Structural and physical properties of SrMn$_{1-x}$Ru$_x$O$_3$ perovskites

S. Kolesnik, B. Dabrowski, and O. Chmaissem
Department of Physics, Northern Illinois University, DeKalb, IL 60115 and Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
(Dated: November 25, 2008)

We combine the results of magnetic and transport measurements with neutron diffraction data to construct the structural and magnetic phase diagram of the entire family of SrMn$_{1-x}$Ru$_x$O$_3$ (0 ≤ x ≤ 1) perovskites. We have found antiferromagnetic ordering of the C type for lightly Ru-substituted materials (0.06 ≤ x ≤ 0.5) in a similar manner to $R_y$Sr$_{1-y}$Mn$_3$O$_3$ ($R$=La, Pr), due to the generation of Mn$^{4+}$ in both families of manganite perovskites by either B-site substitution of Ru$^{4+}$ for Mn$^{4+}$ or A-site substitution of $R^{3+}$ for Sr$^{3+}$. This similarity is driven by the same ratio of $d^8/d^3$ in both classes of materials for equivalent substitution level. In both cases, a tetragonal lattice distortion is observed, which for some compositions (0.06 ≤ x ≤ 0.2) is coupled to a C-type AF transition and results in a first order magnetic and resistive transition. Heavily substituted SrMn$_{1-x}$Ru$_x$O$_3$ materials are ferromagnetic due to dominating exchange interactions between the Ru$^{4+}$ ions. Intermediate substitution (0.6 ≤ x ≤ 0.7) leads to a spin-glass behavior instead of a quantum critical point reported previously in single crystals, due to enhanced disorder.

PACS numbers: 75.30.Kz, 75.50.Ee, 75.50.Lk, 81.30.Dz

I. INTRODUCTION

The substitution of Ru in perovskite manganites has been demonstrated to lead to a variety of interesting physical phenomena. For colossal magnetoresistance manganites La$_{0.5}$Sr$_{0.5}$Mn$_{1-y}$Ru$_y$O$_3$ with ferromagnetic matrix and La$_{0.45}$Sr$_{0.55}$Mn$_1$Ru$_y$O$_3$ with antiferromagnetic matrix, the low Ru doping 0.05 ≤ y ≤ 0.15 induces an enhanced ferromagnetism with an increasing Curie temperature $T_C$. Ru ions in these materials exist mainly in the form of Ru$^{4+}$ with a small quantity of Ru$^{5+}$. A ferromagnetic exchange interaction between Mn$^{3+}$ and Ru$^{4+}$ (Ru$^{5+}$) has been attributed to this enhancement of ferromagnetism. Similarly in charge ordered Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ $T_C$ is significantly increased by substitution of Ru$^{4+}$, but the charge ordering can be destroyed. The incorporation of Ru ions in CaMn$_{1-y}$Ru$_y$O$_3$ perovskites can induce ferromagnetism in a large substitution range 0.1 ≤ y ≤ 0.8 with a maximum Curie temperature $T_C = 210$ K for y = 0.4 and a metallic character for 0.2 ≤ y ≤ 0.4. By substitution of only a few percent of Ru with Mn in Sr$_3$(Ru$_{1-y}$Mn$_y$)$_2$O$_7$ the ground state can be switched from a paramagnetic metal to an antiferromagnetic insulator.

The study of SrRu$_{1-y}$Mn$_y$O$_3$ single crystals in the limited (Ru-rich) range of compositions 0 ≤ y ≤ 0.6 has shown that the Mn substitution can drive the system from the itinerant ferromagnetic (F) state for SrRuO$_3$ through a “quantum critical point” at $y_c = 0.39$ to an insulating antiferromagnetic (AF) state. Salh et al. reported a contradictory finding that the ferromagnetic state may still be observed with higher Mn contents including SrRu$_{0.5}$Mn$_{0.5}$O$_3$ for polycrystalline samples prepared in air at 1200°C. A more complicated phase diagram with the coexistence of F and AF phases in a wide range of substitution and a large magnetoresistance have been reported by Zhang et al. for polycrystalline samples prepared in air at 1150°C. The discrepancy can be traced to the highly inhomogeneous polycrystalline samples obtained to date, containing a large amount of SrRuO$_3$, for which only a fraction of the FM phase changes but not the magnetic phase or transition temperature (see: Ref. 6, Fig. 1; Ref. 7, Fig. 2, Ref. 8, Fig. 3, and Ref. 9, Fig. 3).

The end member of the SrMn$_{1-x}$Ru$_x$O$_3$ family, SrRuO$_3$, is a unique ferromagnetic metal among 4d transition metal based perovskite oxides. Most dopants for low spin Ru$^{4+}$ ($t_{2g}$) decrease the ferromagnetic Curie temperature from 163 K, except for Cr. The other end member, a cubic perovskite SrMnO$_3$, is a G-type antiferromagnet with $T_N = 233$ K. The oxidation state of Mn in the latter material is also 4+. When this valency of Mn is preserved (e.g. as in Sr$_{1-y}$Ca$_y$MnO$_3$), then the G-type AFM ordering is observed in the cubic, tetragonal and orthorhombic crystal structures. $T_N$ is suppressed by the deviation of the Mn-O-Mn bond angle from 180° and by the variance of the average size of the A-site ion via changes in the Sr/Ca ratio.

The substitution of Ru$^{5+}$ for Mn$^{4+}$ in SrMnO$_3$ was considered to stabilize the cubic perovskite structure by the induced Mn valency shift, corresponding to electron doping by Mn$^{3+}$ in the Mn$^{4+}$ matrix. The $L_{2,3}$-edge absorption spectroscopy of Ru and Mn in Sr-rich SrRu$_{1-y}$Mn$_y$O$_3$ (0 ≤ y ≤ 0.5) has revealed the mixed-valence of both Mn$^{3+}$/Mn$^{4+}$ and Ru$^{4+}$/Ru$^{5+}$. $^{55}$Mn NMR on SrRu$_{0.9}$Mn$_{0.1}$O$_3$ has demonstrated that Mn exists in an intermediate Mn$^{3+}$/Mn$^{4+}$ valence state due to fast electron hopping.

In this study, we investigate the complete solubility range of polycrystalline SrMn$_{1-x}$Ru$_x$O$_3$ samples and construct the phase diagram of structural, magnetic, and conducting properties. The polycrystalline samples were characterized by neutron diffraction, magnetic, transport and thermoelectric experiments.
tion of Ru in the SrMnO$_3$ matrix (0.06 $\leq x \leq 0.2$) results in a phase transition to a C-type antiferromagnetic state accompanied by a cubic-tetragonal transition. At slightly higher substitutions (0.3 $\leq x \leq 0.5$) the structural transition temperature is higher than the AF transition temperature. The intermediate substitution level (0.6 $\leq x \leq 0.7$) induces a spin-glass behavior, due to competing ferro- and antiferromagnetic interactions in the tetragonal structure. Close to the maximum Ru substitution (0.8 $\leq x \leq 1$) the material becomes ferromagnetic in the orthorhombic structure.

II. EXPERIMENTAL DETAILS

Samples with $x \leq 0.5$ were prepared using a two-step synthesis method developed for similar kinetically stable perovskites. First, oxygen-deficient samples were prepared in argon at $T = 1300 - 1400^\circ$C. The samples were then annealed in air at lower temperatures to achieve stoichiometric compositions with respect to the oxygen content. The samples with $x > 0.5$ were prepared in air at $1330 - 1340^\circ$C with many (up to 14) intermittent grindings due to difficulty of achieving homogeneous material. An excess of RuO$_3$ was added to compensate for Ru loss due to sublimation at these high temperatures. The process of formation of single-phase and homogeneous material was monitored with x-ray diffraction (Rigaku D-MAX diffractometer) and ac susceptibility (Physical Property Measurement System Model 6000, Quantum Design) measurements. After a few firings, x-ray diffraction indicated formation of single-phase material, though the ac susceptibility measurements clearly showed peaks related to multiple magnetic transitions and hence highly inhomogeneous samples. Fig. 1 shows a sequence of ac susceptibility measurements for the SrMn$_{0.1}$Ru$_{0.9}$O$_3$ sample, which demonstrates the gradual improvement of sample quality. This difficulty to achieve research quality polycrystalline materials may explain the discrepancy in the properties of single crystals and bulk samples reported to date.

The ac susceptibility, resistivity, thermal conductivity and Seebeck coefficient were measured using a Physical Property Measurement System Model 6000 (Quantum Design). The dc magnetization was measured using a Magnetic Property Measurement System Model MPMS-7 (Quantum Design). Time-of-flight neutron powder diffraction data were collected at 300 K (room temperature) for all members of the SrMn$_{1-x}$Ru$_x$O$_3$ series on the Special Environment Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. Data were collected, for the $x = 0.2, 0.7$ and 0.9 samples, at several temperatures between 10 and 320 K using a closed cycle refrigerator. In the refinements, high-resolution backscattering data, from 0.5 to 4 Å $d$-spacing were analyzed using the Rietveld method and the General Structure Analysis System (GSAS) code. Absorption, background and peak width parameters were refined, together with the lattice parameters, atomic positions, and isotropic and anisotropic temperature factors for the cations and oxygen atoms, respectively.

The cationic ratio was determined by energy dispersive x-ray spectroscopy (EDXS) analysis in a Hitachi S-4700-II scanning electron microscope at the Electron Microscopy Center, Argonne National Laboratory. Typically, 5 spot spectra were collected across the surface of sintered pellets. Fig. 2 presents the effective contents $x_{\text{eff}}$ of Ru and Mn ions calculated from the EDXS spectra using a normalization condition $x_{\text{eff}}$(Ru)+$x_{\text{eff}}$(Mn)=1. We observe a good agreement with the nominal compositions drawn as straight lines in Fig. 2. This result is strongly supported by the refined Ru occupancies from the neutron powder diffraction data.

III. RESULTS AND DISCUSSION

A. Neutron powder diffraction and structural details

The well-known perovskite structures of the two end-members of the series, namely SrMnO$_3$ and SrRuO$_3$, have frequently been described as crystallizing in the cubic and orthorhombic space group symmetries, respectively. The Ru spins, in SrRuO$_3$, do not localize (are itinerant) and the material is viewed as an itinerant ferromagnet below 163 K. On the other hand, in SrMnO$_3$, the Mn spins become localized below 233 K in a G-type antiferromagnetic structure.
Room temperature structural refinements \((T = 300 \text{ K})\) for all members of the \(\text{SrMn}_{1-x}\text{Ru}_x \text{O}_3\) series demonstrate that, upon increasing \(x\), the symmetry changes from cubic \(Pm - 3m\) \((x \leq 0.2)\) to tetragonal \(I4/mcm\) (for \(0.3 \leq x \leq 0.7\)) to orthorhombic \(Pbnnm\) for \((x \geq 0.8)\) in agreement with the different magnetic and resistive properties of the materials discussed in the next subsections. Refined Ru and Mn site occupancies were in agreement with the nominal values, within 1-3 standard deviations, as shown in Fig. 2. Refined structural parameters are presented in Fig. 3 as a function of composition. The lattice parameters [Fig. 3(a)] display overall increase associated with a larger ionic size of \(\text{Ru}^{4+}\) (the average bond length \(<\text{Ru}^{4+}-\text{O}> = 1.985 \text{ Å}\)) than \(\text{Mn}^{4+}\) (the average bond length \(<\text{Mn}^{4+}-\text{O}> = 1.903 \text{ Å}\)) as observed in Fig. 3(d). The sequence of structural transitions from high symmetry cubic \(Pm - 3m\) to low symmetry orthorhombic \(Pbnnm\) is thus a consequence of decreasing tolerance factor of the perovskite structure \(t(x) = <\text{Sr}-\text{O}>/<\sqrt{2} < \text{B}-\text{O}> (B = \text{Mn}, \text{Ru})\) from 1 to 0.99 [Fig. 3(f)]. Similar sequence of transitions was observed for \(\text{Sr}_1-x\text{Ca}_x\text{MnO}_3\), for which decrease of tolerance factor was a result of smaller ionic size of \(\text{Ca}\) than \(\text{Sr}\). Since neutron diffraction found no evidence for Mn/Ru cation ordering at any \(x\), the volume would be expected to vary linearly with \(x\) according to the Vegard’s law, presented as a dashed line in Fig. 3(b). However, the unit cell volume exhibits deviations from the linear behavior especially when crossing from the Mn-rich side to the Ru-rich side of the phase diagram [Fig. 3(b)]. These deviations can be solely explained by geometrical considerations of the charge transfer \(\text{Ru}^{4+} (0.62 \text{ Å}) + \text{Mn}^{4+} (0.53 \text{ Å}) \rightarrow \text{Ru}^{5+} (0.565 \text{ Å}) + \text{Mn}^{3+} (0.645 \text{ Å})\) from the fact that the average ionic size of a \(\text{Ru}^{5+}, \text{Mn}^{3+}\) pair \((0.605 \text{ Å})\) is larger than that of a \(\text{Ru}^{4+}, \text{Mn}^{3+}\) pair \((0.575 \text{ Å})\). Following the procedure developed by Williams et al. [12] for \(\text{SrRu}_{1-y}\text{Cr}_y\text{O}_3\), we made linear fits to the data in Fig. 3(b) and obtained a good agreement of the charge transfer model with the data. A similar phenomenon has recently been observed in \(\text{CaRu}_{1-y}\text{Mn}_y\text{O}_3\) and also interpreted in terms of mixed valence \(\text{Ru}^{4+}, \text{Ru}^{5+}, \text{Mn}^{4+}\), and \(\text{Mn}^{3+}\) ions. The latter compound preserves its orthorhombic \(Pnma\) structure within the entire composition range.

Another anomalous feature observed in the data is a large increase of the average \(<\text{Sr}-\text{O}>\) bond length from 2.69 to 2.78 Å [Fig. 3(e)]. In order to interpret the “abnormal” behavior of the \(<\text{Sr}-\text{O}>\) bond length, we performed simple Bond Valence Sum calculations [31] from which we find the calculated oxidation state \(v(\text{Sr})\) of \(\text{Sr}\) to decrease from 2.5 to 2.0 as the Ru content increases from 0 to 1. The unphysical values of the \(\text{Sr}\) oxidation state (i.e., when \(v(\text{Sr}) > 2\)) may be interpreted as evidence for the presence of significant strains in the Mn-rich side of the phase diagram with the strains relaxing as a function of increased Ru content. Strain relaxation would then occur through a series of structural distortions from heavily stressed cubic to moderately stressed tetragonal and finally to “stress-free” orthorhombic structures. Further evidence for stress relaxation may be observed in the behavior of the unit cell volume as seen in the change of slope in Fig. 3(b). Additionally, a changeable \(<\text{Sr}-\text{O}>\) bond length could also be due to the decreasing size of the oxygen ion as a function of hole transfer to it from \(\text{Mn}\), i.e., formation of the ligand holes for \(\text{SrMnO}_3\) compound. The Mn to O charge transfer would not lead to a large change of the \(<\text{Mn}-\text{O}>\) bond length as the overall amount of charge remain constant on the electronically relevant Mn-O network. Another possibility would be that simply the \(<\text{Sr}-\text{O}>\) bond lengths are changeable depending on the B-site ion of the perovskite structure. To unambiguously differentiate between these possibilities extensive x-ray absorption spectroscopy studies would be necessary for both transition metal and oxygen ions. We point out here, however, that peculiar magnetic properties of \(\text{SrMnO}_3\) and lightly substituted compounds, which are discussed in the following sections, may be caused by the charge transfer from Mn to O ions.

Evolution of the structure of the \(x = 0.2\) sample as a function of temperature is shown in Fig. 4. At temperatures above 260 K, the paramagnetic material is best described using the cubic \(Pm - 3m\) symmetry. Below 260 K, a structural phase transition takes place to lower tetragonal \(I4/mcm\) space group symmetry and additional antiferromagnetic peaks become visible. In this space group, a good fit to the magnetic intensities could only be achieved by further lowering the magnetic symmetry to \(I_p\).
range ordering of c-axis oriented Ru/Mn spins takes place to form C-type antiferromagnetically coupled FM chains.

Temperature-dependent neutron diffraction patterns for the tetragonal $x = 0.7$ and orthorhombic $x = 0.9$ samples show no structural change and no extra magnetic intensities at any temperature between 10 and 300 K in good agreement with the materials’ spin-glass and itinerant ferromagnetic properties, respectively. A decrease of the difference between individual B-O bonds [Fig. 3(e)] with increasing temperature as well as a similar effect for lattice parameters [Fig. 4(i)] and B-O-B bond angles [Fig. 4(h)] indicate an incipient transition to the cubic phase for the $x = 0.7$ composition. No such behavior is observed for the orthorhombic $x = 0.9$ composition, for which structural transitions to tetragonal and cubic phases appear to remain at high temperatures similar to SrRuO$_3$.

In addition, the $x = 0.9$ composition does not exhibit a distinctive invar effect, which was observed below Curie temperature for SrRuO$_3$. Suppression of the invar effect with a small amount of Mn substitution in SrRuO$_3$ is similar to both Cr- and La-substitution and introduction of Ru-vacancy.

**B. Magnetic properties**

The dc magnetization measured on cooling in a magnetic field of 1 kOe is presented in Fig. 5. From these results we have determined Néel and Curie temperatures $T_N$ and $T_C$ (defined as the temperatures for which the slope of magnetization $dM/dT$ is maximum and minimum, respectively). On substitution of small amount of Ru for Mn ($0.06 \leq x \leq 0.2$), we observe sharp magnetic
transitions from paramagnetic to a C-type AF ordered state. The Néel transitions in this substitution range are coupled with the structural cubic-tetragonal transitions, i.e. \( T_N = T_s \). This type of behavior has also been observed for Sr-rich \( R_y\text{Sr}_{1-y}\text{MnO}_3 \) \( (R=\text{La, Pr}) \). For larger \( x \), the structural transition takes place at temperatures \( T_s \) higher than \( T_N \). As a result, the magnetic transition is not as sharp and an anomalous magnetization is observed for \( x = 0.3 \) in \( T_N < T < T_s \) before the material becomes paramagnetic above \( T_s \). Further Ru doping decreases \( T_N \), which is maximum for \( x \sim 0.2 - 0.3 \). More substitution of Ru leads to a change of the magnetic ordering from AF to F, although this boundary is not as sharp as reported for single crystals. It is spread over a range of compositions \( (0.6 < x < 0.7) \) where a spin-glass behavior can be observed. In this range of substitution we also observed a cusp in ac susceptibility, which supports the spin-glass behavior.

In Fig. 4 we present the ac susceptibility for \( \text{SrMn}_{0.3}\text{Ru}_{0.7}\text{O}_3 \) measured at several frequencies \( \omega \) in an ac magnetic field of 14 Oe. One can observe a cusp in the ac susceptibility related to spin-glass behavior, a decrease of the ac susceptibility below \( T_f \) with increasing frequency, and a shift of \( T_f \) towards higher temperatures. The linear fit to \( T_f \) gives relative temperature shift vs. frequency \( \Delta T_f/\Delta(\log \omega) = 0.0136 \pm 0.005 \). This value is similar to those observed for the \( \text{SrMn}_{1-x}\text{Fe}_x\text{O}_3 \) perovskite having mixed F and AF interactions. The spin-glass related irreversibility between the “zero field cooled” and “field cooled” magnetization can also be observed (not shown). For lower Ru contents, \( (0.4 < x < 0.6) \) this kind of irreversibility, resembling a spin glass behavior, can also be observed at temperatures below \( \sim 60 \) K in the AF state. This points to a frustrated/disordered AF state, which is sometimes confused with spin glass behavior. A closer inspection of the remanent magnetization after “field cooling” shows that a slight irreversibility persists up to \( T_N \) in these compositions, which points
to a certain level of disorder in the AF state.

The phase diagram in the low Ru substitution regime presented in Fig. 7(a), strikingly resembles the phase diagram for $R_x$Sr$_{1-x}$MnO$_3$ ($R$ = La, Pr). In both classes of materials, the two different substitutions in the parent SrMnO$_3$ compound, A-site and B-site, respectively change the band filling by generating exactly the same amount of Mn$^{3+}$ ions for the same substitution level. The concentration of these ions is not sufficient to induce Mn$^{3+}$ - Mn$^{4+}$ DE interaction, but can induce the same tetragonal lattice distortion, coupled with a C-type AF transition. The only magnetic ions present in La$_y$Sr$_{1-y}$MnO$_3$ are Mn$^{3+}$/Mn$^{4+}$ ions in the ratio $y/(1-y)$. The $d$ shell electronic configuration of Ru$^{3+}$ ions in SrMn$_{1-x}$Ru$_x$O$_3$ is identical with that of Mn$^{4+}$ ($d^3$, $t^{2g}$). Therefore, the ratio of $d^3/d^3$ ions in both classes of materials is identical, which leads to a very similar structural and magnetic behavior. The paramagnetic Curie-Weiss temperature $\Theta$, also presented in Fig. 7(a), was calculated from the molar dc susceptibility $\chi_m = M/H$ in the temperature range 350–400 K, which was fitted to the general Curie-Weiss formula:

$$\chi_m = \chi_0 + (\mu_B N_A / 3k_B) \mu_{\text{eff}}^2 / (T - \Theta),$$

where $\chi_0$ is a temperature-independent background susceptibility, $N_A$ is the Avogadro number, $k_B$ is the Boltzmann constant, $\Theta$ is the paramagnetic Curie-Weiss temperature, $\mu_{\text{eff}} = g \sqrt{\delta(S + 1)}$ is the effective paramagnetic moment, $g = 2$ is the gyromagnetic ratio, $S$ is the magnetic spin. The values of $\Theta$ pretty well coincide with the values of $T_C$ or $T_f$.

The effective paramagnetic moment $\mu_{\text{eff}}$ determined from the magnetization using Eq. (1) is presented in Fig. 7(b). We consider two possible valence states of the Ru dopant, 4+ and 5+. The former case would lead to the following formula SrMn$_{1-x}$Ru$_x$O$_3$ and the expected dependence $\mu_{\text{eff}} = \sqrt{\mu_{\text{eff}}(\text{Mn}) + \mu_{\text{eff}}^2(\text{Ru})}$, plotted as the dashed line in Fig. 7(b) is far from the observed $\mu_{\text{eff}}$ behavior. The latter case would give the following formulas SrMn$_{1-x}$Ru$_x$O$_3$ and SrMn$_{1-x}$Ru$_x$O$_3$ for $x < 0.5$ and $x > 0.5$, respectively. These formulae are plotted as solid lines. In both cases we assume spin only moments. The latter model works well for $x > 0.5$. This is an additional evidence for the presence of Ru$^{5+}$ ions in this material. However, significant deviations from any of the discussed models can be observed for $x < 0.5$, especially for pure SrMnO$_3$. The determined $\mu_{\text{eff}}$ values are much lower in this region (not shown). $\Theta$ is also positive in the $x < 0.5$ solid solution range, which in turn is a sign of ferromagnetic interactions in the paramagnetic state, even if these compositions exhibit an AF order at low temperatures. It is possible that in this doping regime the fitting temperature range is very close to the magnetic and structural transition temperatures and the Curie-Weiss approximation in Eq. (1) is not fully valid. Another explanation for reduced $\mu_{\text{eff}}$ of SrMnO$_3$ and lightly substituted compositions may relate to unusual bond distances observed for these compounds that

FIG. 5: (Color online) dc magnetization for SrMn$_{1-x}$Ru$_x$O$_3$ samples.

FIG. 6: (Color online) Temperature dependence of ac susceptibility for SrMn$_{0.3}$Ru$_{0.7}$O$_3$ at several frequencies. Inset shows the linear dependence of $T_I$ on log frequency.
would require further study.

C. Resistivity

The temperature dependence of resistivity \( \rho(T) \) for SrMn\(_{1-x}\)Ru\(_x\)O\(_3\) samples is presented in Fig. 8. The resistivity demonstrates an insulating character for SrMnO\(_3\) and overly decreases with increasing Ru substitution due to itinerant character of the Ru electrons. It becomes metallic for \( x \geq 0.9 \) with a metal to insulator transition at around 70 K for \( x = 0.9 \). The difference between the characters of resistivity for highly Ru substituted polycrystalline samples and single crystals can be explained by the granular nature of the polycrystalline samples. It has been demonstrated, e.g., for polycrystalline colossal magnetoresistance manganites that the presence of grain boundaries can affect the magnitude of resistivity as well as the low-temperature magnetoresistance, without affecting their magnetic properties. For low Ru contents \( (x \leq 0.2) \) a significant increase of resistivity is observed below the coupled AF-structural transitions. These transitions correspond to a jump in \( \rho(T) \) again similar to rare earth substituted SrMnO\(_3\). This behavior corresponds to a first-order phase transition with a hysteretic behavior of \( \rho \) as illustrated in Fig. 9(a). The transition can be shifted to lower temperatures by applying a magnetic field. A slight magnetoresistance can be observed for higher Ru contents below the Curie temperature. Generally, this effect is rather small although enhanced with respect to pure SrRuO\(_3\). For \( x = 0.3 \), where the structural and magnetic transitions are decoupled, a subtle anomaly in resistivity can be observed at a temperature related to the structural transition along with a smooth resistivity behavior at the AF transition.

D. Thermoelectric properties

For higher Ru contents it has been demonstrated\(^\text{24}\) that the Seebeck coefficient is positive and varies slightly from +34 \( \mu \)V/K for SrRuO\(_3\) to +28 \( \mu \)V/K for SrMn\(_{0.1}\)Ru\(_{0.9}\)O\(_3\) at room temperature. This small change reflects the introduction of Ru\(^{5+}\) ions into the Ru\(^{4+}\) matrix. In Fig. 10 we present thermal conductivity \( \kappa \), Seebeck coefficient \( \alpha \), and the thermoelectric figure of
FIG. 9: (Color online) Magnetoresistance for selected SrMn$_{1-x}$Ru$_x$O$_3$ samples.

FIG. 10: (Color online) (a) Thermal conductivity, (b) Seebeck coefficient, (c) Thermoelectric figure of merit $ZT = \alpha^2 T / (\kappa \rho)$ for selected SrMn$_{1-x}$Ru$_x$O$_3$ samples.

IV. SUMMARY

In summary, we have studied the phase diagram of polycrystalline perovskite SrMn$_{1-x}$Ru$_x$O$_3$ (0 $\leq x \leq$ 1) system. In the low Ru$^{5+}$ substitution regime ($x \leq 0.3$), the structural, magnetic, and transport behavior strikingly resemble those for the SrMnO$_3$ compound with an A-site heterovalent substitution $R_y$Sr$_{1-y}$MnO$_3$ ($R=$La, Pr). In both cases, a tetragonal lattice distortion, for some compositions coupled to a C-type AF transition is observed. This similarity is driven by the same ratio of $d^4/d^3$ ions in both classes of materials for equivalent substitution level. In the moderate Ru$^{5+}$ substitution regime ($x \sim 0.65$) a boundary between the AF-C and F orders in polycrystalline SrMn$_{1-x}$Ru$_x$O$_3$ is broadened with respect to a sharp quantum critical point previously observed in single crystals due to magnetic disorder, which leads to a spin glass behavior. The observation of a spin glass behavior suggests that the AF-C and F states are separated by a first-order transition in the clean limit and they can coexist in the presence of quenched disorder. 

ACKNOWLEDGMENTS

Work at NIU was supported by the NSF (DMR-0706610). Work at Argonne National Laboratory was supported by the U. S. Department of Energy under contract DE-AC02-06CH11357.
[1] Yue Ying, Jiyu Fan, Li Pi, Zhe Qu, Wenqin Wang, Bo Hong, Shun Tan, and Yuheng Zhang, Phys. Rev. B 74, 144433 (2006).

[2] P. V. Vanitha, A. Arulraj, A. R. Raju and C. N. R. Rao, Compt. Rend. Acad. Sci. Paris (J. Rouxel memorial issue) t.2, serie II, 595 (1999).

[3] A. Maignan, C. Martin, M. Hervieu and B. Raveau, Solid State Comm. 117, 377 (2001).

[4] R. Mathieu, A. Asamitsu, Y. Kaneko, J. P. He, X. Z. Yu, R. Kumai, Y. Onose, N. Takeshita, T. Arima, H. Takagi, and Y. Tokura, Phys. Rev. B 72, 092404 (2005).

[5] G. Cao, S. Chikara, X. N. Lin, E. Elhami, V. Durairaj, and P. Schlottmann, Phys. Rev. B 71, 035104 (2005).

[6] R. K. Sahu and S. S. Manoharan, J. Appl. Phys. 92, 4831 (2002).

[7] R. K. Sahu, Z. Hu, M. L. Rao, S. S. Manoharan, T. Schmidt, B. Richter, M. Knapfer, M. Golden, J. Fink, and C. M. Schneider, Phys. Rev. B 66, 144415 (2002).

[8] Xiao-Yu Zhang, Yajie Chen, Zhen-Ya Li, Carmine Vitertoria, and Vincent G. Harris, J. Phys.: Condens. Matter 19, 266211 (2007).

[9] N. Banerjee, R. N. Bhowmik, and R. Ranganathan, J. Phys.: Condens. Matter 13, 9481 (2001).

[10] L. Pi, A. Maignan, R. Retoux, and B. Raveau, J. Phys.: Condens. Matter 14, 7391 (2002).

[11] B. Dabrowski, S. Kolesnik, O. Chmaissem, T. Maxwell, M. Avdeev, P. W. Barnes, and J. D. Jorgensen, Phys. Rev. B 72, 054428 (2005).

[12] A. J. Williams, A. Gillies, J. P. Attfield, G. Heymann, H. Huppertz, M. J. Martinez-Lope, and J. A. Alonso, Phys. Rev. B 73, 104409 (2006).

[13] O. Chmaissem, B. Dabrowski, S. Kolesnik, J. Mais, D. E. Brown, R. Kruk, P. Prior, B. Pyles, and J. D. Jorgensen, Phys. Rev. B 64, 134412 (2001).

[14] B. Dabrowski, O. Chmaissem, J. Mais, S. Kolesnik, J. D. Jorgensen, and S. Short, J. Solid State Chem. 170, 154 (2003).

[15] A. Maignan, C. Martin, M. Hervieu, and B. Raveau, J. Appl. Phys. 91, 4267 (2002).

[16] Z. H. Han, J. I. Budnick, W. A. Hines, B. Dabrowski and T. Maxwell, Appl. Phys. Lett. 89, 102501 (2006).

[17] D. G. Hinks, B. Dabrowski, J. D. Jorgensen, A. W. Mitchell, D. R. Richards and D.-L. Shi, Nature 333, 836 (1988).

[18] J. D. Jorgensen, J. J. Faber, J. M. Carpenter, R. K. Crawford, J. R. Haumann, R. L. Hitterman, R. Kleb, G. E. Ostrowski, F. J. Rotella, and T. G. Worton, J. Appl. Crystallogr. 22, 321 (1989).

[19] A. C. Larson and R. B. von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report No. LAUR 86-748, (2004); B. H. Toby, J. Appl. Cryst. 34, 210 (2001).

[20] T. Taniguchi, S. Mizusaki, N. Okada, Y. Nagata, S. H. Lai, M. D. Lan, N. Hiraoka, M. Ito, Y. Sakurai, T. C. Ozawa, Y. Noro, and H. Samata, Phys. Rev. B 77, 014406 (2008).

[21] I. D. Brown and D. Altermatt, Acta Crystallogr., Sect. B: Struct. Sci. 41, 244 (1985).

[22] B. J. Kennedy and B. A. Hunter, Phys. Rev. B 58, 653 (1998).

[23] B. Dabrowski, M. Avdeev, O. Chmaissem, S. Kolesnik, P. W. Klamut, M. Maxwell, and J. D. Jorgensen, Phys. Rev. B 71, 104411 (2005).

[24] Y. Klein, S. Hébert, A. Maignan, S. Kolesnik, T. Maxwell, and B. Dabrowski, Phys. Rev. B 73, 052412 (2006).

[25] J. Pietosa, A. Wisniewski, R. Puzniak, S. Kolesnik, M. Majjiga, and B. Dabrowski, Acta Phys. Polon. A 111, 159 (2007).

[26] B. Dabrowski, O. Chmaissem, P. W. Klamut, S. Kolesnik, M. Maxwell, J. Mais, Y. Ito, B. D. Armstrong, J. D. Jorgensen, and S. Short, Phys. Rev. B 70, 014423 (2004).

[27] O. Chmaissem, B. Dabrowski, S. Kolesnik, J. Mais, J. D. Jorgensen, and S. Short, Phys. Rev. B 67, 094431 (2003).

[28] S. Kolesnik, B. Dabrowski, J. Mais, D. E. Brown, R. Feng, O. Chmaissem, R. Kruk, and C. W. Kimball, Phys. Rev. B 67, 144402 (2003).

[29] A. Maignan, S. Hébert, L. Pi, D. Pelloquin, C. Martin, C. Michel, M. Hervieu, and B. Raveau, Crystal Eng. 5, 365 (2002).

[30] J. Burgy, M. Mayr, V. Martin-Mayor, A. Moreo, and E. Dagotto, Phys. Rev. Lett. 87, 277202 (2001).