Magnetic structure of NdMnO$_3$ consistently doped with Sr and Ru

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The crystal and magnetic structures of the (Nd$_{1-x}$Sr$_{x}$)(Mn$_{1-y}$Ru$_{y}$)O$_3$ perovskites have been studied by neutron powder diffraction and muon spin relaxation. The simultaneous and consistent doping of the A- and B-sites with Sr and Ru has been used for avoiding the Mn$^{4+}$ formation and hence, suppression of the double exchange. All studied samples (0.825$\leq$ x $\leq$ 0.875) are insulators and show unusual long-range ferromagnetic state, which can be called “statistical ferrimagnet.” with antiferromagnetic coupling between Mn and Ru magnetic moments, and ferromagnetic coupling in the Mn-Mn and Ru-Ru pairs.

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I. INTRODUCTION

Rare earth perovskite manganites of LaMnO$_3$ type continue to be a subject of intensive studies. Upon A-site (substitution of La for Ca or other divalent alkaline earth cations) or B-site (substitution of Mn for Co or other 3$d$ or 4$d$ cations) doping, the manganites exhibit a wide variety of physical properties including colossal magnetoresistance effect (CMR) observed in the family near the temperature of the ferromagnetic ordering, $T_C$ (see, for instance, recent reviews 1,2). Historically, more attention was paid to A-site substitution, leading to appearance of intermediate or mixed Mn$^{3+}$/Mn$^{4+}$ valence states of Mn ions. It has been observed that the metallic phase appeared with doping at low temperatures concomitantly with ferromagnetic ordering. These studies have established that the basic model for understanding of coexistence of the ferromagnetism (FM) and metallicity is the double-exchange model introduced a long time ago by Zener,3 in which strong FM exchange interaction between the localized magnetic moments of Mn$^{3+}$ and Mn$^{4+}$ cations is mediated by the hopping of $e_g$-electrons. However, there are some experimental evidences that the ferromagnetism itself is not necessarily connected with DE interactions.4

The substitution of Mn, or B-site doping, has been much more rarely examined so far. However, it may provide new insights into the understanding of physics in these CMR compounds. In particular, substitution of Mn for Ru is especially interesting because it leads to some unusual consequences both in transport and magnetic properties.5–8 The 4$d$-ion of ruthenium has more extended and, therefore, less localized 4$d$-orbitals than the Mn 3$d$-orbitals, and thus the partial overlapping of the Ru 4$d$-orbitals with the oxygen 2$p$-orbitals is similar and even stronger as compared to the 3$d$-orbitals of Mn. Indeed, SrRuO$_3$ and CaRuO$_3$ are metals and the first one is also ferromagnetic with a high magnetoresistance in the vicinity of Curie temperature.9 Another important feature of Ru ion is that its (4$d$) configuration has a reference energy close enough to one of (3$d$) Mn ion and the hybridization between the orbitals can be strong. Therefore, superexchange interaction between Mn and Ru is large and can significantly affect the physical properties of Ru-doped manganites. Exceptional ability of ruthenium to induce metallicity and ferromagnetism has been discovered for wide composition and doping range of manganites, from the hole rich to the electron rich side. Raveau et al.5,10 have shown that substitution of Mn for Ru (at least up to 12% level) in R$_{1-x}$Ca$_x$MnO$_3$ (R is rare earth element), favors the appearance of FM state and improves their metallic properties. One of the most spectacular effects has been observed for Sm$_{0.4}$Ca$_{0.6}$Mn$_{1-y}$Ru$_y$O$_3$ series,5 where the antiferromagnetic charge ordered phase was readily destroyed by the Ru-doping being replaced by the ferromagnetic metallic state. One of possible explanations of the extreme efficiency of the Ru-doping in inducing the ferromagnetic metallic state in the charge ordered manganites is the possibility for ruthenium to exhibit a mixed valence.5 The substitution of manganese ions Mn$^{3+}$ can be made either by Ru$^{3+}$, Ru$^{4+}$, or Ru$^{5+}$ species.6,11,12 However, the experimental data on the Ru electronic states in manganites contradict each other. Raveau et al.10 believe that in mixed manganites, only Ru$^{4+}$ and Ru$^{5+}$ are possible, while XPS (x-ray photoelectron spectroscopy)11 and x-ray diffraction studies12 suggest Ru$^{3+}$/Ru$^{4+}$ mixed state. In any case, mixed-valence ruthenium ion can cause orbital reorientation and spin reversal of Mn cations in the antiferromagnetic structures together with strong charge fluctuations (Mn$^{3+}$/Mn$^{4+}$) around Ru ion, which should induce the formation of the ferromagnetic metallic clusters.5 This behavior could be still understood by extension of the double exchange model involving both mixed-valence Mn and Ru.
ions even if the exact role of Ru doping on the properties of manganites remains still an open problem.

The experimental approach we propose here is an investigation of manganite compounds for which DE-mechanism is weakened or even completely eliminated. It might be realized by the simultaneous and consistent doping in both A- and B-sublattices of the perovskite structure with di- and four-valence ions, respectively. This kind of doping may allow the realization of the fixed value of the Mn oxidation state (Mn$^{3+}$) and consequently, switching off the double exchange interaction between Mn-ions. We have studied effect of this doping in (Nd$_{1-x}$Sr$_x$)(Mn$_{1-x}$Ru$_x$)O$_3$, considering ruthenium being predominantly four-valence Ru$^{4+}$ in the low-stoichiometry index for $x\leq 0$ composition was found to be optimal for the realization of the fixed value of the Mn oxidation state and B-sublattices of the perovskite structure with di- and four-valence ions.

The single phase (Nd$_{1-x}$Sr$_x$)(Mn$_{1-x}$Ru$_x$)O$_{3+\delta}$ powder samples ($x=0$, 0.125, 0.25, 0.5, 0.75, 0.875, 1.0, $\delta=0$) have been prepared in the ceramic state with the use of the chemical homogenization method. First, ash-free paper was soaked with the water solution of Nd, Sr and Mn nitrates, mixed in the proper ratio, and dried in air at 120°C. Then paper was burned, and the ash was annealed in the air at 700°C during 30 minutes. Resulting powder was mixed with RuO$_2$ powder and pressed in pellets. Sintering was accomplished at 1200°C in air for 16 hours.

Electron probe microanalysis shows satisfactory agreement of the calculated and experimentally measured cation stoichiometry. All the samples with $x\leq 0.875$ reveal semiconducting behavior of the electric resistivity without any peculiarities at the magnetic ordering temperature (Fig. 1). However, in the whole temperature range, the electrical resistance and the conduction activation energy decrease significantly with increasing $x$. This corresponds to approaching the $x=1$ composition which is metallic. Iodometric titration was accomplished as described in Ref. 13. The oxygen nonstoichiometry index for $x=0$ composition was found to be 0.01 but the other compositions reveal higher deviation of the oxygen index from 3.0 ($\delta\approx 0.10$ for $x=0.25$ and $\delta\approx 0.06$ for other samples). Thus, the agreed character of doping in A- and B-sublattices of the perovskite structure is somewhat distorted. According to Ref. 6 in manganites containing ruthenium, the doped holes are mostly captured by ruthenium instead of manganese. It means that for oxygen index $3+\delta$, 2$\delta$ ions of Ru$^{4+}$ are transformed to Ru$^{5+}$, and the extracted magnetic moment of Ru should be regarded as amount of $(x-2\delta)\mu$(Ru$^{4+}$) and $2\delta\mu$(Ru$^{5+}$). At the same time, it is known that the insertion of excess oxygen is not possible in three-dimensional (3D) perovskite structure and the oxygen nonstoichiometry in a sample is incorporated via cation vacancies, with equal amounts in A- and B-sites (see, for instance, Ref. 14). The number of vacancies $y$ in each site can be calculated according to $y=\delta(3+\delta)$, i.e., even for $\delta=0.1$, $y$ is around 0.03, which is at the level of experimental uncertainties in occupation factors. For this reason we used fully occupied A- and B-sites in the Rietveld refinements for all samples.

The magnetic susceptibility was measured in the field of 10–20 Oe at several frequencies between 100 and 1000 Hz. For all samples the frequency dependence of the susceptibility is negligibly small. The compositions with $x=0.125$ and 0.5 demonstrate the ferromagnetic type behavior of the magnetic susceptibility (Fig. 2) with one pronounced phase transition. For $x=0.75$ and 0.875 together with the ferromagnetic transition one can see an additional transition at lower temperatures. It will be discussed later together with $\mu$SR data.

Neutron diffraction (ND) experiments have been performed at several instruments: HRFD at FLNP, JINR at the IBR-2 pulsed reactor, HRPT$^{15}$ and DMC at the SINQ spallation source of Paul Scherrer Institut (Villigen, Switzerland). At high resolution diffractometers HRFD and HRPT crystal structure of the samples with $0\leq x\leq 0.875$ have been studied. Medium resolution DMC instrument was used for magnetic structure studies of all samples except $x=0$ and 1. The diffraction patterns were measured in the regime of heating in the wide temperature range. For the Rietveld refinements, MRIA$^{16}$ and FULLPROF$^{17}$ programs were used. The data on crystal structure were treated in the conventional for manganites with $\langle r_\perp \rangle \approx 1.2$ Å orthorhombic space group Pnma in
SrRuO$_3$ crystal structure was done by Jones et al. The standard setting ($a = c = \sqrt{2}a_c = 5.4$ Å, $b = 2a_c = 7.6$ Å, where $a_c \approx 3.8$ Å is the lattice spacing of the ideal cubic pervoskite). Typical high resolution neutron diffraction pattern and the Rietveld refinement for the sample with $x=0.5$ is shown in Fig. 3. More detailed description of $(\text{Nd}_{1-x}\text{Sr}_x)(\text{Mn}_{1-y}\text{Ru}_y)_3$O$_3$ compound preparation and characterization is given elsewhere.\textsuperscript{18}

In further analysis we will limit ourselves to the properties of the $(\text{Nd}_{1-x}\text{Sr}_x)(\text{Mn}_{1-y}\text{Ru}_y)_3$O$_3$ with $x > 0.1$. The properties of NdMnO$_3$ in which there are both ferromagnetic and antiferromagnetic couplings between the Mn spins, resulting in a noncollinear structure below 75 K,\textsuperscript{19} are quite different from the properties of the compositions with $x \approx 0.1$ being ferromagnets. The precision refinement of the SrRuO$_3$ crystal structure was done by Jones et al.\textsuperscript{20} This compound is known as a ferromagnet (see, for instance, Ref. 21) with $T_C=160$ K with saturation moment reported is between $\mu_{Ru}=1.1$ $\mu_B$ obtained from the magnetization measurements in high magnetic field,\textsuperscript{22} and $\mu_{Ru}=(1.4\pm0.4)\mu_B$ from neutron diffraction.\textsuperscript{23}

III. RESULTS

A. Crystal structure

The partial substitution Nd and Mn for equal amounts of Sr and Ru leads at first to a sharp decrease of the unit cell volume and orthorhombic distortion ($a/c \approx 1.067$ and 1.011 for $x=0$ and 0.25 correspondingly), and equalizing of (Mn/Ru)-O interatomic distances. Upon further doping ($x$ increases to 1), unit cell volume grows up practically linearly [Fig. 4(a)], oxygen octahedra become even more regular, i.e., all three independent bond lengths (Mn/Ru)-O1 (along $b$ axes), (Mn/Ru)-O21 and (Mn/Ru)-O22 (in $a-c$ plane) converge at $\sim 1.985$ Å, which well corresponds to the Ru-O bonds in SrRuO$_3$. Both valence angles (Mn/Ru)-O1-(Mn/Ru) and (Mn/Ru)-O2-(Mn/Ru) are slowly increasing with $x$, which corresponds to the decrease of the oxygen octahedra tilt magnitudes both about $b$-axis and in the $a-c$ plane. This increase is consistent with the noticeable growth of the tolerance factor upon substitution of Nd$^{3+}$ for Sr$^{2+}$ and of Mn$^{2+}$ for Ru$^{4+}$. These features, the most important of which is practical absence of the oxygen octahedra distortion starting from $x=0.25$, are illustrated in Fig. 4. Another important conclusion from the high-resolution neutron diffraction data is that there is no indication of either phase separation, or cation ordering. It means in particular that Mn substitution for Ru occurs statistically homogeneous. The Rietveld refinements of neutron diffraction data confirm also that Mn and Ru relative concentrations in B-sites are corresponding to the nominal stoichiometry. For instance, in the composition with $x=0.25$ the occupation factors for Mn and Ru are: $n(\text{Mn})=0.760\pm0.008$, $n(\text{Ru})=0.240\pm0.008$. Their ratio is equal to 3.17±0.11, i.e., within $\approx 5\%$ limits is equal to 0.75:0.25. Since there is no proper way of distinguishing between Nd and Sr with neutrons, the ratio $n(\text{Nd})/n(\text{Sr})$ has been fixed to $n(\text{Mn})/n(\text{Ru})$.

For the $x=0.5$ sample the high-resolution diffraction patterns were measured in wide temperature range. Temperature dependencies of the structural parameters (lattice constants, interatomic distances, and valence angles) are quite monotonic (see, our paper, Ref. 18), which is conventional for manganites in an insulating state. The ferromagnetic phase transition at $T_C=200$ K is not revealed in these temperature dependencies.

B. Magnetic ordering

Comparison of the neutron diffraction patterns of Nd$_{0.5}$Sr$_{0.5}$Mn$_{0.3}$Ru$_{0.7}$O$_3$, measured at DMC at the room temperature and 10 K (Fig. 5) shows an increase in the intensity of some diffraction peaks due to the appearance of the FM contribution. No additional reflections were detected in the neutron diffraction patterns down to $T=8$ K. The similar behavior, appearance of FM order with the temperature de-
crease, was observed for all samples except for the one with \( x = 0.75 \). For this particular composition, no significant variations of the peak intensities were found in the whole temperature range.

For the compositions with \( x = 0.125 \) and 0.25, the characteristic changes in the temperature dependence of the Bragg peak intensities below 50 K (upturn and decrease in intensity of (101)/(020) and upturn and much faster increase in intensity of (121)/(002) and (200) peaks) indicate the ordering of the magnetic moments in the A-sublattice parallel to the magnetic moments in the B-sublattice. The refinement of magnetic moment direction gives reliable result for the samples with \( x = 0.125 \) and 0.25. The best fit is obtained for the B-site magnetic moments \( M_B \) along \( b \)-axis. For other compositions the reliable determination of the magnetic moment direction is not possible because of the pseudo-cubic lattice symmetry. Figure 6 shows an example of the temperature dependencies of the magnetic moments at A- and B-sites for the composition with \( x = 0.25 \) and 0.50.

The ferromagnetic transition temperatures and the experimental low-temperature magnetic moments for the A- and B-sites are listed in Table I. Ordering of the Nd (A-site) magnetic moments occurs only if the concentration of Nd is high enough (1−\( x = 0.875 \) and 0.75). The experimental low-temperature ordered magnetic moment per one cation on a B-site can be properly described as \( M_B = m_{Mn} m_{Ru} \) even for rough estimation with \( m_{Mn} = 4 \) (low-spin \( t_{2g}^3e_g^1 \) state) and \( m_{Ru} = 4 \) (low-spin \( t_{2g}^3e_g^1 \) state). Such a description corresponds to the situation of anti-parallel ordering of Mn and Ru magnetic moments. Assumptions on the parallel ordering of Mn and Ru moments, or ordering of the solely Mn or Ru moments, cannot fit the experimental val-

FIG. 4. Dependencies of the unit cell volume (a), the unit cell parameters (b’=\( b/\sqrt{2} \)) (b), the (Mn/Ru)-O bond lengths (c), and the (Mn/Ru)-O-(Mn/Ru) valence angles (d) of \( (Nd_{1-x}Sr_x)(Mn_{1-x}Ru_x)O_3 \) at room temperature on the (Sr,Ru) content \( x \). Data for \( x = 1 \) are taken from Ref. 20. The symbol sizes are larger than the experimental errors (a) and (b) or comparable with ones (b) and (c).

FIG. 5. Diffraction pattern of the \( (Nd_{0.5}Sr_{0.5})(Mn_{0.5}Ru_{0.5})O_3 \) sample, measured at the DMC at \( T = 10 \) K and treated with the Rietveld method. Experimental points, calculated profile and difference function are shown. In the inset, the patterns (in 36–60 degree range) measured at 10 and 300 K are compared. The higher intensity at low temperature is due to the appearance of the FM ordering.

FIG. 6. Temperature dependence of the ordered magnetic moment in B-site \( (Mn/Ru) \) and A-site \( (Nd) \) for the sample with \( x = 0.25 \) (●), and B-site \( (Mn/Ru) \) for the sample with \( x = 0.5 \) (▲). The solid lines are results of the calculation according to the molecular field theory (see the discussion section).
ues. A reasonable correspondence between the experimental and calculated $M_B$ values can be obtained if $\mu_{Mn}=4\mu_B$ and $\mu_{Ru}=1.45\mu_B$ are used. The last value is taken from spin-density functional theory calculation\textsuperscript{21} for SrRuO$_3$. The fit of the experimental data to the linear function $M_B(x)=1-(1-x)\mu_{Mn}-x\mu_{Ru}$ gives $\mu_{Mn}=(3.74\pm0.15)\mu_B$ and $\mu_{Ru}=(1.34\pm0.25)\mu_B$. One can see (Fig. 7) that the experimental points are excellently fitted by straight line (except $x=0.125$) with the values of $\mu_{Mn}$ and $\mu_{Ru}$ which are in good agreement with the expected magnetic moments of Mn and Ru. Results of the calculation are also listed in Table I.

In the proposed model, the absence of any measurable magnetic moment in the $x=0.75$ composition is simply an effect of nearly ideal compensation of Mn and Ru contributions to the magnetic structure factors. Indeed, $M_{Mn}=(1-x)\mu_{Mn}=(0.935\mu_B$, $M_{Ru}=x\mu_{Ru}=1.005\mu_B$ for $x=0.75$ and $\mu_{Mn}=3.74\mu_B$, $\mu_{Ru}=1.34\mu_B$. For anti-parallel ordering of Mn and Ru magnetic moments, the magnetic structure factors are proportional to the difference $|M_{Mn}-M_{Ru}|=0.07\mu_B$ which is too small to be measured in the powder diffraction experiment.

To prove the presence of frozen magnetic moments and better identification of the temperature magnetic state of the $x=0.75$ sample we have exploited also the $\mu$SR technique. The $\mu$SR measurements with the same sample have been carried out using DOLLY spectrometer on the $\mu$E4 beam line at PSI. The powder sample was packed in an aluminum container, mounted in the helium flow cryostat.

No spontaneous muon spin precession in zero external magnetic field ($ZF$) was detected at low temperatures. The $ZF$ muon spin polarization function $P(t)$ is rapidly relaxed at initial times ($<10$ ns), making practically impossible to study the fast relaxing part of $P(t)$. However, this behavior of the polarization function proves that the magnetic moments of Mn$^{3+}$ and Ru$^{4+}$ are static at low temperature, thus confirming the idea of the B-sublattice ferromagnetic moment compensation following from the ND data. Due to the large magnetic moment of Mn$^{3+}$, the local magnetic fields at the muon in the perovskite manganites are expected to be very large [e.g., the muon precession frequency $\sim 80$ MHz is observed in La$_{0.67}$Ca$_{0.33}$MnO$_3$ (Ref. [24]) corresponds to the local field of $\sim 5$ kG]. Due to the strong local disorder the dispersion of the local magnetic fields is large leading to the completely relaxed $P(t)$ at $t>10$ ns.

The sample volume occupied by the magnetically ordered state is better determined in the transverse external field (TF) experiment in the weak magnetic field of 100 Oe, which is much less than the internal magnetic field. The asymmetry (or amplitude) $A_{TF}$ of the muon spin precession with the frequency corresponding to the external magnetic field is a direct measure of the paramagnetic volume fraction. Figure 8 shows the temperature dependence of $A_{TF}$ together with magnetic susceptibility in (Nd$_{0.5}$Sr$_{0.5}$)(Mn$_{0.25}$Ru$_{0.75}$)O$_3$. The values of $A_{TF}$ are given for the muon spin polarization component perpendicular to the initial muon spin polarization direction. For this component, any contribution from the magnetically ordered (short or long-range) regions of the sample volume is averaged to zero. Above 170 K the whole sample volume is in the paramagnetic state and the precession asymmetry is given by the total experimental asymme-

![FIG. 7. Dependence of the ordered magnetic moment on B-site (Mn/Ru) of (Nd$_{1-x}$Sr$_x$)(Mn$_{1-x}$Ru$_x$)O$_3$ on the (Sr/Ru) content x. For $x=0.125$, 0.25, 0.50, 0.75, and 0.875, the values obtained in the present paper are shown. The value $\mu_{Ru}=1.45\mu_B$ for $x=1$ is taken from Ref. 21. The dashed line is calculation for theoretical values $\mu_{Mn}=4\mu_B$ and $\mu_{Ru}=1.45\mu_B$, the solid line is the least square approximation (in the $0.25\leq x\leq 1.0$ range) by linear function with $\mu_{Mn}=3.74\mu_B$ and $\mu_{Ru}=1.34\mu_B$.](image-url)
try $A_{TF}=0.26$. Below $T_2=160\,\text{K}$ which corresponds to a peculiarity in the magnetic susceptibility $\chi(T)$, the frozen atomic magnetic moments begin to appear in the part of the sample volume, causing the decrease in $A_{TF}$. Below $T=115\,\text{K}$, the $A_{TF}(T)$ curve changes its slope, becoming more rapidly decreasing function. The temperature $T_1=92\,\text{K}$ of the maximum of $\chi(T)$ roughly corresponds to the middle of the transition by $A_{TF}(T)$. The residual muon spin precession asymmetry at low temperature $A_{TF}=0.05 (\sim 20\%)$ gives the fraction of the muon stops in the sample holder and in the part of sample volume which remained paramagnetic.

The slow relaxing part of the ZF polarization function has an exponential form $P_{ZF}=A_{ZF}\exp(-\lambda t)$ with noticeable $\lambda=0.2\,\mu\text{s}^{-1}$ even at the low temperatures $T\leq 50\,\text{K}$, implying that a slow dynamics of the local fields is present. The asymmetry $A_{ZF}$ well corresponds to the expected $1/3$ of the total experimental asymmetry.

For the sample with $x=0.75$ we cannot assign the ferromagnetic transition temperature to either $T_1$ or $T_2$. However, a comparison of the susceptibilities of the samples with $x=0.75$ and $x=0.875$ shows that the both compositions have two peculiarities at the temperatures $T_1$ and $T_2$.

The transition at $T_2$ in the sample with $x=0.875$ well corresponds to the ferromagnetic Curie temperature $T_C$ determined from the temperature dependence of the integrated neutron intensities (Fig. 9). Since the net ferromagnetic moment in the sample with $x=0.875$ is small we present in Fig. 8 the sum of two most intense ferromagnetic Bragg peaks. By analogy we can assign the transition at $T_2$ to the ferromagnetic Curie temperature in the sample with $x=0.75$. The transition at $T=T_1$ is not revealed in the neutron diffraction data, and thus is probably related to a spin-glass-like or another short-range ordering effects.

**IV. DISCUSSION**

Good correspondence between the model calculations and the experimental data in the wide interval of Sr/Ru concentration allows us to conclude that proposed interactions and obtained magnetic moments are intrinsic properties of Mn and Ru ions in the compound. The deviation of $x=0.125$ point is natural; for the small values of $x$ the compound has to turn into the noncollinear (mainly A-type antiferromagnetic) state with close to zero ferromagnetic component of the ordered moment at B-site. For the undoped NdMnO$_3$ compound, an antiferromagnetic A-phase is stabilized due to the orbital ordering and its energy is only slightly lower than the energy of FM order. Ru$^{4+}$ is not Jahn-Teller active ion and serves as a defect for the orbitally ordered state. Therefore, even at small concentration of Ru$^{4+}$, the AFM order turns into FM.

As follows from the fitting procedure discussed above, the resulting interaction between the Mn and Ru ions should be antiferromagnetic. The nature of such an interaction can be understood by considering electron energy levels for both manganese and ruthenium ions. Their reference energies are $e_{Mn}^{\text{d}3}=-15.27\,\text{eV}$ and $e_{Ru}^{\text{d}4}=-14.59\,\text{eV}$, correspondingly. These energies are very close to each other and allowing a significant overlapping between some of the orbitals. As Ru ion is in the low spin configuration, the crystal field splitting is essential and Ru $e_g$ orbitals have rather high energy. As a result they are located high above the Mn $e_g$ states and do not cross their Fermi energy and do not participate in the formation of the band. Thus the ferromagnetic superexchange between quarter-filled $e_g$ band of Mn$^{3+}$ and empty $e_g$ band of Ru is suppressed. The resulting exchange between Ru and Mn ions is therefore the superexchange between half-filled $t_{2g}(3d)$ band of Mn and more than half-filled $t_{2g}(4d)$ band of Ru which should be antiferromagnetic according to Goodenough–Kanamori rules. Note, that if $e_g$ states of Ru would lie close enough to the $e_g$ states of Mn, the double exchange mechanism would work fine, Ru and Mn ions would be ferromagnetically coupled, and compound would show metallic behavior (see, for example, Ref. 10).

The antiferromagnetic superexchange interaction between Mn and Ru gives a state with a finite magnetic moment...
which temperature dependence can be described in frame of the molecular field theory.\textsuperscript{25} Let us divide the lattice of magnetic atoms (B-sites) into two “statistical sublattices” B1 and B2 such that Mn\textsuperscript{3+} and Ru\textsuperscript{4+} occupy the B1 and B2 sites correspondingly. Since Mn and Ru ions are located randomly in the whole volume of the compound, we are using the term “sublattices” only for convenience. We consider the case of a magnetically isotropic crystal with ferromagnetic interaction within both sublattices and antiferromagnetic interaction between them. The Hamiltonian of the system can be written as
\[ H = -J_{11} \sum S_{1i}S_{1j} - J_{22} \sum S_{2i}S_{2j} + J_{12} \sum S_{1i}S_{2j}. \]

Here \( J_{11} \) and \( J_{22} \) are ferromagnetic exchange constants for Mn-Mn and Ru-Ru, respectively, and \( J_{12} \) is antiferromagnetic exchange constant constant Mn-Ru, \( S_{1} \) and \( S_{2} \) are the spin operators of Mn\textsuperscript{3+} and Ru\textsuperscript{4+} ions, the sums are taken over nearest neighbors of corresponding sublattices. The system of molecular field equations may be written in the form:
\[ \alpha_1 = z(1-x)J_{11}S_1 \sigma_1 + zJ_{12}S_2 \sigma_2, \]
\[ \alpha_2 = zJ_{22}S_2 \sigma_2 + z(1-x)J_{12}S_1 \sigma_1, \]

where \( z=6 \) is the coordination number, and \( \alpha_1, \alpha_2 \) are relative magnetizations per site in sublattices B1(2):
\[ \alpha_1 = 1 - B_S(\alpha_1/2)/S_1, \quad \alpha_2 = 1 - B_S(\alpha_2/2)/S_2. \]

\( B_S \) is the Brillouin function:
\[ B_S(x) = \frac{2x}{\sum_{n=0}^{\infty} \frac{n! e^{-nx}}{2^n n!}}. \]

This system of equations must be solved self-consistently to give \( \sigma_1 \) and \( \sigma_2 \) as functions of temperature \( T \). The total magnetization can be written as
\[ M = M_1 - M_2 = M_{10} \sigma_1 - M_{20} \sigma_2, \]

where \( M_{10} = (1-x)S_1 \mu_{Mn} \) and \( M_{20} = xS_2 \mu_{Ru} \) is a concentration of Ru, \( \mu_{Mn} \) and \( \mu_{Ru} \) are magnetic moments of Mn and Ru ions. We performed the calculations with experimentally obtained values \( \mu_{Mn} = 3.74 \) \( \mu_B \) and \( \mu_{Ru} = 1.34 \) \( \mu_B \). From the experimental value of the Curie temperature \( T_C = 160 \text{K} \) \textsuperscript{22,23} in SrRuO\textsubscript{3} we calculate the Ru-Ru exchange constant \( J_{12} = 21 \text{meV} \) using the above formulas of the molecular field approximation. The ferromagnetic superexchange between Mn ions was fixed to \( J_{11} = 2.1 \text{meV} \). This value is in the range reported in the literature for the planar ferromagnetic exchange in LaMnO\textsubscript{3}.\textsuperscript{26} The antiferromagnetic exchange \( J_{12} \) was considered as a free parameter. Good agreement with the experimental temperature dependencies of magnetization has been obtained with \( J_{12} = 23 \text{meV} \) (Fig. 6). The calculated values of \( T_C \) are shown in Table I together with the experimentally measured ones.

Calculations reproduce satisfactorily well the temperature dependencies of magnetic moments, in particular for \( x = 0.25 \) and \( x = 0.5 \). However, there is a difference between calculated and experimentally measured values of \( M(T) \). This quantitative disagreement can be understood as a consequence of the mean field approximation which neglects spin fluctuations and overestimates total magnetic moments \( M_1(T) \) and \( M_2(T) \) both for Mn- and Ru-sublattices. However since Mn ions have larger value of spin \( S = 2 \) the molecular field theory is working better for Mn-sublattice than for Ru-sublattice with \( S = 1 \). Moreover at low doping Ru ions can be considered as impurities for Mn-sublattice which worsens the application of the mean field theory. As a result, the magnetization \( M_2(T) \) of Ru-sublattice is significantly overestimated. As Mn- and Ru-sublattices are antiferromagnetically coupled, the calculated total magnetic moment is under- or overestimated depending on the sign of total magnetic moment \( M(T) \).

V. SUMMARY

Neutron diffraction, \( \mu \)SR, and electrical resistivity measurements have been performed to study the magnetic, structural, and electrical properties of NdMnO\textsubscript{3} upon simultaneous and consistent doping of A- and B- sites by Sr and Ru, respectively. The end members of the series (Nd\textsubscript{1-x}Sr\textsubscript{x})(Mn\textsubscript{1-x}Ru\textsubscript{x})O\textsubscript{3} are A-type antiferromagnetic insulator (\( x = 0 \)) and ferromagnetic metal (\( x = 1 \)). The Sr and Ru doping assures an increase of the tolerance factor at higher \( x \), which must favor an appearance of the metallic state. Nevertheless, the metallic state in our samples is not present, they are all insulators, and we do not observe any peculiarities on the resistivity curves at magnetic transition temperatures. This implies, that the DE mechanism, which is practically excluded in (Nd\textsubscript{1-x}Sr\textsubscript{x})(Mn\textsubscript{1-x}Ru\textsubscript{x})O\textsubscript{3}, is very important for correlation between FM order and metallic state as it is well known for the doped manganites. Good correspondence between the experimental data and model calculations for the low-temperature Mn and Ru magnetic moments as function of (Sr/Ru) concentration in a wide range of \( x \), indicates that hypothesis about FM correlation magnetic moments within both Mn-Mn and Ru-Ru pairs and AFM correlation of the moments in Mn-Ru pairs is correct. The electronic states are \( t_{2g}^4e_{g}^1 \) for Mn\textsuperscript{3+} and high-spin \( t_{2g}^3e_{g}^0 \) for Ru\textsuperscript{4+}, respectively, with quite different values of the moments: \( \mu_{Mn} = 3.74(15) \mu_B \) and \( \mu_{Ru} = 1.34(25) \mu_B \). Due to random distribution of Mn and Ru over B-sites (as it follows from diffraction patterns) the obtained magnetic state can be called “statistical ferrimagnet.” The concentration dependencies of the ferromagnetic transition temperatures and the saturated magnetic moments calculated in the mean field approximation are in rather good agreement with the proposed magnetic state.

The discovered unusual interaction between Mn and Ru magnetic moments can provide also a new insight to the anomalies of the ferromagnetic state which were observed in Ru doped perovskite manganites earlier (see Ref. 6 for review).
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