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Effects of Fe doping in $La_{0.67}Sr_{0.33}CoO_3$

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The effects of Fe doping in $La_{0.67}Sr_{0.33}CoO_3$ has been studied by the measurements of magnetic, electrical transport, and magnetoresistance properties. It is found that no apparent structure change is introduced by Fe doping up to $x=0.3$. But the Curie temperature T_c and magnetization M are strongly lowered by Fe substitution. The electrical resistivity exhibits metallic behavior in low-doped ($x\leqslant 0.1$) samples while semiconducting behavior in high-doped ($x=0.2$ and 0.3) samples. In addition, Fe doping weakens the MR peak near T_c but enhances the low-temperature MR. The origin of CMR and the effect of Fe doping in $La_{0.67}Sr_{0.33}CoO_3$ are interpreted in terms of the spin-state transition induced by applied magnetic field.

The recent discovery of colossal magnetoresistance (CMR) in mixed valence $R_{1-y}A_yMnO_3$ perovskite (where R and A stand for rare-earth and alkaline-earth elements, respectively) has generated renewed interest in this family of compounds due to its scientific significance as well as possible potential applications.[1] The underlying physics of this system has been traditionally interpreted in terms of the double-exchange model (DEM), suggested by Zener.[2] Recently, the importance of strong electron-phonon interaction due to the Jahn-Teller (JT) distortion associated with Mn^{3+} ion in addition to the DEM has been stressed and discussed intensively.[3]

Although most of the attention has been focused on the system of R-A-Mn-O, CMR has also been observed in materials based on $RCoO_3$.[4] As a typical sample of it, the system of $La_{1-y}Sr_yCoO_3$ has been extensively studied.[5–12] The parent compound $LaCoO_3$ had been known to exhibit unusual transport and magnetic properties as a result of thermally induced spin-state transition of trivalent cobalt ion.[13,14] At the lowest temperatures the Co^{3+} ions are all in low-spin (LS) state $Co^{3+}(t_{2g}^6,\ S=0)$ because the crystal-field splitting strength $(10Dq)$ is slightly larger than the Hund's-rule coupling energy. However, the small energy difference ($\approx$0.03 eV) allows thermal excitation of high-spin (HS) state $(t_{2g}^4e_g^2,\ S=2)$ or intermediate-spin (IS) state $(t_{2g}^5e_g^1,\ S=1)$ with increasing temperature. There had been controversy on the nature of high-temperature spin state of Co^{3+}, namely, whether it is the HS or IS state. Recent finding of the appreciable local lattice distortion during the spin-state transition suggests the presence of Jahn-Teller distortions in the high-temperature spin state, supporting the IS $(S=1)$ state model.[15] Substitution of Sr on La sites oxidizes part of Co^{3+} into Co^{4+}. The spin configuration of Co^{4+} was proposed by different investigators to be low spin $(t_{2g}^5,\ S=1/2)$,[16] high spin $(t_{2g}^3e_g^2,\ S=5/2)$,[5] and even intermediate spin $(t_{2g}^4e_g^1,\ S=3/2)$,[17] depending on Sr content and temperature. While $LaCoO_3$ has a ground state as nonmagnetic insulator, the resistivity of $La_{1-y}Sr_yCoO_3$ decreases with increasing y and the system becomes metallic when Sr content exceeds 0.2. The magnetic phase diagram of $La_{1-y}Sr_yCoO_3$ has been studied in detail.[12,18] Three phases were identified: (i) For $y\leqslant 0.18$, a spin-glass phase at low temperature below ferromagnetic Curie temperature T_c, (ii) for $0.18<y\leqslant 0.25$, a cluster-glass phase below a temperature $T_g<T_c$, (iii) for $0.25\leqslant y\leqslant 0.5$, long-range ferromagnetic order at all temperatures $T<T_c$. At high temperature, $La_{1-y}Sr_yCoO_3$ exhibits a paramagnetic phase.

Since the magnetic and electrical properties of rare earth transition metal oxides with perovskite type structure is strongly dependent on the valence state and spin state of metal ions, it will be worthwhile to investigate the influence of the substitution on Co sites with other elements, which has not yet been studied extensively. In the present work, we choose Fe as the doping element because Fe^{3+} ion has almost identical ionic radii with Co^{3+}/Co^{4+} ion so that no strong lattice effect would be introduced and the change due to electronic structure become accessible. Very recently, Sathe *et al.* explored the magnetic and structural properties of $La_{0.7}Sr_{0.3}Co_{1-x}Fe_xO_3$ by neutron diffraction and magnetization measurements.[19] A transition from rhombohedral to orthorhombic structure was observed with $x=0.5$. Ferromagnetic behavior was observed for $x\leqslant 0.4$ while antiferromagnetic nature was observed for $x\geqslant 0.8$. The intermediate compositions $x=0.5,0.6,0.7$ showed complex behavior arising from the presence of both ferromagnetic and antiferromagnetic structure. In this paper, we present an extended study of $La_{0.67}Sr_{0.33}Co_{1-x}Fe_xO_3$ on the magnetic, electrical transport, and magnetoresistance properties.

Bulk polycrystalline samples with nominal composition $La_{0.67}Sr_{0.33}Co_{1-x}Fe_xO_3$ ($x=0.0,0.05,0.1,0.2,0.3$) were prepared by the solid state reaction method. Powder x-ray diffraction (XRD) patterns indicate the single-phase rhombic perovskite structure of all samples, as shown in Fig. 1. It also proves that no apparent structural change is introduced by Fe doping up to $x=0.3$. The resistivity under zero and 6 T magnetic field was measured by standard four-probe method. Magnetization measurements were performed in 50 G magnetic field using a vibrating sample magnetometer (VSM) after zero-field cooling from room temperature.

The magnetization measured in 50 G field is shown in Fig. 2. It can be seen that Fe doping not only weakens magnetization but also drives Curie temperature T_c to lower temperature. The inflection T_c of all samples, which is defined as the inflection point in M-T curve, are summarized in Table I.

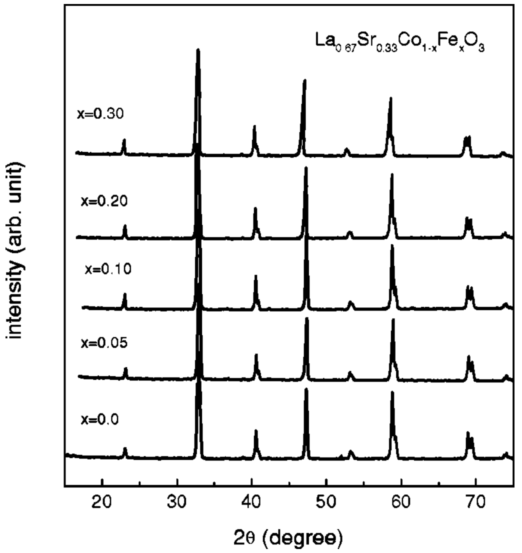

FIG. 1. X-ray diffraction patterns of $La_{0.67}Sr_{0.33}Co_{1-x}Fe_xO_3$ ($x = 0.0, 0.05, 0.1, 0.2$, and 0.3).

For $x \leq 0.10$ samples, magnetization displays a slight drop below 80 K which may indicate the spin-state transition of Co^{3+} with cooling. For $x = 0.2$ sample, there is a sharp peak of magnetization near 110 K. We think it could be a sign of complicated magnetic structure, such as cluster glass due to the introduction of competing antiferromagnetism by Fe doping. When Fe content reaches 0.3, the magnetization becomes very small and shows a bump at 70 K. The compression of magnetization and the decrease of T_c suggests that Fe doping destorys the ferromagnetic interaction in the system.

The temperature dependence of resistivity under zero and 6 T magnetic field is demonstrated in Figs. 3(a) and 3(b). For low doped samples ($x \leq 0.10$), the behavior of resistivity is metallic in most of the temperature range, with a rise at very low temperature. For $La_{0.67}Sr_{0.33}CoO_3$, this rise of ρ at low temperature can arise from several mechanisms such as electron-electron interaction, weak localization by disorder effect or even Kondo effect. However, since it was ever found that the low-temperature rise of ρ appears around the same temperature for different Sr doping level in $La_{1-x}Sr_xCoO_3$,[6] other causes such as the spin-state transition of Co^{3+} ion can also be a possible mechanism. For Fe-doped samples, the frustration of ferromagnetism by Fe doping should play a dominating role in this rise of ρ. From Fig. 3(a), it is clear that there is a steep change in the slope of resistivity at $T = T_c$, which suggests that the onset of long-range FM order promotes the conduction. For high-doped samples ($x = 0.2$ and 0.3), the resistivity exhibits insulating behavior in all the temperature range studied. We found that the low-temperature resistivity of these high-doped samples can be fitted by Mott's law of variable-range hopping model,

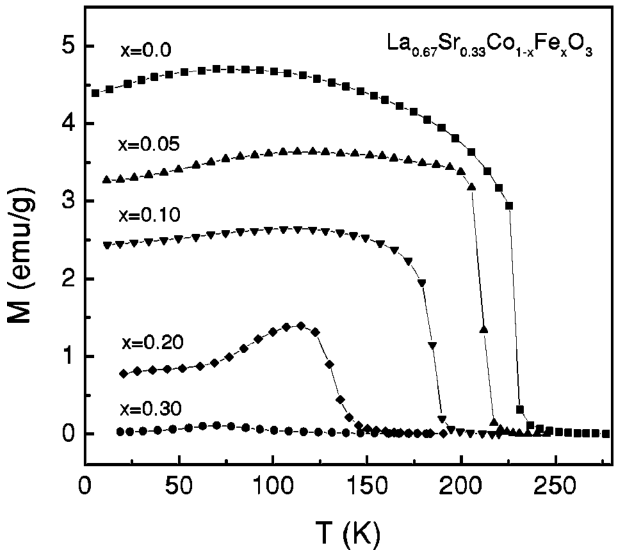

FIG. 2. Temperature dependence of magnetization in 50 Oe magnetic field for all samples.

TABLE I. Inflection T_c of all samples studied and parameter T_0 of VRH model for high-doped samples ($x = 0.2$ and 0.3).

sample	$x = 0.0$	$x = 0.05$	$x = 0.1$	$x = 0.2$	$x = 0.3$
T_c (K)	228	212	184	133	80
T_0 (K)				3.54×10^5	1.15×10^6

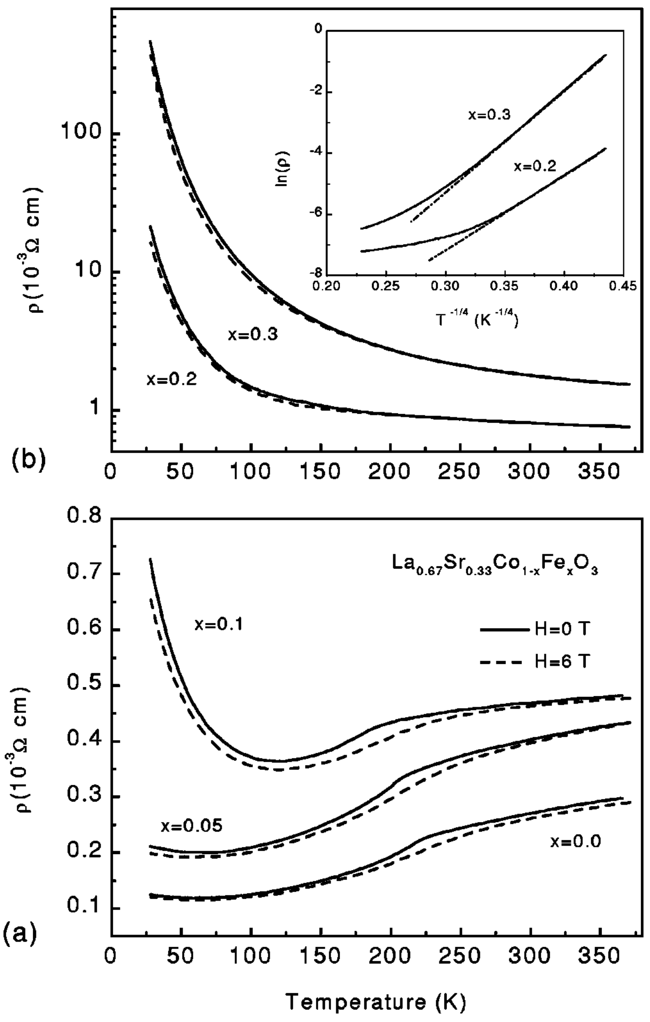

FIG. 3. Resistivity in zero and 6 T magnetic field as a function of temperature for (a) low-doped samples ($x \leq 0.1$) and (b) high-doped samples ($x = 0.2$ and 0.3). The inset shows the fits to VRH model.

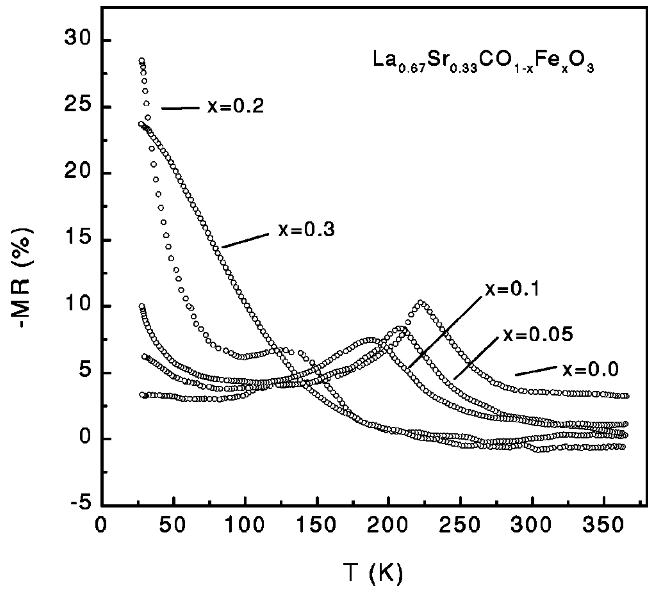

FIG. 4. Dependence of MR on temperature for $La_{0.67}Sr_{0.33}Co_{1-x}Fe_xO_3$ ($x=0.0, 0.05, 0.1, 0.2$, and 0.3).

$\rho=\rho_\infty \exp(T_0/T)^{1/4}$, as shown in Fig. 3(b). This means that Fe doping on Co sites increases the extent of disorder in the lattice so as that the carriers are trapped in localized state by severe potential fluctuation. The parameter T_0 is related to localization length L by the expression $kT_0=18/[L^3N(E)]$, where k is Boltzmann constant, $N(E)$ is electronic density of states. Since the value of T_0 for $x=0.3$ sample is nearly three times of that for $x=0.2$ sample (see Table I), this large change of T_0 cannot be caused by the slight variation of $N(E)$ and should consequently reflect the change of localization length L with increasing Fe content. Thus, the relatively bigger T_0 in $x=0.3$ sample corresponds to a smaller localization length and implies a more severe disorder in the lattice due to Fe doping.

Under applied magnetic field, the resistivity of $La_{0.67}Sr_{0.33}Co_{1-x}Fe_xO_3$ is compressed in most of the temperature though the extent of change is not so great as in mixed-valence manganites. In Fig. 4, we depict the temperature dependence of MR response. For the parent compound $La_{0.67}Sr_{0.33}CoO_3$, MR shows a peak near T_c, consistent with previous extensive reports.[6,20] With increasing Fe content, MR peak near T_c is weakened while the low-temperature MR is enhanced. When $x=0.3$, MR keeps increasing with cooling and no MR peak appears. The substitution of Fe on Co sites depresses the peak of MR near T_c but enhances the low-temperature MR, which suggests that the mechanism of low-temperature MR is different from that of the high-temperature MR near T_c. Morever, it can also be inferred that the CMR in R-A-Co-O perovskites is somewhat different from that in R-A-Mn-O perovskites because it was ever reported that Fe doping in $La_{0.67}Ca_{0.33}MnO_3$ enormously enhances CMR near T_c.[21]

The different effects of Fe doping between R-A-Mn-O and R-A-Co-O should have its origin from the distinct feature of the microscopic electronic and spin configuration between two systems. In $R_{1-y}A_yMnO_3$, the only channel for carrier transport is Mn^{3+}-O-Mn^{4+}. In contrast, the transport channel in $La_{1-y}Sr_yCoO_3$ could be diverse. Co^{3+}(LS, $t_{2g}^6e_g^0$)-O-Co^{4+}(HS, $t_{2g}^3e_g^2$), Co^{3+}(LS, $t_{2g}^6e_g^0$)-O-Co^{4+}(IS, $t_{2g}^4e_g^1$), Co^{3+}(IS, $t_{2g}^5e_g^1$)-O-Co^{4+}(LS, $t_{2g}^5e_g^0$),Co^{3+}(LS, $t_{2g}^6e_g^0$)-O-Co^{3+}(IS, $t_{2g}^5e_g^1$), and Co^{4+}(LS, $t_{2g}^5e_g^0$)-O-Co^{4+} (IS, $t_{2g}^4e_g^1$ or HS, $t_{2g}^3e_g^2$), all are possible channels for carrier motion. This richness of transport channels leads to the high conductivity. With Fe substituion on Co sites, part of the channels are blocked and the resistivity is enhanced. But the resistivity is less than 1 Ω cm even with Fe content $x=0.3$. As a strong contrast, the resistivity of $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$ reaches 10^8 Ω cm at low temperature.[21] This great difference confirms our above argument that there are more electrical transport channels in $La_{1-y}Sr_yCoO_3$ than in $R_{1-y}A_yMnO_3$ perovskites. Although there also exists mixed-valence state, it was ever argued that the double-exchange interaction has little possiblity to occur in $La_{1-y}Sr_yCoO_3$ due to the absence of both the half-filled t_{2g} level providing the core spin and a strong Hund's rule coupling.[6] So the ferromagnetism in $La_{1-y}Sr_yCoO_3$ may mainly come from the superexchange interaction rather than the DE interaction. Moreover, the complex magnetic phase diagram of $La_{1-y}Sr_yCoO_3$, especially the spin-glass state that usually results from the competition between ferromagnetic and antiferromagnetic interaction, indicates the superexchange interaction could also be antiferromagnetic between certain valence states and spin states of Co ion. Another possible reason for the relative insensitivity of resistivity to Fe doping is that Fe ion could take part in the conduction due to the identical electron configuration ($t_{2g}^3e_g^2$) of Fe^{3+} with Co^{4+}(HS) ion. If the energy difference between the e_g bands of Fe^{3+} and Co^{4+}(HS) is small enough, the Fe^{3+} could act as Co^{4+}(HS) and contribute to the conduction.

Though it has been recognized that the mechanism of CMR in $La_{1-y}Sr_yCoO_3$ is different from that in La-A-Mn-O, there are still much controversy on the origin of CMR in this system. The suppression of spin-disorder scattering by applied magnetic field, though could contribute partly to MR, is unlikely to be the dominating mechanism. Recent finding of huge anisotropic magnetostriction in $La_{1-y}Sr_yCoO_3$ provides new insight to the role of applied magnetic field, i.e., a spin-state transition of Co^{3+} induced by the magnetic field.[11] As we mentioned above, the LS Co^{3+} ions can be thermally activated into IS Co ions due to the small energy difference between these states. When in a magnetic field of the order of several T, these LS Co^{3+} ions are under the influence of the local magnetic field due to the ferromagnetic clusters and the externally applied magnetic filed. The effective magnetic field at LS Co^{3+} sites could transform the LS Co^{3+} into the close energetic configuration of IS Co^{3+}. Hence, the conduction would be promoted because more channels are opened through Co^{3+}(IS, $t_{2g}^5e_g^1$)-O-Co^{4+}(LS, $t_{2g}^5e_g^0$) or Co^{3+}(IS, $t_{2g}^5e_g^1$)-O-Co^{3+}(LS, $t_{2g}^6e_g^0$). As a result, a negative MR appears. This case happens when most of the Co^{4+} ions are in LS state. However, if the ground state of Co^{4+} is IS (or HS), the spin-state transition of Co^{3+} ion by magnetic field would enhance the resistivity and cause a positive MR. This case could happen for certain Sr doping level because the spin configuration of Co^{4+} may also be doping dependent. In fact, the positive MR has been reported in $La_{1-y}Sr_yCoO_3$ at $y\approx0.5$.[6] On another hand, an interesting and still open question is whether a spin-state transition of Co^{4+} by applied magnetic field could occur and share the responsibility for CMR. Our present results of $La_{0.67}Sr_{0.33}Co_{1-x}Fe_xO_3$ could be a supporting evidence to the view of spin-state transition by applied magnetic field. The decrease of CMR by Fe doping may be ascribed to two aspects. One is to decrease the proportion of Co ion; the other is to weaken the effective local magnetic field on Co sites. Both aspects are against the occurence of CMR. In addition, the enhancement of low-temperature MR by Fe doping indicates that CMR can occur even without long-range ferromagnetic order. The complicated magnetic structure such as spin glass or cluster glass seems also a favorable circumstance for CMR. The mechanism of CMR in this spin-glass (or cluster-glass) state has not been well understood yet and deserves more devotion to it.

In summary, we have presented the study of the effects of Fe doping in $La_{0.67}Sr_{0.33}CoO_3$ on the magnetic, electrical transport, and magnetoresistance properties. The distinctive effects of Fe doping suggest the different mechanism of CMR between manganites and cobalt oxides. The origin of CMR and the effect of Fe doping in $La_{0.67}Sr_{0.33}CoO_3$ are interpreted in terms of the spin-state transition induced by applied magnetic field. The peculiar and confused properties of $R_{1-y}A_yCoO_3$ compounds are believed to be ascribed to the uncertainty of spin state of either trivalent or tetravalent Co ion. Although some investigations have been performed to explore the exact nature of spin state of either Co^{3+} or Co^{4+} ion, there is no concurrence reached yet and more efforts are needed to this subject.

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