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Reinforcement of double-exchange ferromagnetic coupling by Ru in $La_{1.24}Sr_{1.76}Mn_{2-y}Ru_yO_7$ manganite system

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ABSTRACT

The effect of Mn-site doping on magnetic and transport properties in the bilayer manganites $La_{1.24}Sr_{1.76}Mn_{2-y}Ru_yO_7$ (y = 0.0, 0.04, 0.08 and 0.15) has been studied. The undoped compound $La_{1.24}Sr_{1.76}Mn_2O_7$ exhibits a ferromagnetic metal to paramagnetic insulator transition at T_C = 130 K and the substitution of Ru shifts the transition temperatures to higher temperature values. The increased metal–insulator transition by Ru substitution, obtained from temperature dependence of resistivity measurements, indicates that the Ru substitution enhances the metallic state at low temperature regime and favours the Mn–Ru pairs in the Ru doped samples. Moreover, the activation energy values calculated from the temperature dependence of resistivity curves suggest that the Ru substitution weakens the formation of polarons. The increased magnetoresistance ratio from 108% to 136% by Ru substitution, measured at 5 K, points out that the Ru substitution also enhances the inter-grain tunneling magnetoresistance. Thus, the ferromagnetic order and metallic state in $La_{1.24}Sr_{1.76}Mn_2O_7$ system have been enhanced by the presence of Ru in the Mn-site. These reinforcements of ferromagnetic metallic state and magnetoresistance have been interpreted by the ferromagnetically coupled high spin states of Ru with Mn ions in the Mn–O–Ru network.

1. Introduction

The bilayer manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ system which is the n = 2 member of the Ruddlesden-Popper series ($R_{n+1}Mn_nO_{3n+1}$), presents a very rich magnetic phase diagram including the notable colossal magnetoresistance (CMR) phenomenon [1,2]. Experimental and theoretical studies in layered manganites exhibit interesting features like tunneling type magnetoresistance (MR) effect, enhanced ferromagnetic transition and magnetic field induced phenomena due to layered crystal structure [3–5]. In bilayer manganite system, the ferromagnetic metallic MnO_2 layers are separated by a rock-salt type block layer $(La, Sr)_2O_2$ and hence it exhibits highly anisotropic transport behaviour and determines an extremely large inter-plane tunneling magnetoresistance. Indeed, the charge transport and magnetic properties observed in these materials are strongly related to charge, spin and orbital ordering interactions.

The basic conduction mechanism in manganites is explained by the double exchange (DE) interaction, where the conductivity is attributed to electrons hop from Mn^{3+} to O^{2-} which is accompanied by a simultaneous hop from the later to Mn^{4+} [6]. According to Anderson and Hasegwa [7], in DE the hopping amplitude of the e_g electron from one site to another is a function of relative spin alignment at the two sites. Thus the hopping amplitude 't' can be written as $t = t_0 \cos(\theta/2)$, where θ is the angle between the neighboring t_2g spins. This model explains why a properly doped manganite at low temperature is a ferromagnetic metal which will become a paramagnetic insulator at elevated temperatures. The DE can occur only if the spins of each carrier is parallel to the local ionic spin and the hopping is highly dependent on the overlap of Mn–O–Mn network. Thereby, the Mn–O bond length and Mn–O–Mn bond angle are considered as the important crystallographic factors in manganites. Besides the DE mechanism, the Jahn–Teller effect, phase separation and antiferromagnetic super exchange interactions also play an important role in manganites [8,9].

The double-perovskite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ bilayer manganite allows a wide variety of doping and the La-site substitution has

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brought out the importance in the carrier density (n), Mn–O bond length and Mn–O–Mn bond angle which control the physical properties of manganites [1,2,10,11]. The parent compound $La_{2-2x}Sr_{1+2x}Mn_2O_7$ with $x = 0$ is a Mn^{3+} based antiferromagnetic insulator (AFI) with no local lattice distortion. When the divalent ion (Sr^{2+}) is doped in the trivalent (La^{3+}) site, the doping leads to a mixed valence $La^{3+}_{2-2x}Sr^{2+}_{1+2x}Mn^{3+}_{2-x}Mn^{4+}_{x}O_7$ system and it exhibits interesting phenomena in charge transport and magnetic properties. Magnetic phase diagram of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ system, determined by neutron diffraction in a wide range of doping was reported by several groups [3,5,10,11]. This system shows a ferromagnetic metal in a narrow doping range $0.30 \leq x \leq 0.42$ and a phase separation between ferromagnetic metallic (FMM) and antiferromagnetic (AF) is observed for the doping level $0.42 \leq x \leq 0.48$. The increased Sr concentration in La site results a canted AF order at $0.48 \leq x \leq 0.5$. The A, C and G type AFI are observed in the high doped regime ($x > 0.5$). Thus, the physical properties of layered manganites are extremely sensitive to small changes in La-site doping. Even though the La-site doping presents interesting phenomena by changing Mn to a mixed valence state, Mn-site doping gives more attention and considered as an effective method to modify the charge carrier and Mn–O–Mn network.

In this paper, we report the low temperature magnetization, electrical resistance and magnetoresistance of $La_{1.24}Sr_{1.76}Mn_{2-y}Ru_yO_7$ ($y = 0.0$, 0.04, 0.08 and 0.15) system in order to investigate the effect of Mn-site doping. Numerous studies have been reported on Mn-site doping in bilayer manganite system by substituting Fe, Co, Cr, Cu, Hf and Al [12–15]. We have also studied the Ru doped $La_{1.32}Sr_{1.68}Mn_2O_7$ system and reported that the Ru is coupled antiferromagnetically with Mn and weakens the ferromagnetic metallic state [16]. Indeed, both the $La_{1.32}Sr_{1.68}Mn_2O_7$ and $La_{1.24}Sr_{1.76}Mn_2O_7$ compounds are ferromagnetic below T_C and paramagnetic at elevated temperatures but its ground state spins are oriented differently. The magnetic moments of $La_{1.32}Sr_{1.68}Mn_2O_7$ system align ferromagnetically along the c-axis and the later one align to the ab-plane [2,17]. Since, manganites are spin dependent transport compounds, it will be interesting to study the effect of Mn-site doping in two differently spin oriented systems.

2. Experimental details

Polycrystalline samples of the series $La_{1.24}Sr_{1.76}Mn_{2-y}Ru_yO_7$ for $y = 0.0$, 0.04, 0.08 and 0.15 were prepared by the conventional solid-state reaction method. High purity La_2O_3, $SrCO_3$, Mn_2O_3 and RuO_2 powders were taken in stoichiometric proportions, and the mixtures were thoroughly ground, calcined at 1100 °C for 24 h, and pressed into pellets with several intermediate grindings. The pellets were finally sintered at 1300 °C for 36 h in controlled oxygen atmosphere. The room temperature powder XRD patterns of the final products were recorded with CuK_α radiation using a Phillips diffractometer in the 2θ range $20^\circ - 80^\circ$. The patterns were analyzed with the Rietveld method using the GSAS program [18].

A commercial SQUID magnetometer (Quantum design) was used to perform all the magnetization measurements reported in this paper. The electrical resistance measurements at low temperatures have been carried out by the standard four probe method with the electrical contacts made by silver epoxy (Alfa Aesar) and Pt wires of 25 μm. An oxford He^4 cryostat was used to execute all the low temperature measurements which admits a wide temperature range from 4.2 to 300 K and an external magnetic field up to 5 T. The electrical resistance was measured by a Linear Research (model LR-700) AC-resistance bridge. A LakeShore temperature controller (LakeShore-340) was used to measure and control the temperature.

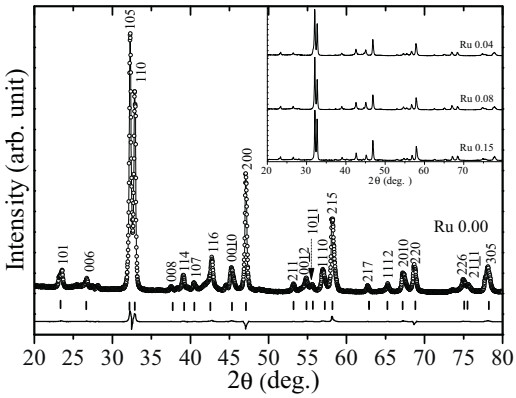

Fig. 1. Room temperature powder X-ray diffraction pattern processed by the Rietveld method for the $La_{1.24}Sr_{1.76}Mn_2O_7$ system. The inset shows the XRD patterns of Ru-doped samples.

3. Results

3.1. XRD measurement

The powder XRD patterns for all the samples were recorded at room temperature by step scanning over the angular range $20^\circ \leq 2\theta \leq 80^\circ$ at a step size of 0.02° with a counting time of 5 s per step. Fig. 1 shows the XRD pattern refined with Rietveld method for the $La_{1.24}Sr_{1.76}Mn_2O_7$ compound and the inset shows the XRD profile for Ru doped compounds. The patterns indicate that all the samples are single phases without detecting any secondary phase or impurity phase. All the diffraction peaks were indexed to the $Sr_3Ti_2O_7$ type tetragonal structure and all the samples belong to the space group I4/mmm.

The lattice parameters were refined using GSAS program and listed in Table 1. Lattice parameters were determined assuming a tetragonal crystal structure and the calculated unit cell parameters for the undoped sample ($y = 0.00$) are in good agreement with the values reported earlier [17]. The lattice parameters 'a' and 'c' were found to be increase linearly with the substitution of Ru. The appreciable increase in lattice parameters is expected, because the ionic radius of Ru (0.68 Å) is larger than that of Mn (0.52 Å). Since, the Ru is substituted in the site of Mn, the Ru is also expected to be in mixed valence states.

3.2. Magnetization measurements

The field dependence of magnetization M(H) measurements were executed for all the compounds of $La_{1.24}Sr_{1.76}Mn_{2-y}Ru_yO_7$ ($y = 0.0$, 0.04, 0.08 and 0.15) at 5 K and the obtained results are displayed in Fig. 2. In the measurements, it is clear that all the samples show saturation at high magnetic field and all the samples are found to be ferromagnetic at 5 K. We find that the calculated magnetic moments were increased from 3.44 μ_B for the undoped compound to 4.95 μ_B for the highly doped compound ($y = 0.15$). There are several studies on the calculation of Ru magnetic moments and those results reported that the high spin state of Ru^{4+}

Table 1
Lattice parameters, important magnetic parameters and magnetoresistance ratio for different Ru doped compounds.

Ru con. (y)	a(Å)	c(Å)	$M(\mu_B/Mn)$	H_C (mT)	T_C (K)	MRR (%)
Ru 0.00	3.871(3)	20.191(7)	3.44	0	130	108
Ru 0.04	3.874(4)	20.225(6)	3.87	25	136	118
Ru 0.08	3.878(1)	20.252(3)	4.52	55	144	125
Ru 0.15	3.882(8)	20.306(8)	4.95	77	148	136