Magnetism and electronic transport in Sr$_{4-x}$La$_x$Ru$_{2-x}$Mn$_x$O$_9$: Interplay of Mn and Ru redox chemistry

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(Submitted on 9 November 2004; published online 28 April 2005)

Sr$_2$RuO$_3$ has a P6$_2$C space group and differs from the Ruddelsden–Popper series of the strontium ruthenate family where Ru is distinctly present in Ru$^{5+}$ state with no Jahn–Teller activity. A significant increase in magnetic moment and coercivity is observed along with lowering of resistivity, especially around a critical concentration of $x=0.2$ in Sr$_{1-x}$La$_x$Ru$_{2-x}$Mn$_x$O$_9$. Such an unusual effect is correlated to the mixed magnetic pair effect arising out from the variable oxidation states of Ru as suggested by x-ray photoelectron spectroscopic studies. Our results substantiate the long-range ferromagnetism observed for Ruthenium-substituted three-dimensional manganites. © 2005 American Institute of Physics. [DOI: 10.1063/1.1847913]

The colossal magnetoresistive (CMR) property in rare-earth manganites is introduced along with the paramagnetic to ferromagnetic transition (PM–FM) and metal to insulator transition (MIT) due to the presence of mixed-valence Mn$^{3+}$/Mn$^{4+}$ ions. These mixed-valence ions of Mn, often referred to as Zener pair, induce a double-exchange (DE) mechanism, wherein an $e_g$ electron of Mn$^{3+}$ ion couples ferromagnetically with the Mn$^{4+}$ ion by means of strong Hund’s coupling. More recently it has been observed that ruthenium chemistry offers a variety of DE-mediated magnetic coupling between Mn and Ru ions in the La(Sr)Mn$_{1-x}$Ru$_x$O$_3$ (Ref. 4) series. This opens up a new series of perovskite oxides showing correlated magnetic and electronic behaviors due to an unusual presence of Ru$^{5+}$ state (which is iso-ortibital with the Mn$^{4+}$)\(^{2,3}\). Substitution of ruthenium in manganites leads to (i) long-range ferromagnetism,\(^{5–7}\) (ii) induces ferromagnetism,\(^{8,9}\) (iii) removes charge ordering by means of orbital rotation,\(^{10,11}\) and (iv) forms a new magnetic pair analogous to Zener pair.\(^{12,13}\) An unusual magnetic pair making ability of Ru and Mn lies in the ease with which Mn$^{4+}$ and Ru$^{4+}$ can undergo a redox reaction, leading to a reduced Mn$^{3+}$ and to oxidized Ru$^{5+}$ states. Such a trend has also been verified via a reverse doping effect wherein Mn doping in SrRuO$_3$ seems to lead to unusual Mn and Ru states.\(^{14}\) The solid solutions of SrRuO$_3$ and SrMnO$_3$ show long-range ferromagnetic ordering and enhancement of magnetoresistance (MR) ratio due to the induced DE-mediated coupling coming from (Ru$^{4+}$/Ru$^{5+}$) of Ru and (Mn$^{3+}$/Mn$^{4+}$) of Mn states.\(^{15}\)

The effect of Mn doping in other Ruddelsden–Popper (R–P) analogs of SrRuO$_3$, namely, Sr$_2$RuO$_4$ and in Sr$_3$Ru$_2$O$_7$ has also been verified recently,\(^9\) wherein a spin-glass transition is observed at 16 K in Sr$_2$Ru$_{0.5}$Mn$_{0.5}$O$_4$ and at 25 K in Sr$_3$RuMnO$_7$ systems. In both systems, magnetic transition was accompanied by a reduction in the zero-field electrical conductivity. On the other hand, Sr$_2$Ru$_2$O$_9$ is not a member of the R–P series, having Ru in a pentavalent state. Hence, this compound serves as a reference compound for Ru$^{5+}$ state in spectroscopic analysis.\(^{16}\) Our interest in the present study is twofold: (1) to understand the Mn substitution effects in Ru$^{5+}$ sites and (2) to probe if unusual magnetic signatures are evident due to the redox reactions between Ru$^{5+}$ and Mn$^{3+/4}$ pair. In this paper we demonstrate an increased conductivity and magnetic moment with an increase in ($T_c$) for a critical concentration of $x=0.2$ in Sr$_{4-x}$La$_x$Ru$_{2-x}$Mn$_x$O$_9$ (0 $\leq$ $x$ $\leq$ 0.25). We attribute this to the exchange interactions between Ru and Mn because of the presence of mixed valence of Ru and Mn in the Ru–O–Mn basal plane.

Polycrystalline samples of Sr$_{4-x}$La$_x$Ru$_{2-x}$Mn$_x$O$_9$ (0 $\leq$ $x$ $\leq$ 0.25) were prepared by the solid-state reaction method. Appropriate proportions of SrCO$_3$, La$_2$O$_3$, Ru$_2$O$_7$, and MnO$_2$ pure oxides were mixed thoroughly according to the desired stoichiometric, calcined at 850 °C for 36 h in the presence of O$_2$ atmosphere, and subsequently sintered under O$_2$ atmosphere at 950 °C for 36 h. The homogeneity of the samples was checked with x-ray powder diffraction. Standard four-probe techniques were employed to study the transport properties. Magnetization measurements were carried out using a vibrating-sample magnetometer (VSM) Oxford instrument.

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The higher analog of Ruthenates, namely, Sr$_4$Ru$_2$O$_9$, having a nominal valence of Ru$^{5+}$, has a 2H hexagonal perovskite structure, which can be considered as forming from the stacking of perovskite like layers. The average Ru–O distance within the octahedra is 1.98 Å in Sr$_4$Ru$_2$O$_9$, which is closer to the Mn–O bond length of 1.91 Å, as noted in rare-earth manganite. In order to maintain the charge neutrality in the unit cell, La was substituted at the Sr site, in proportion to Mn doping concentration at the Ru site. In this way we exclude any other possible crystal-field effects other than those coming from the oxidation states of Mn and Ru for long-range ferromagnetism. The room-temperature x-ray powder-diffraction patterns of Sr$_{4-x}$La$_x$Ru$_2_x$Mn$_x$O$_9$ ($0 \leq x \leq 0.25$) show (Fig. 1) a single phase pattern for all the samples. All the reflections are indexed to a hexagonal symmetry. Beyond $x=0.25$ of Mn, a multiphase x-ray pattern was observed.

In Fig. 2 we show the magnetization as a function of temperature for the Sr$_{4-x}$La$_x$Ru$_2_x$Mn$_x$O$_9$ ($0 \leq x \leq 0.25$) series. $M$ vs $H$ loop [inset (a) and (b) to Fig. 2] shows the ferromagnetic behavior for all the samples with a maximum coercive field ($H_C$) for the $x=0.2$ sample. In accordance with a $T_C$ of 30 K in Sr$_2$RuO$_4$ sample. It is noteworthy that the substitution of Mn at the Ru site results in a nearly monotonic decrease in moment and $H_C$ until we reach up to $x=0.2$ composition. For $x=0.2$ a large increase in magnetic moment and a distinct change in Curie temperature ($T_C$) are noted. Such an increase is observed in Ru-doped bulk polycrystalline La$_{0.5}$Ca$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_2$ two-dimensional (2D) perovskite, which shows an increase in the $T_C$ and $T_{MRT}$ by 15–20 K for $x=0.2$ compound. This increase in $T_C$ and $T_{MRT}$ is attributed due to a dominant double-exchange mediated transport, aided by the presence of Ru$^{5+}$ ions, which is metrically and chemically similar to Mn$^{4+}$ ions. The presence of Ru$^{5+}$ state ensures that the effective hole carrier density essentially remains the same, hence the itinerant $e_g$ electron of Mn$^{3+}$ is delocalized to the Ru$^{5+}$ center via O: 2$g$ orbital, as in the case of Mn$^{3+}$–O–Mn$^{4+}$. A substantial increase in saturation moment $H_C$ and $T_C$ appears to come from an induced interaction between Ru and Mn mixed-valence states. The moments are substantially high enough to exclude the possibility of a typical spin-glass behavior. However, if the magnetic signatures were to originate from the presence of a SrRuO$_3$ impurity phase, the moment is significantly lower compared to $T_C \approx 1.4\mu_B$/Ru for the SrRuO$_3$ phase. Several competing interactions can be noted for this magnetic behavior. According to Goodenough–Kannamori–Anderson (GKA) rule similar ions couple antiferromagnetically and different ions couple ferromagnetically. We anticipate that mixed-valence oxidation states appear to bring about such a ferromagnetic response, more so for the $x=0.2$ sample.

All the compositions show a weak to strong semiconducting behavior as a function of increasing Mn doping. The low-temperature upturn in resistivity increases sharply with Mn doping. However for $x=0.2$ sample, in accordance with a large increase in magnetization, $H_C$, and $T_C$, the sample shows a sharp decrease in resistivity compared to $x=0.1$, $x=0.15$ samples (Fig. 3). We observe that a correlated response between magnetic and transport behaviors occurs whenever Ru and Mn translate to different valence states. In the present case when Ru$^{5+}$ is substituted by Mn$^{4+}$, at an optimum concentration of $x=0.2$, a clear redox reaction occurs promoting Ru$^{5+}$ to Ru$^{4+}$ and reducing Mn$^{4+}$ to Mn$^{3+}$ states.

Recently Sahu et al. have shown that SrRu$_{1-x}$Mn$_x$O$_3$ ($0 \leq x \leq 0.5$) reveals the coexistence of a mixed-valence redox pair involving both redox pairs Mn$^{3+}$/Mn$^{4+}$ and Ru$^{4+}$/Ru$^{5+}$, which induces DE mediated ferromagnetism and metallic behavior compared to the superexchange interaction.
observed in the parent SrRuO$_3$. Further the x-ray absorption studies in La$_{0.4}$Pb$_{0.6}$Mn$_{1−x}$Ru$_3$O$_9$ confirmed the presence of Mn$^{3+}$/Mn$^{4+}$ ↔ Ru$^{5+}$/Ru$^{6+}$ redox pairs up to $x=0.4$, where the coexistence of $T_C$ and $T_P$ shows evidence for sustained double-exchange interactions. In the present study we observe Ru to be in the pentavalent state for the parent Sr$_2$Ru$_2$O$_9$ compound. With La doped in proportion to Mn doping concentration (to keep up the charge neutrality) in Sr$_{1−x}$La$_x$Ru$_2$O$_9$, any change in Ru or Mn valence should therefore occur only due to a redox reaction behavior of Ru and Mn ions. We indeed observe such a redox reaction leading to mixed valency, which in turn modifies the magnetic and electronic transports. As a result of the presence of Mn$^{3+}$ and Ru$^{5+}$/Mn$^{4+}$ redox pairs, a weak double-exchange mediated interaction occurs between the $e_g$ electron of Mn$^{3+}$($t_{2g}^3e_g^1$) ions with Ru$^{5+}$($t_{2g}^{2}e_g^0$) ions for a critical concentration around $x=0.2$ in the Sr$_{1−x}$La$_x$Ru$_2$O$_9$ series.

In order to elucidate the presence of mixed-valence states in Ru and Mn we have probed the Ru 3$d$ states using X-ray photoelectron spectroscopy (XPS). The presence of mixed valency in Ru (Ru$^{5+}$/Ru$^{6+}$) is evident from the XPS data, which are shown in the inset to Fig. 3. Signatures of Sr 3$p$ and Cl 1$s$ core-level peak of adventitious carbon contamination are seen, along with a doublet for Ru3$d_{5/2}$ for the $x=0.2$ composition. The Ru 3$d_{5/2}$ peak shows a splitting corresponding to 283.1 and 282.1 eV (Refs. 24 and 25) binding energy peaks which suggests the presence of a redox couple involving Ru$^{6+}$/Ru$^{5+}$ for the $x=0.2$ compound. In the event of Ru$^{5+}$ going to Ru$^{6+}$ state there is a reduction of Mn$^{4+}$ state to Mn$^{3+}$ state. This induces ferromagnetic interactions between the Mn$^{3+}$($t_{2g}^3e_g^1$) state with the Ru$^{5+}$($t_{2g}^{2}e_g^0$) states for the $x=0.2$ sample, where the $e_g$ electron of Mn$^{3+}$ ion can couple ferromagnetically with the Ru$^{5+}$($t_{2g}^3e_g^1$) electrons via oxygen center. This unusual magnetic interaction seems to happen for an optimum $x=0.2$ compound which results in the increase of the magnetic moment, $T_C$, and distinctly low resistivity.

In summary, $x=0.2$ compound shows an increase in the magnetic moment with $T_C$ and $H_C$ due to an induced interaction between Mn$^{3+}$ and Ru$^{5+}$/Ru$^{6+}$ redox pairs. This is another model system wherein the presence of Ru$^{5+}$ and Mn$^{4+}$ initiates a redox mechanism leading to mixed-valence states of Mn$^{3+}$/Mn$^{4+}$ and Ru$^{5+}$/Ru$^{6+}$.

One of the authors (B.S.) thanks CSIR—INDIA for a senior research fellowship. Financial grant from ESPRC, UK to SSM for a visiting fellowship is greatly acknowledged. We thank Professor C. M. Schneider IFF—Jülich for fruitful discussions.