

Evolution of Structural and Physical Properties of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ with Mn Concentration

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Layered ruthenates are prototype materials with strong structure-property correlations. We report the structural and physical properties of double-layered perovskite $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ single crystals with $0 \leq x \leq 0.7$. Single crystal x-ray diffraction refinements reveal that Mn doping on the Ru site leads to the shrinkage of unit-cell volume and disappearance of $(\text{Ru}/\text{Mn})\text{O}_6$ octahedron rotation when $x > 0.16$, while the crystal structure remains tetragonal. Correspondingly, the electronic and magnetic properties change with x . The electrical resistivity reveals metallic character ($d\rho/dT > 0$) at high temperatures but insulating behavior ($d\rho/dT < 0$) below a characteristic temperature T_{MIT} . Interestingly, T_{MIT} is different from T_{M} , at which magnetic susceptibility reaches maximum. T_{MIT} monotonically increases with increasing x while T_{M} shows non-monotonic dependence with x . The difference between T_{MIT} and T_{M} ($T_{\text{MIT}} > T_{\text{M}}$) becomes larger when $x > 0.16$. The constructed phase diagram consists of five distinct regions, demonstrating that the physical properties of such a system can easily be tuned by chemical doping.

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Transition metal oxides (TMOs) have attracted extensive attention due to the strong correlations between charge, lattice, orbital, and spin degrees of freedom. The Ruddleson-Popper (RP) $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ (n =integer) series are prototype strongly correlated systems, since both theoretical and experimental investigations indicate intimate relationships between structural, electronic and magnetic properties [1–5]. A small change in structure often results in different ground states, as seen in single-layered ($n=1$) $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ [6, 7]. Different from the rest of the RP series, $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n=2$) shows unique physical properties. Although the electrical resistivity varies smoothly with temperature without any anomaly, the magnetic susceptibility of $\text{Sr}_3\text{Ru}_2\text{O}_7$ reveals a characteristic peak around 16 K [2]. Neutron scattering measurements confirm that the susceptibility peak corresponds to a short-range antiferromagnetic (AFM) correlation [8, 9]. Under the application of hydrostatic pressure, the ground state of $\text{Sr}_3\text{Ru}_2\text{O}_7$ reveals ferromagnetic (FM) instability [2]. On the other hand, the application of magnetic field leads to a metamagnetic transition at low temperatures [10]. These phenomena strongly suggest that both AFM and FM interactions exist in $\text{Sr}_3\text{Ru}_2\text{O}_7$.

It was reported that a slight substitution of Ru by Mn drives the ground state from a paramagnetic metal (PM) to an AFM insulator, and a phase diagram of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ was mapped out up to

$x=0.2$ [11]. The central question is how Mn doping leads to the change of ground state properties. X-ray absorption spectroscopy (XAS) revealed that the Mn dopant has an oxidation state different from Ru^{4+} , while x-ray photoemission spectroscopy (XPS) showed no sign of doping-induced multiple Ru valences up to $x=0.2$ [12, 13]. We have studied $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ in the doping range of $0 \leq x \leq 0.7$. According to its electronic and magnetic properties, a phase diagram is constructed which has two phase boundaries: one is a metal-insulator crossover line and the other is the magnetic transition line.

Single crystals of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ ($0 \leq x \leq 0.7$) were grown by the floating-zone technique in an image furnace (model: Canon SC1-MDH20020). All selected crystals for physical property measurements in this Letter were characterized by powder and single crystal x-ray diffraction (XRD). The crystal structure and Mn concentration (x) were determined by single crystal XRD refinement. Magnetic susceptibility measurements were carried out in a superconducting quantum interference device (SQUID) magnetometer. Measurements of the resistivity and specific heat were performed in a Quantum Design Physical Properties Measurement System (PPMS).

For all $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ samples, single crystal XRD data show that their structure can be described by the space group $I4/mmm$ with the details described previously [14]. The left panel of Fig. 1 displays the unit-cell representation of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ (top) and the three oxygen sites of the $(\text{Ru}/\text{Mn})\text{O}_6$ octahedron (bottom). Fig. 1(a)-(d) shows the x dependence of lattice parameters a

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and c , the volume of unit cell (V), and ratio c/a at 298 K and 90 K, respectively. Note that, with increasing x , the lattice parameter a increases for $0 \leq x \leq 0.2$ and decreases for $x > 0.2$, while the lattice parameter c decreases monotonically. This results in a monotonic decrease of V and c/a with increasing x . For comparison, the structural information obtained from polycrystalline $\text{Sr}_3\text{Mn}_2\text{O}_7$ ($x=1$) is also presented [15], which has a higher c/a ratio than that for $x=0.7$. Nevertheless, the Ru-O(3) bond length [Fig. 1(g)] remains more or less unchanged, while both the Ru-O(1) [Fig. 1(e)] and Ru-O(2) bond lengths [Fig. 1(f)] decrease with increasing x . With this information, the Jahn-Teller distortion (Δ_{JT}) can be calculated via $\Delta_{\text{JT}} = [\text{Ru-O}(1) + \text{Ru-O}(2)] / [2 \times \text{Ru-O}(3)]$, which decreases from 1.04 for $x=0$ to 1 for $x=0.7$ (not shown). This suggests that Mn doping makes the (Ru/Mn) O_6 octahedron less distorted. Further support can be found from the reduction of rotation angle of the (Ru/Mn) O_6 octahedron, as shown in Fig. 1(h). Note that the rotation angle (Φ) of the (Ru/Mn) O_6 octahedron decreases with increasing x and becomes undetectable for $x > 0.16$.

The temperature dependence of the in-plane (ρ_{ab}) and out-of-plane (ρ_c) electrical resistivity of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ single crystals are shown in Fig. 2(a) and 2(b), respectively. For the undoped compound ($x=0$), both $\rho_{\text{ab}}(T)$ and $\rho_c(T)$ are metallic in the measured temperature range. Upon doping, both ρ_{ab} and ρ_c are not only enhanced in magnitude but also change sign in slope at a characteristic temperature T_{MIT} from positive (metallic) at high temperatures to negative (insulating) at low temperatures. This result is consistent with the previous report that a metal-insulator transition (MIT) occurs when introducing the Mn dopant into $\text{Sr}_3\text{Ru}_2\text{O}_7$ [11]. With increasing x , T_{MIT} is quickly pushed to higher temperature and becomes less pronounced.

However, the magnetic properties of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ reveal a different trend. Fig. 2(c) and 2(d) show the temperature dependence of the in-plane (χ_{ab}) and out-of-plane (χ_c) magnetic susceptibility under zero-field-cooling (ZFC) condition for $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$, respectively (χ_{ab} and χ_c measured under field-cooling condition are very similar). For $0 \leq x \leq 0.7$, both χ_{ab} and χ_c always display a characteristic peak at T_{M} . For $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($x=0$), T_{M} is about 16 K, in agreement with previous results [2]. With increasing x , T_{M} initially increases then decreases, with a maximum near $x \sim 0.16$.

In order to understand why T_{M} varies with x non-monotonically, we analyze χ_{ab} and χ_c at high temperatures. Both $\chi_{\text{ab}}(T)$ and $\chi_c(T)$ can be fitted with a formula $\chi(T) = \chi_0 + \chi_{\text{CW}}(T)$ between 175 K and 390 K. Here χ_0 is the temperature independent term and

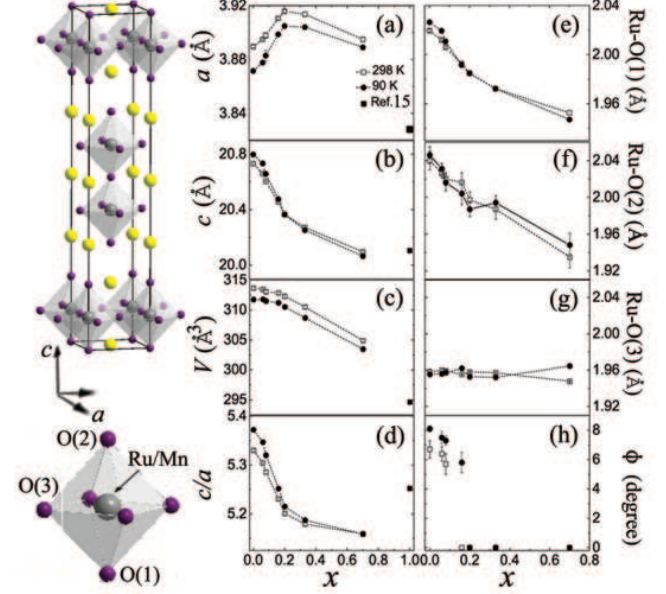


FIG. 1: (Color online) Unit-cell representation of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ in space group $I4/mmm$ (left top) and the configuration of the (Ru/Mn) O_6 octahedron (left bottom), where the Mn atoms partially occupy the Ru site. (a)-(d) are the Mn concentration (x) dependence of the lattice parameters a and c , the unit cell volume (V), and the ratio c/a at 298 K (empty squares) and 90 K (solid circles), respectively. The solid square in (a)-(d) indicate the values of a , c , V and c/a of polycrystalline $\text{Sr}_3\text{Mn}_2\text{O}_7$ at 300 K obtained from Ref.15. (e)-(g) are the bond length of Ru-O(1) (inner apical), Ru-O(2) (outer apical), and Ru-O(3) (equatorial) as a function of x at 298 K (empty squares) and 90 K (solid circles), respectively. (h) is the x dependence of the rotation angle Φ of the (Ru/Mn) O_6 octahedron at 298 K and 90 K, respectively. Dashed lines are guides for the eye.

$\chi_{\text{CW}}(T) = C / (T - \Theta_{\text{CW}})$ is the Curie-Weiss term with Curie constant $C = N_{\text{A}} p_{\text{eff}}^2 \mu_{\text{B}}^2 / (3k_{\text{B}})$ and Curie-Weiss temperature Θ_{CW} (N_{A} is Avogadro number, p_{eff} is the effective Bohr magneton number, μ_{B} is the Bohr magneton, and k_{B} is the Boltzmann constant). Θ_{CW} and p_{eff} obtained from the fitting for $0 \leq x \leq 0.7$ are plotted in Fig. 2(e) and Fig. 2(f), respectively. Note that both $\Theta_{\text{CW}}^{\text{ab}}$ and Θ_{CW}^c are negative with similar magnitude and increase with increasing x for $0 \leq x \leq 0.16$. For $x > 0.2$, $\Theta_{\text{CW}}^{\text{ab}}$ is positive but Θ_{CW}^c is negative. The sign change of $\Theta_{\text{CW}}^{\text{ab}}$ is likely caused by the change from AFM to FM interaction in the ab plane, while the dominant magnetic interaction in c direction remains AFM ($\Theta_{\text{CW}} < 0$). Indeed, the in-plane magnetization (M_{ab}) vs field (H) plot shows FM character when $x > 0.16$ (see Fig. 2(g)).

Although $\rho_c \gg \rho_{\text{ab}}$ with $\rho_c / \rho_{\text{ab}} \sim 30$ for $x=0$ and ~ 10 for $x > 0.16$ at room temperature, the magnetic anisotropy is much smaller with $\chi_c / \chi_{\text{ab}} \sim 1$ for $x > 0.16$ (see Fig. 2(h)). The above fitting also showed

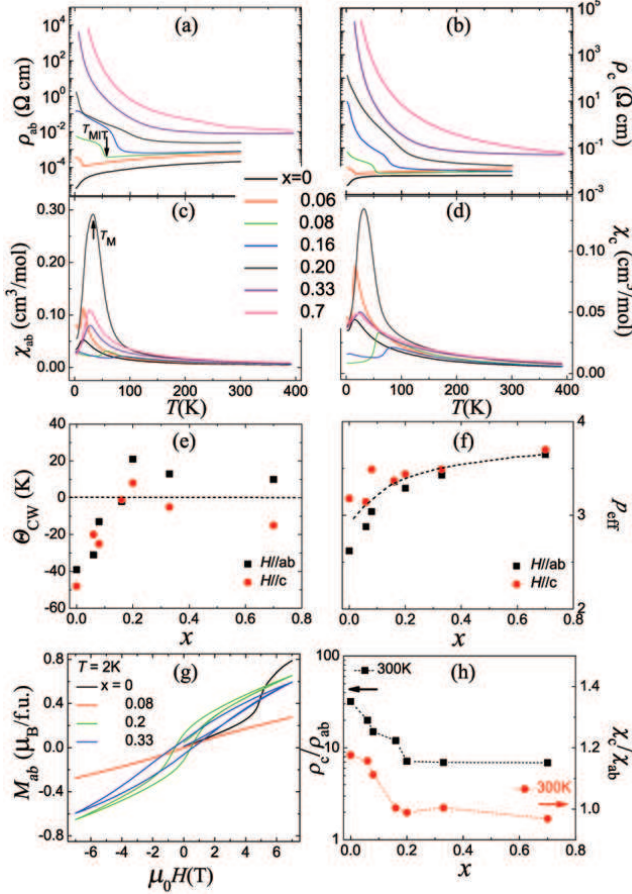


FIG. 2: (Color online) (a) and (b) are the temperature dependence of $\rho_{ab}(T)$ and $\rho_c(T)$ with different x , respectively. The arrow in (a) shows an example of the temperature defined as T_{MIT} for $x=0.08$. (c) and (d) are $\chi_{ab}(T)$ and $\chi_c(T)$ as a function of T with different x , respectively. The arrow in (c) shows an example of the temperature defined as T_M for $x=0.2$. (e) and (f) are the derived Θ_{CW} and p_{eff} from Curie-Weiss law fitting as a function of x , respectively. Squares (circles) denote fitting values under $H||ab$ ($H||c$). (g) shows magnetization $M(H)$ hysteresis loops at 2 K for $H||ab$ for $x=0$ (black), 0.08 (red), 0.2 (blue) and 0.33 (green). (h) shows the x dependence of ρ_c/ρ_{ab} (left axis) and χ_c/χ_{ab} (right axis) at 300 K. Dashed lines are guides for the eye.

that $p_{eff}^{ab} \sim p_{eff}^c$. Interestingly, both p_{eff}^{ab} and p_{eff}^c increase with x and tend to saturate for $x > 0.16$. For $x=0$, $p_{eff} \sim 2.8$, corresponding to $S=1$, according to $p_{eff} = g\sqrt{S(S+1)}$ with $g=2$ for transition metals. For $x > 0.16$, $p_{eff} \sim 3.7$, corresponding to $S=3/2$.

The temperature dependence of the resistivity and magnetic susceptibility reveals two characteristic temperatures (T_{MIT} and T_M) in $Sr_3(Ru_{1-x}Mn_x)_2O_7$. The question is whether they correspond to true phase transitions. The specific heat data shown in Fig. 3(a) allow us to determine the nature of T_{MIT} and T_M . In Fig. 3(a), we plot the specific heat as C_p/T vs

T , and shift the data for each doping level for clarity. For $x=0$, C_p varies with x smoothly without any anomaly at $T_M \sim 16$ K (see Fig. 2c). This indicates that there is no true phase transition in the undoped compound, consistent with neutron scattering measurements [8]. For $x=0.06$, there is a clear specific heat anomaly at T_M , indicating a true second order phase transition. Since $T_M \sim T_{MIT}$ for $x=0.06$, it is unclear whether the phase transition originates from magnetic ordering and/or a metal-insulator transition. Specific heat data for higher doping levels can clarify this. Note that, for $x=0.16$, the specific heat anomaly presents at $T_M \sim 80$ K but not at $T_{MIT} \sim 140$ K. This implies that T_M in the region of $0.06 \leq x \leq 0.16$ corresponds to a true phase transition, while T_{MIT} represents a crossover temperature from metallic behavior at high temperatures to insulating character at low temperatures. Recent neutron scattering experiment confirms a long-range AFM ordering below T_M for $x=0.16$ [16]. Theoretically, the entropy removal upon magnetic ordering is expected to be $S_M = R \ln(2S+1) = 1.09R$ for $S=1$ and $1.39R$ for $S=3/2$ ($R=8.314$ J/mol K). We may estimate the actual entropy removal at T_M by subtracting the background by fitting the experimental data outside of the transition region using a polynomial (dashed line in Fig. 3(a)). By integrating $\Delta C_p/T$ in the transition region, we obtain $\Delta S_M \sim 0.077R$ for $x=0.06$, $0.64R$ for $x=0.08$, and $0.77R$ for $x=0.16$. These values are considerably smaller than the expected values, indicating that only a fraction of the spins are ordered. It is also possible that some of entropy has been removed above T_M . Nevertheless, the specific heat anomaly at T_M can no longer be detected when $x > 0.16$ (see Fig. 3(a)), suggesting that there is no long-range magnetic ordering at high Mn doping levels.

As shown in the inset of Fig. 3(b), the low temperature (2 K) specific heat decreases with increasing x , quickly dropping to a very small value as $x > 0.16$. This is most likely due to the reduction of electronic specific heat, because of the insulating ground state when $x \neq 0$. The electronic specific heat becomes negligible at high Mn doping concentrations. However, the low temperature (below 10 K) C_p/T does not seem to vary linearly with T^2 (Fig. 3(b)). Such a deviation should be attributed to magnetic contributions of the system.

Based on the above observations, we construct a phase diagram for $Sr_3(Ru_{1-x}Mn_x)_2O_7$, covering $0 \leq x \leq 0.7$. Fig. 4 shows the $x-T$ phase diagram, which consists of two boundary lines: T_{MIT} and T_M . In terms of physical properties, it can be divided into five regions, as marked in the phase diagram. Region I represents a paramagnetic (PM) metallic (PM-M) phase, which covers temperature range above T_{MIT} . Region

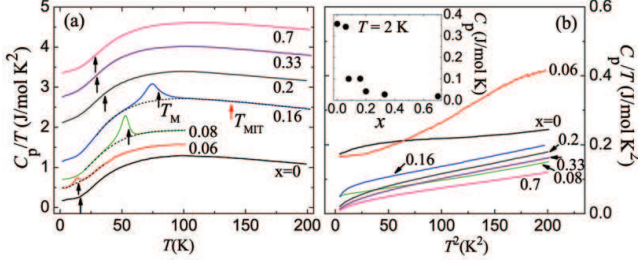


FIG. 3: (Color online) (a) Temperature dependence of specific heat C_p of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ at zero field, plotted as $C_p(T)/T$ versus T and shifted for clarity. The black arrows indicate T_M for each concentration. The red arrow indicates T_{MIT} for $x=0.16$. Dashed lines in the $x=0.06$, 0.08 and 0.16 plots represent the polynomial fit to the specific heat background. (b) Low temperature specific heat plotted as C_p/T versus T^2 . The inset of (b) shows C_p at 2 K for each x .

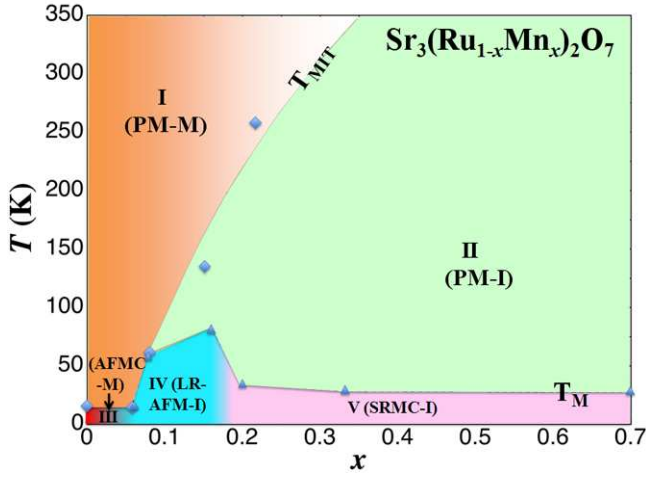


FIG. 4: (Color online) The x - T phase diagram of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ ($0 \leq x \leq 0.7$). Diamonds and triangles represent T_{MIT} and T_M , respectively. Region I is a paramagnetic metallic (PM-M) phase. Region II is a paramagnetic insulating (PM-I) phase. Region III is a metallic phase with AFM correlation (AFMC-M), where the correlation is enhanced upon Mn doping. Region IV represents a long-range AFM insulating phase (LR-AFM-I). Region V is an insulating phase with short-range magnetic correlation (SRMC-I).

II is a PM insulating (PM-I) phase, where the system is non-metallic with $d\rho/dT < 0$ but remains paramagnetic. Region III ($0 \leq x < 0.06$) represents metallic phase with AFM correlation (AFMC-M), where the correlation is enhanced upon Mn doping. Region IV is a long-range (LR) AFM insulating (LR-AFM-I) phase, where LR AFM ordering forms below T_M and the specific heat anomaly emerges at T_M . Since there is lack of specific heat anomaly in Region V, this region is an insulating phase with short-range magnetic correlations (SRMC-I).

In light of all of the structural and physical prop-

erties, it becomes clear that the variation of electronic and magnetic properties is intimately connected with the change of structure of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$. Due to partial replacement of Ru by Mn with smaller ionic radius, the unit cell becomes smaller and $(\text{Ru}/\text{Mn})\text{O}_6$ becomes less distorted. This is reflected in both rotation angle (see Fig. 1 (h)) and Δ_{JT} (not shown). This weakens the FM interaction, according to the theoretical calculations for the single layered ruthenate $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ [5], and leads to long-range AFM ordering accompanied by a metal-insulator transition in Region IV. When $x > 0.16$, the structure of $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ is no longer distorted which gives rise to competitive AFM and FM interactions (see Fig. 2(e)). As a result, the system can no longer form long-range magnetic ordering (Region V). On the other hand, the electrical transport is dominated by impurity scattering, leading to the increase of T_{MIT} with x . Given the fact that the spin varies from $S \sim 1$ for $x=0$ to $S \sim 3/2$ for $x > 0.16$ (derived from p_{eff} shown in Fig. 2(f)), it is likely that the oxidation state of Mn in $\text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ is $4+$, independent of x . In principle, $S=3/2$ could also result from Ru^{5+} , but there seems to be lack of support according to XAS and XPS results [12, 13].

In summary, we have investigated the structural and physical properties of Mn-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ and constructed a rich phase diagram for $0 \leq x \leq 0.7$. Two characteristic temperatures (T_{MIT} and T_M) are required to accurately describe the change of the physical properties. T_{MIT} shows a monotonic change, while T_M reveals a non-monotonic dependence with x . Three distinct regions are identified below T_M . This work illustrates the coupling between structure and physical properties which can be tuned by chemical doping.

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