excitation source ($h\nu=1253.6$ eV). Binding energy was calibrated with a reference of surface contaminated C 1s (E$_b$=284.6 eV). The basic vacuum was about 1×10$^{-9}$ mbar.

**RESULTS AND DISCUSSION**

XRD patterns for as-synthesized (AS) samples with various Ca content, $x$, are shown in Fig. 1. No any visible impurity peak in XRD patterns is observed for all samples. All the peaks can be indexed using the space group $I\overline{m}2$. It demonstrates all the samples are single phase materials and have the orthorhombic structure. The lattice parameters determined from the XRD patterns with the Rietveld method in GSAS program are plotted against $x$ in Fig. 2 (Noted that the c-axis here were referred to the layer piling direction as typically employed for the structures of high-T$_c$ superconductors, and a-axis is along the CoO$_{1+\delta}$ chain.). With increasing Ca content $x$, the lattice parameter of a-axis slightly increases, while b-axis shrinks a little. An increase of c-axis parameter with $x$ demonstrates that the doped Ca ions have entered into Y sites instead of Sr sites. The reason is that the radius of Cu$^{2+}$ is larger than Y$^{3+}$ but less than Sr$^{2+}$, thus substitution of Sr$^{2+}$ by Cu$^{2+}$ should cause a shrinkage of c-axis. It has been reported that the oxygen content in Ca-doped Co1212 almost remains constant, thus replacing partial trivalent Y ion by divalent Ca ion results in excess holes to system.

Figure 3 shows the temperature dependence of the dc magnetization (M) of annealed samples $x=0.0$~0.4. The magnetization of Ca-free sample shows a broad maximum around 145 K and then a shallow downturn followed by a up-turn with decreasing temperature, which well agrees with the previous reports. The analogous FC M(T) curve has been observed in Sr$_2$CoCu$_2$O$_6$[17], Sr$_2$CuMnO$_4$S[18], Sr$_2$Mn$_2$Sn[19], and Sr$_2$Mn$_3$O$_{8-\delta}$Cl[20], in which the broad maximum was thought to be indicative of low-dimensional magnetic feature. The inverse of magnetization displays an up-turn deviation from linear behavior with decreasing temperature, indicative of antiferromagnetic ordering. Considering the 3D magnetic character of high-T$_c$ system, the low dimensional antiferromagnetic feature most likely originates from the Co-O layers instead of Cu-O planes. In addition, magnetization remains almost unchanged for $x=0.1$ and $x=0.2$ except for a little lowering of the temperature of maximum, indicating that the holes induced by Ca doping enter into the Cu-O plane. The drastic drop of resistivity with $x$ increasing from 0.0 to 0.2 confirms this speculation, which will be discussed later. As shown in fig.3, for higher Ca doping, however, the temperature of maximum decreases dramatically, and for the sample with $x=0.4$, there only exhibits a small kink in M(T) curve. From Fig. 3b, the inverse of M(T) of sample $x=0.4$ shows a downturn deviation from high temperature linear behavior with decreasing temperature, which indicates that at low temperature the sample $x=0.4$ shows a weak ferromagnetism. The branching of the ZFC and FC data shown in the inset of figure 3 approves the ferromagnetism in the sample $x=0.4$. The change of magnetic behavior by Ca-doping may arise from following aspects: 1) some holes enter into CoO$_{1+\delta}$ and destruct the effective antiferromagnetic coupling; 2) intermixing of Cu and Co ion induced by Ca doping breaks the Co-O chain; 3) some structure transformation changes the Co coordination. The following results will suggest that the first supposition may be the most possible.

Resistivity as a function of temperature is displayed in Fig. 4 for the annealed samples $x=0.0$~0.4. Substitution of Y by Ca reduces the resistivity fiercely with magnitude change of three orders at room temperature from $x=0.0$ to 0.4. A metal-insulator transition induced
by doping Ca is clearly observed with increasing doping level. In contrast to the large resistivity and insulator-like behavior in Ca-free Co1212 sample, the resistivity of the sample x=0.2 is reduced dramatically by nearly 1000 times at room temperature, and it exhibits a metallic behavior with a positive slope within a wide temperature region below room temperature. Doping Ca up to x=0.4, the resistivity at room temperature is very close to that of the superconducting cuprates. Since the conductive unit in high-T_c cuprates is CuO_2 plane, drastic drop of resistivity induced by Ca substitution for Y ion demonstrates that doped holes enter into CuO_2 plane indeed. The variation of resistivity with doping is associated with the magnetic results discussed above. However, none of all the samples shows superconducting (SC) at the temperature down to 2 K. The reason for absence of SC has been ascribed to that slight Co ions enter into CuO_2 plane and this destroys its integrity or that some holes are trapped in the CoO_{1+δ} charge reservoir. It is excluded for the former interpretation since it can be become superconducting by annealing AS samples in 5 GPa oxygen (this seems to be unable to rearrange the occupational sites). Otherwise, our results seem to demonstrate that the charge reservoir participates in charge transport, that is, there exist holes in CoO_{1+δ} layers.

In Fig. 4, there exists a small peak at low temperature for the samples of x=0.2, 0.25, 0.3 and 0.4 with a noticeable change in the slope (dρ(T)/dT). In Fig. 5, the derivative of the resistivity for the four samples x=0.2, 0.25, 0.3, 0.4 shows a shallow dip-hump feature. It is found that the temperature at maximum of M(T) corresponds to this dip-hump zone for these four samples. It suggests that the peak observed in resistivity is related to the maximum of the magnetization M(T). In order to find out the correlation between resistivity and magnetization, the curvature (d^2ρ(T)/dT^2) and M(T) curves are shown in Fig.6. The temperatures of maximum of M(T) are almost the same as that corresponding to the minimum of d^2ρ(T)/dT^2 for the four samples, with the largest difference less than 10 K for the sample x=0.2. These results indicate that when Ca content x is as large as 0.2, electrical transport behavior becomes related to magnetic properties closely.

What is the nature of this correlation between charge transport and magnetic behavior? As mentioned previously, the CuO_4 chains participate in the b-axis charge transport in Cu1212, and give slightly contribution to the resistivity and lead to a different temperature dependence from that of the a-axis. In our case, magnetic properties in this system originate from the CoO_{1+δ} charge reservoir, and the main conducting unit is CuO_2 plane. Two possible reasons can be considered to interpret the fact that the charge transport is closely related to magnetic properties: i) the couplings between the itinerant charge carrier in the CuO_2 planes and the localized ordered spin in the CoO_{1+δ} charge reservoir lead to the correlation; ii) likely to Cu1212, the charge reservoir participates in charge transport, so that magnetic transition occurred in CoO_{1+δ} influences the charge transport. The behavior exhibited in Cu1212 is not the former case because the correlation between magnetic and charge transports is different from that in Ru1212 and Ru1222, in which there exists a ferromagnetic transition in RuO_2 plane, but no apparent change in resistivity is observed at Curie temperature. This assumption is further tested by the magnetotransport data discussed later. In this way, the system contains contributions from two types of conducting layer: CoO_{1+δ} layers and CuO_2 planes although the component arising from the charge reservoir layers may be rather little. Therefore, an apparent change in resistivity is observed when a magnetic transition takes place in CoO_{1+δ}, then the dip-hump structure on dρ(T)/dT is related to magnetic transition on the charge reservoir layers.

This speculation is confirmed by the magnetotransport data. As shown in Fig. 7, the sample x=0.3 exhibits positive magnetoresistance (MR), less than 1% at magnetic field as high as 14 Tesla, while the sample x=0.4 shows a negative MR, larger than 14% at 14 Tesla, which seems to be like the behavior in ferromagnetic metal. These contrasting behaviors manifest that the magnetism is transformed from low-dimensional antiferromagnetism in the sample x=0.3 to weak ferromagnetism in the sample x=0.4, a different MR behavior occurs and the change in resistivity behavior with Ca doping is closely associated with that in magnetism. Furthermore, the different MR behavior associated with the different magnetic properties located on the CoO_{1+δ} layers further confirms that the CoO_{1+δ} charge reservoir participates in charge transport. In Ru-1212 and Ru1222, a maximum negative MR is observed at T_{curie} (Ferromagnetic transition temperature). This MR behavior has been attributed to the interaction between Ru moment in RuO_2 planes and itinerant carriers in CuO_2 planes. However, the sample x=0.4 in Co1212 shows a different MR behavior from Ru1212 and Ru1222. An increase in negative MR with decreasing temperature is observed in Co1212 and the MR in Co1212 is much larger than that in Ru1212 and Ru1222. These differences between Co1212 and Ru1212 (Ru1222) is also an indication for significant current flowing in CoO_{1+δ} layers. The Kohler’s plot for the samples is shown in the inset of figure 7. It should be noted that the MR of the samples with x=0.3 and 0.4 does not obey Kohler’s rule. This is because below 110 K the charge becomes localized instead of a metal as above 110 K. The MR of the sample x=0.3 is proportional to square of magnetic field, while that of the sample x=0.3 shows saturation at high field. In addition, the evolution of the magnetic properties with Ca doping supports minor charge carrier in CoO_{1+δ} layers. For the samples with Ca content x ≤ 0.2, the holes induced
by Ca substituting for Y are completely introduced into $CuO_2$ planes, so that the resistivity decreases apparently and the magnetic behavior originated from $CoO_{1.5}$ layers does not change with Ca doping. However, further doping Ca leads to a dramatic change in the magnetic behavior and an associated change in resistivity with magnetic behavior. It suggests that the change of magnetic properties is induced by the transfer of the holes into the netic behavior. It suggests that the change of magnetic behavior originated from $CoO_{1.5}$ layers when the Ca content $x > 0.2$. It should be pointed out that the ferromagnetism occurred in $RuO_2$ layers does not change with the doping level.

The consideration that holes enter into the $CoO_{1.5}$ charge reservoir for the high Ca doping samples is confirmed by XPS results further. The $Co_{2p}$ spectra obtained for the sample $x=0.1$ and $x=0.4$ were shown in figure 8. Comparing to the spectrum of the sample $x=0.1$, the binding energy of the two main components $Co 2p_{3/2}$ and $2p_{1/2}$ in the spectrum for the sample $x=0.4$ shift toward higher energy as shown by the solid straight line in the figure. The spectra were analyzed using a peak synthesis program in which a non-linear background is assumed. For the sample $x=0.1$, the $Co_{2p}$ spectrum shows two main components at about 779.3 eV and 794.8 eV which are attributed to $Co^{3+}$ ions. In comparison with the spectrum of the sample $x=0.1$, the two peaks corresponding to the two components $Co 2p_{3/2}$ and $2p_{1/2}$ become broad, especially, an apparent doublet is observed for the component $Co 2p_{1/2}$. The peaks in the spectrum of $x=0.4$ have to be fitted by two components. By fitting, the doublet positions are determined to be at 797.0 and 795.3 eV for the $Co 2p_{1/2}$, and at 781.2 and 779.8 eV for the $Co 2p_{3/2}$, respectively. As pointed out in Ref. 24, the binding energies of 779.8 and 795.3 eV correspond to $Co^{3+}$ ions, while 781.2 and 779.0 eV are attributed to $Co^{4+}$ ions. This is evident by the presence of an obvious shoulder on the high-energy side of the $Co 2p_{1/2}$ component (marked by the arrow in the figure). These facts clearly show the increase of the valence of $Co$ and confirm the transfer of the holes into the $CoO_{1.5}$ layers by increasing the Ca doping level.

It has been reported that $CoO_4$ tetrahedra in Ca-free Co1212 has a rigid configuration in terms of the oxygen content, and annealing in flowing $Ar$ or $O_2$ have little effect on oxygen stoichiometry. It is found that no obvious difference in resistivity value or its behavior is observed in AS, 175 atm oxygen annealing, and 195 atm oxygen annealing for $x=0.1$, 0.2, 0.25, 0.3 and 0.4 (not shown here). From the analysis on magnetic and transport behavior above, doping of Ca does induce holes into $CoO_{1.5}$ although the amount of these holes may be much smaller than that of holes entering into $CuO_2$ planes for the same Ca doping level. From iodometric titration experiment by Morita et al., the oxygen content almost remains constant, thus holes entering into $CoO_{1.5}$ increase the oxidation state of $Co$. When magnetic ordering occurs in insulating $Co^{3+}$-$O$ matrix, the magnetism occurred in $CoO_{1.5}$ layers has very weak effect on the charge transport. The magnetic effect on resistivity originates from the coupling between the itinerant carrier and the local ordered spin in the $CoO_{1.5}$ layers. When hole is doped into $CoO_{1.5}$ layers, ferromagnetic metal (FM) cluster containing $Co^{3+}$ ions may reduce the resistivity apparently, especially for the sample $x=0.4$ in which weak ferromagnetism shows up. This picture has been used to interpret the noticeable change of the slope in $\rho(T)$ of $La_{0.85}Sr_{0.15}CoO_3$ and $La_{0.75}Sr_{0.25}CoO_3$ films. In fact, in the inset of figure 3, the ZFC and FC magnetization curves of the samples $x=0.25$ and 0.4 start branching around the temperatures corresponding to the maximum of magnetization, indicative of some ferromagnetic component. However, as reported in ref.11, for the Ca-free sample no ZFC and FC branching are observed. These results suggest that Ca-free sample contains no ferromagnetic component, while as Ca doping level is higher than 0.2, the system becomes a intermixture of antiferromagnetic and ferromagnetic component. The temperature dependence of the magnetization for the sample $x=0.2$, 0.25, 0.3 exhibit antiferromagnetism, indicating that in these samples ferromagnetic component is rather small. While for the sample $x=0.4$, it exhibits weak ferromagnetism, indicating that in this sample the ferromagnetic component is already preponderant. This may interpret the large MR in the sample $x=0.4$ while rather small MR in the sample $x=0.3$. It is not clear whether the partly intermixing between $Co$ and $Cu$ has any effect on the resistivity. More microscopic studies on the electronic state of $Co$ ions($Co^{3+}$ or $Co^{4+}$) in the charge reservoir is needed to explain this phenomena completely.

**CONCLUSION**

We have synthesized polycrystalline $CoSr_2Y_{1-x}Ca_xCu_2O_{7+\delta}(x=0.0\sim0.4)$, and investigated their magnetic and transport properties. In the sample $x=0.0\sim0.2$, magnetization shows broad maximum at low temperature (almost the same temperature), indicative of low-dimensional antiferromagnetic nature originated from $CoO_{1.5}$ layers. The temperature of such maximum for the sample $x=0.3$ drops dramatically, and for the sample with $x=0.4$ a weak ferromagnetism shows up. Ca doping reduces resistivity quickly. $d\rho(T)/dT$ shows dip-hump feature at low temperature for the samples with $x=0.2\sim0.4$, which is ascribed to a contribution of holes in $CoO_{1.5}$ charge reservoir and magnetic transition within the layers. The speculation is confirmed by the fact that small positive MR exhibits in the sample $x=0.3$, while the large negative MR in the $x=0.4$ sample.
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FIGURE CAPTIONS

Figure 1: XRD patterns for the as-synthesized samples of $CoSr_2Y_{1-x}Ca_xCu_2O_{7+\delta}(x=0.0\sim0.4)$.

Figure 2: Lattice parameters for the as-synthesized samples of $CoSr_2Y_{1-x}Ca_xCu_2O_{7+\delta}$.

Figure 3: (a) The temperature dependence of magnetization measured for the annealed $CoSr_2Y_{1-x}Ca_xCu_2O_{7+\delta}$ samples in field-cooled process at the field of 100 Oe. Inset: ZFC (dashed line) and FC (solid line) data at the field of 100 Oe plotted against the temperature for the samples $x=0.25$ and 0.4. (b) The temperature dependence of inverse magnetization for the sample $x=0.0\sim0.4$.

Figure 4: The resistivity as a function of temperature for the annealed $CoSr_2Y_{1-x}Ca_xCu_2O_{7+\delta}$ samples.

Figure 5: The resistivity and its derivative as a function of temperature for the samples with $x=0.2, 0.25, 0.3, 0.4$.

Figure 6: The temperature dependence of the resistivity curvature($d^2\rho/d^2T$) and magnetization for the samples with $x=0.2, 0.25, 0.3, 0.4$.

Figure 7: The plot of magnetoresistance ($MR=[\rho(T,H)-\rho(T,0)]/\rho(T,0)\times100\%$) vs. magnetic field($\mu_0H$) for the samples with $x=0.3, 0.4$. Insets: the same data are shown in Kohler’s plot.

Figure 8: The Co2p XPS spectra for the sample $x=0.1$ and 0.4.
Fig. 1  X. G. Luo et al.
Fig. 2 X. G. Luo et al.
Fig. 3 X. G. Luo et al.
Fig. 4 X. G. Luo et al.
$\rho (m\Omega \text{ cm})$ $x = 0.2$ $x = 0.25$ $x = 0.3$ $x = 0.4$

$\frac{d\rho}{dT} \left( 10^{-1} \text{ m}\Omega \text{ cm K}^{-1} \right)$

$T (K)$

Fig. 5 X. G. Luo et al.
Fig. 6 X. G. Luo et al.
Fig. 7  X. G. Luo et al.
Fig. 8  X. G. Luo et al.