Atomic and magnetic structures, disorder effects, and unconventional superexchange interactions in A_2 MnGaO_{5+ δ} (A=Sr, Ca) oxides of layered brownmillerite-type structure

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Crystal and magnetic structures of complex manganese oxides $Sr_2GaMnO_{5+\delta}$ (δ =0.01,0.52) and $Ca_2GaMnO_{5+\delta}$ ($\delta \simeq 0.05$) were studied by neutron powder diffraction (ND) and μ SR technique in the temperature range 2-300 K. The crystal structures contain single MnO₂ layers separated by three nonmagnetic cation-oxygen layers. The principal difference between the $\delta \simeq 0$ and $\delta \simeq 0.5$ compounds is the Mn valence: Mn^{3+} or Mn^{4+} , and the structure of the $(GaO_{1+\delta})$ buffer layer, which is formed by tetrahedra or partially filled octahedra, respectively. The magnetic moments of the manganese ions are coupled antiferromagnetically in the MnO_2 plane, but antiferromagnetically (G type) or ferromagnetically (C type) between the planes for the reduced and oxidized compositions, respectively. The transition from the G- to C-type magnetic structure by oxygen doping is explained by strong diagonal 180° superexchange antiferromagnetic interaction between Mn⁴⁺-ions in the adjacent layers through additional oxygen atoms in the GaO buffer layer. The magnetic moments in Sr-based samples are appreciably reduced in comparison with the spin-only values of the corresponding Mn ion. By using complementary information on local magnetic field distribution from μ SR we show that the reduced magnetic moments seen by ND are caused by the presence of locally flipped Mn spins and a short-ranged (40 Å) antiferromagnetic phase. The magnetic disorder can be caused by the disorder observed in the oxygen positions of the $GaO_{1+\delta}$ layer, because the coupling between the MnO₂ layers is mediated by the geometry of the superexchange path through these oxygen atoms.

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I. INTRODUCTION

The unusual physical properties, especially colossal magnetoresistance (CMR), of complex manganese oxides are closely connected with the features of their crystal and magnetic structures, which were the subject of intensive investigations in the recent years. The studies are to a large extent concentrated on the three-dimensional perovskites of the type $R_{1-x}A_x$ MnO₃ (*R* is La or a rare earth metal and *A* is a divalent cation), but recent works also deal with systems of reduced dimensionality, which are promising, in particular, for the possibility of observing CMR at low fields. Among these compounds, the most thoroughly explored ones are Ruddlesden-Popper (RP) phases $(R,A)_{n+1}Mn_nO_{3n+1}$ which exhibit CMR at appropriate doping level. Crystal and magnetic structures of both three-dimensional (3D) and quasi-2D manganites are supposed to be already well known (see, for instance, recent reviews^{1,2}), despite the fact that some physical properties, such as the homogeneity of the ground state, orbital effects, and long-scale phase separation, still remain under discussion. Among the layered CMR manganites the main attention was paid to the n=2 RP phases, which contain double perovskite layers interleaved with (AO)(OA)rock-salt-type blocks. Thus, the particular magnetic structure of the n=2 RP phase depends on several Mn-Mn interactions: in plane, within the bilayer, and between nearestneighboring bilayers (both ferromagnetic and antiferromagnetic interactions are possible) (see, for instance, Ref. 3, where data on 25 various compositions are cited). One may expect a two-step change in magnetic properties: at higher temperature due to the coupling within the layers, and at lower temperature because of the interlayer tunneling. Indeed, this type of behavior was observed for La_{1.4}Sr_{1.6}Mn₂O₇ (Ref. 4) and for La_{2-2x}Ca_{1+2x}Mn₂O₇ (for 0.2 < x < 0.5),⁵ though later it was found⁶ that the two-dimensional magnetic behavior of La_{1.4}Sr_{1.6}Mn₂O₇ had an extrinsic nature and was attributed to intergrowths.

Recently, new complex manganese layered oxides Ca_2GaMnO_5 and Sr_2GaMnO_5 with brownmillerite-type structure were synthesized.^{7–9} These compounds contain single MnO₂ layers separated by three cation-oxygen layers (AO)(GaO)(AO) instead of two, as for interbilayer separation of the n=2 RP system. Both Ca- and Sr-based brownmillerites have an orthorhombically distorted structure with $a_p\sqrt{2}$ dimensions in plane and $4a_p$ in the perpendicular direction, where $a_p \approx 3.8$ Å is a lattice parameter for cubic perovskite structure. The shortest Mn-Mn in-plane distance is normal for manganites ($\simeq 3.8$ Å), but as a result of the additional GaO layer, the out-of-plane separation of neighboring manganese atoms is about 8 Å. A specific feature of these oxides is the doping possibility through the incomplete oxygen anion sublattice (in both 3D manganites and the Ruddlesden-Popper layered phases, the oxygen sublattice is completely filled). The oxygen content can be adjusted in the range from $O_{5,0}$ to $O_{5,5}$, corresponding to a Mn formal oxidation state between +3 and +4, respectively. The intermediate valence of Mn can lead to a partially filled electron band and to the activation of the double exchange mechanism, which implies the ferromagnetic metallic state with CMR effect (although it is not always the case, e.g. in the single-layer RP system.¹⁰) There are several open questions about the crystal structure of these layered manganites, mainly connected with true space symmetry and ordering of oxygen vacancies. For instance, x-ray data for the reduced Sr compound taken in Refs. 8 and 9 gave ordered and disordered arrangements of oxygen atoms in (GaO) layers (corresponding to *Ima2* and *Imcm* space groups, respectively). Similar brownmillerite system SrCaMnGaO_{5+ δ} was also studied in Ref. 11 using a variety of techniques. In the present paper we address the problem of magnetic ordering of the Mn ions in these brownmillerites and its relation to the crystal structure parameters.

We present a detailed neutron diffraction and μ SR study of the crystal and antiferromagnetic structures and local magnetic disorder effects and the theory of the magnetic ordering type in the end members of the series with $\delta \approx 0$ and 0.5. Preliminary data on the crystal and magnetic structures were published in Ref. 12. The single phase compositions with the intermediate Mn valence ($0 < \delta < 0.5$) which we were able to synthesize, reveal no ferromagnetic metallic state, but their magnetic structures are a superposition of the antiferromagnetic structures observed in the end members of this family. A detailed report on our studies of the intermediate compositions will be published separately.

II. SAMPLES. EXPERIMENTAL

The Sr₂GaMnO₅ and Ca₂GaMnO₅ samples were synthesized by a solid state reaction in evacuated silica tube at 1000°C. Details of the sample preparation procedures were described in Refs. 7 and 8. The Sr₂GaMnO_{5.5} sample was prepared by annealing of the Sr2GaMnO5 compound under 20 bar oxygen pressure at 415 °C for 12 h. Both samples were checked by x-ray powder analysis, and showed a high degree of purity. The oxygen stoichiometry index, which was determined from chemical analysis (iodometric titration), is $\delta = 0.01(2)$ and $\delta = 0.52(2)$ for the Sr-based reduced and oxidized samples, respectively, and $\delta = 0.05(2)$ for the Cabased sample. Hereafter we will use the nominal compositions Sr2GaMnO5, Ca2GaMnO5 and Sr2GaMnO55 for the samples, keeping in mind that the real stoichiometry is slightly different, as shown above. All the samples are insulators according to the electrical resistivity measurements. Neutron powder diffraction experiments were carried out at the SINQ spallation source of Paul Scherrer Institute (PSI). The crystal structures of the samples were determined from the data taken with the high-resolution HRPT diffractometer¹³ with the neutron wavelength $\lambda = 1.49$ Å. The data on the magnetic ordering were obtained by means of the DMC powder diffractometer¹⁴ situated at a supermirror coated guide for cold neutrons at SINQ ($\lambda = 2.56$ Å). The refinements of the crystal and magnetic structure parameters were carried out with FULLPROF (Ref. 15) program, with the use of its internal tables for neutron scattering lengths and magnetic form factors.

To access the information on local magnetic ordering effects, we involved the μ SR (the muon spin relaxation¹⁶) measurements. This technique allows the observation of the time evolution of the spin polarization of muons implanted in a sample. The magnetic fields at the muon reflect the local magnetic environment of the muon site. On the other hand, the experimental μ SR-signal is an average of the spin polarization of the muons distributed isotropically over the entire sample volume. Thus the technique is a bulk method for measuring local magnetic fields, complementary to the neutron diffraction. The μ SR measurements with the same samples have been carried out using the DOLLY spectrometer on the μ E4 beam line at PSI. The powder samples were packed in aluminum containers, mounted on the cold finger of the helium cryostat. The muon beam was collimated to a narrow spot, sufficient to avoid muon stops in the container walls.

III. RESULTS

A. Crystal structure

Typical neutron diffraction patterns and the Rietveld refinements for the reduced and oxidized Sr-based compositions are shown in Fig. 1. One can see a pronounced difference between the patterns, caused by the change of the space symmetry upon oxygen doping. The reduced phase possesses brownmillerite structure, which can be represented by a stacking sequence of layers:- $(SrO)-(MnO_2)-(SrO)-(GaO)-$. However, different polytypes of the brownmillerite



FIG. 1. An example of the Rietveld refinement pattern and difference plot of the neutron diffraction data (HRPT/SINQ) for Sr_2MnGaO_5 (top) and $Sr_2MnGaO_{5.5}$ (bottom). The top row of the hkl-tics shows the nuclear phase calculated diffraction peaks positions. Next row shows the calculated positions of the peaks of the AF sublattices of the *G*- and *C*-type magnetic structures for the compositions with oxygen contents of 5 and 5.5, respectively.

structure are known, and there is a discrepancy in space symmetry of Sr₂GaMnO₅ reported by different scientific groups. This discrepancy mainly concerns the signs of cooperative rotation of GaO₄ tetrahedra forming infinite chains. Two opposite directions of atomic displacements in GaO layers, resulting in two mirror-related orientations of the tetrahedral chains can be marked as left (L) and right (R). The crystal structure of Sr₂GaMnO₅ has been refined in a model with acentric space group Ima2 which corresponds to the presence of a chain of one type only (either R or L), as proposed from x-ray diffraction data.8 The refined structural parameters at T = 300 K are given in Table I. The authors of Ref. 17 found that centrosymmetric *Imcm* space group with a complete disorder of L and R chains fits better to their powder neutron diffraction data. The Imcm model implies that L and *R* chains alternate in the structure with equal probability, giving a disorder in (GaO) positions in the Ga buffer layer. The refinement in a model with *Imcm* space symmetry and with the disorder in z-positions of Ga and O3 (see Table I) gives slightly better R factors. An important improvement in the Imcm model with the (GaO) disorder is more realistic

TABLE I. The structural parameters and Mn-O interatomic distances in Sr₂MnGaO₅ [sp.gr. *Ima*2, no. 46 in comparison with sp.gr. *Imcm*, no. 74] and Sr₂MnGaO_{5.5} (sp.gr. *P4/mmm*, no. 123) at room temperature. The data are refined from the diffraction patterns measured at HRPT/SINQ, $\lambda = 1.494$ Å.

	Sr ₂ GaMnO ₅ Ima2	Sr ₂ GaMnO ₅ Imcm	Sr ₂ GaMnO _{5.5} P4/mmm
a, Å	16.1971(3)	16.1966(3)	3.8007(1)
b, Å	5.5257(1)	5.5257(1)	
c, Å	5.3863(1)	5.3864(1)	7.9602(2)
x,y,z (Mn)	0	0	0
$B_{\rm iso}({\rm Mn}), {\rm \AA}^2$	0.98(8)	0.82(9)	1.1(1)
x (Sr)	0.1111(1)	0.1112(1)	0.5
y (Sr)	0.0118(4)	0.0116(4)	0.5
z (Sr)	0.4986(33)	0.5	0.2347(4)
$B_{\rm iso}({\rm Sr}), {\rm \AA}^2$	0.41(3)	0.59(3)	0.86(6)
x (Ga)	0.25	0.25	0.054(5)
y (Ga)	0.9331(6)	0.0675(5)	0
z (Ga)	0.0363(34)	0.0423(6)	0.5
$B_{\rm iso}({\rm Ga}),~{\rm \AA}^2$	1.22(8)	0.54(7)	2.6(3)
x (O1)	0.9959(2)	0.0040(2)	0.5
y (O1)	0.2545(14)	0.25	0
z (O1)	0.2504(36)	0.25	0
$B_{\rm iso}({\rm O1}),~{\rm \AA}^2$	0.46(4)	0.59(4)	0.67(5)
x (O2)	0.1449(2)	0.1455(2)	0
y (O2)	0.0419(4)	-0.0428(4)	0
z (O2)	0.0016(36)	0	0.2457(4)
$B_{\rm iso}({\rm O2}), {\rm \AA}^2$	0.745(3)	0.91(4)	1.14(9)
x (O3)	0.25	0.25	0.5
y (O3)	0.6259(9)	0.3760(7)	0.090(2)
z (O3)	0.1155(33)	0.8869(9)	0.5
$B_{\rm iso}({\rm O3}),~{\rm \AA}^2$	1.47(11)	0.87(9)	2.6(2)
n (O3)	1	1	1.57(2)
Mn–O1	1.949(15)	1.9302(1)	1.9003(0)
Mn-O1	1.911(15)	-	-
Mn-O2	2.358(3)	2.368	1.956(3)
R _{Bragg}	7.8	6.8	6.0
R_{wp}	6.4	6.0	7.4
R _{expt}	1.9	1.9	1.8

thermal parameters of the Ga atoms. Following Ref. 17 we have also estimated the occupancy of Ga sites substituted by Mn ions, and vice versa. This disorder is small: the refined amount of substituted atoms is only 2%. This disorder is twice as small as that found by the authors of Ref. 17, probably reflecting a difference in the sample synthesis temperature. Our sample was prepared at 1000 °C whereas the authors of Ref. 17 used a much higher temperature of 1350 °C that is favorable for a formation of disordered structure.

Due to the Jahn-Teller effect, for the Mn^{3+} ion, MnO_6 octahedra are strongly elongated with four short equatorial

 $(2 \times 1.911$ Å and 2×1.949 Å) and two long apical (2.358 Å) distances. The long axes of the octahedra are almost aligned along the *x* direction (perpendicular to the MnO₂ planes), i.e., the orbital ordering type, is different from the antiferrodistorsive orbital ordering within the MnO₂ planes observed in LaMnO₃. The crystal structure of Cabased oxygen reduced composition Ca₂GaMnO₅ is also orthorhombic, with orderings of *L* and *R* chains described by the *Pnma* space group. The details of the crystal structure refinement are given in Refs. 7 and 8.

The diffraction pattern of the oxidized composition Sr₂GaMnO_{5.5} (Fig. 1) was indexed with tetragonal unit cells of $a = b \simeq b_0 / \sqrt{2}$ and $c \simeq a_0 / 2$ (where b_0 and a_0 denote the lattice constants of Sr₂GaMnO₅ in the orthorhombic unit cell). Satisfactory agreement between the observed and the calculated profiles was obtained with a model which includes: Mn (0,0,0) and O1 (0.5,0,0) forming the MnO₂ layer, O2 (0,0, z_1) and Sr (0.5,0.5, z_2) with $z_1 \approx z_2 \approx 0.25$ forming the buffer SrO layer, and Ga (x,0,0.5) and O3 (0.5, y, 0.5) forming a GaO_{1.5} layer. All Ga cations in the Sr₂GaMnO_{5.5} are formally in the octahedral coordination. However, the oxygen positions in the GaO_{1.5} layer, forming an equatorial plane of GaO_{6-x} octahedra, are only partially filled with an occupancy g = 0.78(2), which is close to 3/4, according to the oxygen index $O_{5.5}$ determined by chemical analysis. Incomplete oxygen environment causes static disordered displacements of Ga and O atoms in the $(GaO_{1,5})$ plane which are reflected in large values of thermal parameters. If one assumes no disorder at the Ga and O3 sites, i.e., x and z coordinates fixed to zero, then the values of thermal displacement parameters B are unphysically high, being B= 3.3 and 5.5 $Å^2$ for Ga and O3, respectively. The disorder of the type (x,0,0.5) for Ga cations and (0.5,y,0.5) for O3 anions improves the thermal parameters significantly. The refined structure parameters are given in Table I. The refinement gives of course only an average structure whereas local or irregular ordering of oxygen atoms and vacancies may occur, which could be related to an ordered appearance of Ga atoms in a complete octahedral or tetrahedral coordination. The refined oxygen composition is very close to the nominal $O_{5.5}$ value, implying the Mn^{4+} state. The Mn-O distances are practically equalized, unlike in the reduced composition, because Mn⁴⁺ is a Jahn-Teller inactive ion. The crystal structures of both compositions are shown in Fig. 2. One can see that the principal difference between the two structures is the coordination of Ga ions, which is tetrahedral in the reduced composition and octahedral in the oxidized one.

B. Magnetic ordering

All three samples Sr_2GaMnO_5 , Ca_2GaMnO_5 , and $Sr_2GaMnO_{5.5}$ are antiferromagnets (AF's) at low temperature. Figure 3 shows low scattering angle section of the neutron diffraction patterns and the refinement curves at the temperature T=1.5 K for the Sr-based samples. The magnetic structure of the Ca-based composition is equivalent to that of the Sr-based reduced composition. In Fig. 3 and further on, we use the indexing of the magnetic peaks in the *Ima2* orthorhombic setting (long axis—x) for both compositions.



FIG. 2. The crystal and magnetic structures of (left) Sr_2MnGaO_5 (sp.gr Ima2) and (right) $Sr_2MnGaO_{5.5}$ (sp.gr P4/mmm). Note the principal difference between two crystallographic structures is the structure of (GaO) buffer layer. It is formed by GaO_4 tetrahedra in Sr_2GaMnO_5 and partially filled GaO_6 octahedra in $Sr_2GaMnO_{5.5}$. Sr atoms are not shown. The antiferromagnetic structures of Mn magnetic moments can be denoted as *G* type for Sr_2GaMnO_5 and *C* type for $Sr_2GaMnO_{5.5}$ according to the classification proposed in Ref. 18.

This is convenient for a comparative analysis of the magnetic structures. The corresponding magnetic structures are shown in Fig. 2. The magnetic moments of the Mn ions are coupled antiferromagnetically in the MnO₂ plane for both compositions, but antiferromagnetically or ferromagnetically between the planes for the reduced and oxidized compositions, respectively. These magnetic structures are denoted as G and C types, respectively using the notations of the magnetic structures accepted for the 3D perovskite manganese oxides.¹⁸ The rules for the allowed magnetic Bragg peaks are h=2n+1, (k+l)=2m+1 for the G type structure, and h =2n, (k+l)=2m+1 for the *C* type structure (*n* and *m* are integers). That is, for the reduced composition one can see in Fig. 3 the presence of (110)/(101) and (301)/(310) magnetic Bragg peaks expected for a G type structure and the absence of (010)/(001) and (210)/(201) peaks that would correspond to the C-type configuration. Note that for the Ima2 space symmetry the reflections (hk0), h+k=2n are allowed, so there is a nuclear contribution in the (110) and (310) Bragg peaks. For the oxidized composition, there are only peaks corresponding to the C-type structure, but G-type peaks are extinct. Since the shift in the lattice parameters (reduced to the same orthorhombic elementary cell) between the two compositions is not large, one can directly compare the patterns, as shown by vertical dotted lines in Fig. 3. Analysis of the magnetic Bragg peak intensity ratios (by means of the Rietveld refinement) yields the direction of magnetic moment parallel to the x axis. Direct evidence for this is the zero intensity of the (100) peak for the *G*-type structure (Fig. 3).



FIG. 3. Neutron diffraction patterns, Rietveld refinement, and difference plots for the Sr_2GaMnO_5 and $Sr_2GaMnO_{5.5}$ samples at the temperature T=1.6 K measured at DMC/SINQ with $\lambda = 2.56$ Å. One can see (110)/(101) and (301)/(310) magnetic Bragg peaks expected for a *G*-type antiferromagnetic structure of Sr_2GaMnO_5 and (010)/(001) and (210)/(201) magnetic Bragg peaks for the *C*-type structure, shown in Fig. 2. The peak indexing is given for the orthorhombic setting (the long axis perpendicular to the MnO₂ planes is the *x* axis).

Magnetic *R*-factors R_M (integrated intensities) for the refinements, shown in Fig. 3 amount to 5.8% and 25% for Sr₂GaMnO₅ and Sr₂GaMnO_{5.5}, respectively. An increased value of R_M in the oxidized composition is connected with the presence of diffuse-like scattering centered around 2θ $\simeq 30^{\circ}$. The choice of the appropriate shape of the background, fitted to this diffuse scattering, reduces R_M to 12%. The refined size of the low temperature magnetic moment is not affected by the selected background shape. Figure 4 shows fragments of the diffraction patterns of Sr₂GaMnO₅₅ near $2\theta = 30^{\circ}$ for two temperatures: well above the magnetic transition at 220 K and in the vicinity of the transition at 100 K. One can see the broad peak situated between the two sharp Bragg peaks (010) and (210). The position of the broad peak is excellently indexed as the (110)/(101) magnetic peak, implying that there is a certain contribution of the shortranged magnetic structure of G type in the predominant C-type magnetic structure of Sr₂GaMnO_{5.5} composition. This diffuse peak (110)/(101) corresponds to $(1/2 \ 1/2 \ 1/2)$ for P4/mmm, and is definitely absent for the nuclear structure. Assuming that the width of this broad peak is given only by a size effect, one estimates the range of the G-type



FIG. 4. Sections of the diffraction patterns from $Sr_2GaMnO_{5.5}$ near $2\theta = 30^\circ$ for two temperatures: well above the magnetic transitions at 220 K (shown by thin lines) and at 100 K (experimental points are shown by filled circles and the fit curve is shown by thick line). One can see the broad peak (110)/(101) corresponding to a *G*-type structure situated between two sharp Bragg peaks (010)/ (001) and (210)/(201) of the *C*-type structure.

correlation to $L \approx 40$ Å according to the formula $L \approx \lambda / [\Delta(2\theta)\cos\theta]$, where $\Delta(2\theta)$ is the full width at half maximum of the peak. Figure 5 shows temperature dependencies of the integrated intensities of several magnetic diffraction peaks for both compositions. The Néel temperatures



FIG. 5. Temperature dependencies of the integrated intensities of the characteristic magnetic diffraction peaks in the Sr_2MnGaO_5 (top) and $Sr_2MnGaO_{5.5}$ (bottom). The peaks (110), (101) and (301) represent the *G*-type magnetic structure in the Sr_2MnGaO_5 sample. In the $Sr_2MnGaO_{5.5}$ sample, the *C*-type magnetic structure is represented by two peaks (010)/(001) and (210)/(201), while short ranged magnetic correlations of *G* type are shown by the integrated intensity of the diffuse (110)/(101)peak. The peak indexing is given in the orthorhombic setting.

are $T_N \approx 180$ and 110 K for the reduced (G-type) and oxidized (C-type) Sr-based compositions, respectively. The Mn-Mn distance between the MnO₂ planes is about 8 Å, which is more than twice longer than the in-plane Mn-Mn distances. Due to the layered structure one could expect a two step change in the magnetic properties: at higher temperature due to the coupling within the layers, and at lower temperature because of interlayer tunneling interaction. However, the magnetic diffraction peaks with nonzero indices h [e.g., (101), (210)] and the same temperature dependencies of the (010)/(001) and (210)/(201) peaks justify the purely 3D character of the magnetic ordering. A specific feature of the oxidized composition Sr₂GaMnO_{5.5} is the presence of the short-ranged correlations of G type inside the dominant C-type magnetic structure. The temperature dependence of the integrated intensity of the G-type peak (110)/(101) is shown in Fig. 5. The diffuse peak starts to develop below the Néel temperature of the G-type structure $(\simeq 180 \text{ K})$. Then, below the transition to the long-range antiferromagnetic state of C type, the diffuse G-type peak is suppressed, but remains visible down to the lowest temperatures. This suggests that the C-type magnetic ordering suppresses the G-type antiferromagnetic fluctuations developed at higher temperatures.

The Bragg peak (210)/(201), corresponding to (1/2 1/2 1) for the P4/mmm, should not be present for the nuclear structure. This peak would be also extinct for the orthorhombic Ima2 symmetry; however it is experimentally observed above the Néel temperature with constant intensity (Fig. 5), implying that there are small deviations from the basic crystal structure given by P4/mmm. The analysis of this peculiarity is beyond the scope of the present paper. Presence of this nuclear peak reduces the accuracy of the Rietveld refined value of the ordered magnetic moment in the vicinity of the Néel temperature.

The temperature dependencies of the refined Mn magnetic moment value for the reduced and oxidized Sr-containing compounds are given in Fig. 6. The magnetic moment is also presented for the Ca₂GaMnO₅ sample, which possesses the same magnetic structure as the Sr-based reduced phase. The lines in Fig. 6 are fits to the phenomenological formula $M(T) = M(0) [1 - (T/T_N)^{\alpha}]^{\beta}$, which fits well to experimental M(T) at all temperatures. This formula gives the correct expression for M(T) in two limiting cases in the vicinity of $T_N[M(T) \sim ((T - T_N)/T_N)^{\beta}]$ and near T = 0. The Néel temperatures determined from the fit to the above formula are 183 and 160 K for the Sr- and Ca-based oxygen reduced compositions, respectively. Lower value of T_N in the Cabased sample can be caused by a slightly different crystal structure or different oxygen content (5.05 in a Ca-based structure vs 5.01 in a Sr-based structure). The low temperature saturated magnetic moments are $M(0) = 3.61(5)\mu_B$ for Ca_2GaMnO_5 and $3.16(6)\mu_B$ for Sr_2GaMnO_5 . The critical exponent β , representing the steepness of the M(T) curve in the vicinity of the Néel transition, amounted to 0.38(3) and 0.60(3) for the Ca- and Sr-based oxygen reduced compositions. The experimental values of β should be considered as very rough estimations, because in the fits to the phenomenological formula shown above we used all the experimental



FIG. 6. The ordered magnetic moments of Mn in Sr_2MnGaO_5 (squares), Ca_2MnGaO_5 (circles), and $Sr_2MnGaO_{5.5}$ (diamonds) as a function of temperature. The lines are the fits to the function described in the text.

points below T_N , rather than ones in a restricted temperature range near T_N . The β values give an idea of quantitative difference of M(T) behavior between the samples in the vicinity of T_N . β for the Ca-based sample has typical a value for a 3D Heisenberg antiferromagnet (β =0.36), while for the Sr-based one the exponent β is much larger. The possible reason for this unconventional temperature behavior of M(T) as well as the small saturated magnetic moment M(0)in Sr₂GaMnO₅ could be a disorder in the spin configuration, which is much higher in Sr-based sample as shown in the next section.

In the oxidized Sr₂GaMnO_{5.5} composition, the low temperature magnetic moment of the Mn⁴⁺ ion is 2.1(1) μ_B , being significantly less than the expected spin-only value of $3\mu_B$. This reduction of the *C*-type magnetic moment can be caused the presence of the short-ranged *G*-type fluctuations, which effectively reduce the number of the *C*-type ordered Mn spins. The temperature dependence of the magnetic moment M(T) is very different from the one observed in the reduced compositions. The β parameter is close to 1. The observable M(T) can be distorted by the temperature dependence of the long range ordered volume fraction v(T), because the moment *M*, obtained from the diffraction intensities, is reduced by the factor of $v^{1/2}$.

C. µSR results and discussion of the local magnetic disorder effects

In this section we present the results on the local magnetic field distribution studied in the μ SR experiments performed with the same samples. We concentrate on the comparative analysis of the μ SR and ND data with respect to the problem of the homogeneity of the local magnetic configuration. The spontaneous muon spin precession in a zero external magnetic field (ZF) was detected in all samples below the magnetic ordering temperatures, confirming the long range or-

dered state observed by neutron diffraction. 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 (much less than the internal magnetic field of several kGauss). 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. Above the Néel temperature the whole sample volume is in the paramagnetic state and the precession asymmetry is given by the total experimental asymmetry $a_{TF} = 0.261(2)$. The residual muon spin precession asymmetry at low temperature $a_{TF} = 0.009(2)$ (3% of the total asymmetry) corresponds well to the estimated fraction of the muon stops in the sample holder, implying that the whole sample volume is magnetically ordered in all the samples.

The examples of the ZF muon spin polarization function P(t) measured in the zero external field are shown in Fig. 7. The polarization function P(t) has two components P(t) $=a_1G(f_1,\sigma_1,t)+a_2G_2(f_2,\sigma_2,t)$. The first component with the precession frequency $f_1(0) \approx 23$ MHz in Ca₂GaMnO₅ (corresponding to $B_{\mu} \simeq 1.7$ kG) has a relatively small damping σ_1 , and corresponds to approximately 50% of the total asymmetry. The second component has a ~ 4 times higher precession frequency $f_2(0) \approx 88$ MHz, and complements the precession asymmetry to approximately the total value. Due to both the higher frequency and the damping of the second component, its parameters are determined with less accuracy than the parameters of the first component, which are reliably determined in the whole temperature interval. The two components correspond to two magnetically inequivalent muon sites in the crystal lattice. The same muon spin precession frequencies have been observed in Sr₂GaMnO₅ sample, possessing the same G-type antiferromagnetic structure. Below we discuss the first component of P(t).

Calculation of the dipole magnetic field from the Mn spins allows us to get an idea about the muon site in the crystal structure (contribution of the contact hyperfine field is assumed to be small, although it cannot be calculated theoretically). We assume that the muon is coupled with the oxygen ion, forming a typical μ -O bond of 1 Å. There are three oxygen ions in the given crystal structure: O1 in the MnO_2 plane, apical O2 oxygen just above the MnO₂ plane and O3 in the (GaO) buffer layer (see Table I). The required dipole field $B_{dip} = 1.7$ kG observed for the G-type magnetic structure can be found near apical oxygen O2 and in the MnO₂ plane near oxygen O1. Around O2 there are plenty of sites where the dipole field would match the experimentally measured magnetic field (the dipole field gradient is small ~ 1 kG/Å). One can choose the muon site which is most symmetric with respect to surrounding ions. Reasonable candidate could be near the plane going through the O2-O2 line perpendicular to the MnO₂ plane [e.g., at (0.187, 0.135, 0.097)in Sr₂GaMnO₅, taking 3.6 μ_B per Mn ion]. The unit cell of Ca_2GaMnO_5 is a bit smaller (a=15.30, b=5.47, c) = 5.27 Å), so the muon site in Ca_2GaMnO_5 where the dipole field is the same should be slightly shifted to keep similar distances to the Mn ions (otherwise assuming the same site the dipole field would be larger by +15%, implying that



FIG. 7. (a) Time dependence of the muon spin polarization P(t) in zero external field in the oxygen reduced compositions Ca₂GaMnO₅ and Sr₂GaMnO₅ (P(t) is shifted by -0.12) at T = 4 K. (b) P(t) in the oxidized sample Sr₂MnGaO_{5.5} at T = 4 and 90 K. P(t) for T = 90 K is shifted by -0.15.

there is noticeable contribution of the hyperfine contact field). One can also place the muon near the oxygen ion O1 [at (0.004, 0.344, 0.091)]. The dipole field is canceled between the Mn ions in the MnO₂ plane, and the field has very large values close to Mn ions. The field gradient is much larger (about 10 kG/Å), so there is less choice for the muon sites matching the experimental field near O1. The muon sites around O3 are less probable because of significantly smaller dipole fields.

In the oxidized composition $Sr_2GaMnO_{5.5}$, the muon spin precession frequency is approximately two times higher than that in the oxygen reduced composition (Fig. 8), reflecting a completely different local Mn-spin configuration around the muon site. The crystal structure of $Sr_2GaMnO_{5.5}$ has a different structure of the GaO layer, which can potentially give different muon sites in $Sr_2GaMnO_{5.5}$. Since the field gradient near O1 is very large one can easily find the muon site very close to the site in Sr_2GaMnO_5 with a two times larger



FIG. 8. (a) The spontaneous muon spin precession frequency in Sr_2MnGaO_5 (circles) and Ca_2MnGaO_5 (diamonds) and $Sr_2MnGaO_{5.5}$ (triangles) as a function of temperature measured in zero external field. The lines show the temperature dependencies of the ordered moments seen by neutron diffraction (from Fig. 6) scaled in order to match the f(0) value (for the reduced compositions, the solid line corresponds to the case of Ca_2GaMnO_5). (b) Temperature dependencies of the corresponding muon spin relaxation rates σ and (c) the precession asymmetries *a*. The lines are guides for the eye in (b) and (c). The arrows mark the Néel temperatures.

field. Assuming similar to Sr₂GaMnO₅ muon site near O2 (like in Sr₂GaMnO₅) one estimates that the magnetic moment of the Mn⁴⁺-ion in the *C*-type structure should be around $3\mu_B$, which also does not contradict the experimental data.

The experimental polarizations G(t) can be approximated by the analytical function¹⁹ corresponding to the Gaussian smeared internal magnetic field in a polycrystalline sample: $G(t) = \frac{1}{3} + \frac{2}{3}e^{-(\sigma t)^{2}/2} [\cos \omega t - (\sigma^{2}t/\omega)\sin \omega t]$, where the muon spin precession frequency $f = \omega/2\pi = \gamma_{\mu}/2\pi B_{\mu}$ is given by the modulus of local magnetic field acting on the muon averaged over the sample volume (γ_{μ} is the muon spin gyromagnetic ratio $\gamma_{\mu}/2\pi = 13.55$ MHz/kG). The muon spin relaxation rate σ is given by the Gaussian variance of the internal magnetic field $\sigma = \gamma_{\mu} \langle \Delta B^{2} \rangle^{1/2}$. The above mentioned formula is valid for any ratio σ/ω and has the Gaussian damped cosine function and the Kubo-Toyabe function as

the limiting cases for $\sigma/\omega \rightarrow 0$ and $\omega/\sigma \rightarrow 0$, respectively. An alternative analytical semi-empirical function of the polarization in the case of the Lorentzian distribution of the internal fields²⁰ reads: $G(t) = \frac{1}{3} + \frac{2}{3}e^{-\sigma t}[\cos \omega t - (\sigma/\omega)\sin \omega t]$. The actual internal magnetic field distribution in our samples is more complicated than the simple Gaussian or Lorentzian one. The experimental χ^2 is better for the Lorentzian G(t) in Ca₂GaMnO₅, but in Sr₂GaMnO_{5+ δ}, where the relaxation is larger, the χ^2 is slightly better for Gaussian G(t). The relaxation rates σ and the precession frequencies f practically do not depend on the choice of the relaxation function G(t). The asymmetries *a* are appreciably larger in the case of the Lorentzian G(t), implying that the values of the asymmetry are model dependent and cannot represent an absolute measure of the volume fraction occupied by the ordered state. However, we believe that the relative values of the asymmetries obtained with the same polarization functions can be compared between the different samples. Below we present the experimental parameters obtained from the fits to the Gaussian polarization function.

Figure 8 shows the precession frequencies f, the relaxation rates σ , and the precession asymmetries a of the first component as a function of temperature for all samples. The low temperature values of the frequencies in both Sr- and Ca-based oxygen reduced samples perfectly match each other, indicating that the locally averaged magnetic moments of the Mn-atoms are the same. On the other hand, the magnetic moment M, refined from the ND data in the Sr₂GaMnO₅ sample, is about 10% less than in the Ca one. One explanation could be that a part of the sample volume V $(\simeq 20\%)$, because the diffraction intensity is proportional to the VM^2) does not have the long range magnetic ordering. In this case the precession asymmetries would differ by $\simeq 20\%$. Experimentally, the precession asymmetries a at low temperature are equal within the experimental error bars in both oxygen reduced samples. The increase in the asymmetries with temperature is apparently connected with a systematic error caused by the Gaussian approximation of the internal field distribution. A second possibility is that there are violations of the long range ordering, which effectively reduce the average value of the magnetic moment M seen by ND, but only slightly change the average local magnetic field acting on the muon. This type of disorder can be realized as local spin-flips. In the G-type magnetic structure, two Mn moments can be locally coupled ferromagnetically along the x axis (as in the C-type structure). The superexchange interaction between MnO₂ planes is mediated by the geometry of the GaO layer, as shown in Sec. IV. Thus the disorder of the oxygen distribution in the (GaO) layer could be the possible reason for the local spin-flips. As a result, the observed magnetic moment will be reduced by a value proportional to the fraction of these casual incoherent "C-type" fluctuations (more strictly, the moment will be reduced by $\delta M/M = 2c$, where c is the fraction of the flipped spins). For the local magnetic field distribution these fluctuations give an increase in the field inhomogeneity, leaving the average local field intact for small concentration of the flips. This "configurational" disorder should be distinguished from the disorder when each Mn spin has a small disordered spin-glass-like component (e.g., a casual canting of the spin, or a fluctuation of the magnitude of the magnetic moment due to certain Mn^{4+} concentration). In this case the muon spin precession frequency would be given by the mean value of the magnetic moment M similar to ND, whereas the muon spin relaxation would be proportional to the magnitude of the disordered component. In the case of the "configurational" disorder the average dipole field is proportional to the local magnetic moment M_0 . The dipole field is determined by the nearest neighbors of the muon (1-2 coordination spheres), while the more distant spins give a very small contribution to the net dipole field because of their antiferromagnetic structure. Thus the average dipole field is very slightly affected by spin-flips with a small concentration c_f (when $c_f^{-1/3}$ is much larger than the radius of convergence of the dipole sum). Since the dipole field strength is proportional to $1/r^3$ (r is the distance to the flipped spin) the shape of the field distribution from the flipped spin should be Lorentzian-like for small c_f , and the field variance σ (hereafter we omit γ_{μ}) has to be proportional to the flipped spin concentration $\sigma \propto c_f M_0$. In the limit of large c_f the local field distribution has a more Gaussian-like shape because of the cancellation of the dipole fields from the distant spin-flips, however, the specific type of distribution can be quite complicated and is site dependent. It is obvious that the field variance $\sigma(c_f)$ should be a linear function of c_f , with a linear coefficient which does not depend on the muon site in the limit of small flip concentration c_f . This helpful feature of the local field distribution can be used to obtain a quantitative estimation of the c_f . To obtain specific values of the field variance for the given crystal lattice and the spin-flip concentrations we have done Monte Carlo calculations of the local field distribution in the muon sites in Sr₂GaMnO₅ mentioned above. The dipole field was calculated from the Mn spins in the volume of sphere with radius of 120 Å. The distribution of the dipole field component $B_i(i=x,y,z)$ is excellently fitted by Lorentzian function $\sim 1/[(B_i - B_{0i})^2 + \sigma^2]$ for a small flip concentration $c \leq 1\%$, where c is given relative to the Mn-spin concentration (Fig. 9). The Lorentzian shape of distribution gives a better fit in comparison with the Gaussian one up to c \simeq 5%, depending on the field component and muon site. The linear dependence $\sigma(c) = \alpha(c/100)M_0$ is well obeyed for concentrations below $c \approx 5\%$, with a mean value of α $\simeq 7 \text{ G}/\mu_B$. The average dipole field **B**₀ is practically constant for these concentrations.

The experimental muon spin polarization P(t) in Ca₂GaMnO₅, where the relaxation σ is small, has the exponential damping corresponding to the Lorentzian distribution in the limit of small c. In Sr₂GaMnO₅, where the relaxation rate σ [see Fig. 8(b)] is indeed much larger the local field distribution is changed to Gaussian one. The increase in relaxation $\Delta \sigma \approx 10 \mu s^{-1}$ corresponds to the field variance ≈ 230 G. Assuming a Mn³⁺ moment $M_0 \approx 4 \mu_B$, we estimate that the concentration of flips in Sr₂GaMnO₅ is larger by $c \approx 8\%$, that is, in reasonable agreement with the value of 5% obtained from the difference in the ordered magnetic moments seen in the ND experiment.



FIG. 9. An example of the distribution of the dipole field component B_z in the AF structure of Sr₂MnGaO₅ at the muon site near the apical oxygen O2 calculated with the Monte Carlo method for the spin-flip concentration c = 0.4%. The line shows the fit to the Lorentzian function. See the text for details.

The lines in Fig. 8(a) show the temperature dependencies of the ordered moments [from Fig. 6(a)], scaled to match the low temperature value of the muon precession frequency f(T=0). For the Ca₂GaMnO₅ sample, which has a little disorder, the temperature dependencies of the average magnetic moment M(T) (solid line) and the local magnetic moment given by the muon spin precession frequency f(T) are in satisfactory agreement. However, the increase in σ at T <100 K with the temperature lowering is not typical for an antiferromagnet, and could originate from the development of the disorder in the Mn-spin system similar to the one discussed above. In the Sr₂GaMnO₅ sample, the disorder in Mn spins given by σ is larger and, as we have shown above, reduces the average magnetic moment observed by ND. In addition, the reduced temperature dependencies of f(T) and M(T) are significantly different above 100 K. This difference can be connected with the decrease in the fraction of the "C-type" fluctuations with the temperature increasing above 100 K.

In the oxidized composition Sr₂GaMnO_{5.5}, the muon spin precession frequency f(T) and the magnetic moment M(T)seen in the ND experiment have completely different temperature dependencies above 70 K. The muon spin relaxation rate σ drastically increases above 70 K [Fig. 8(b)], and above 90 K the precession signal completely disappears, while the average ordered magnetic moment is still seen by ND until 100 K [Fig. 8(a)]. This is also illustrated in Fig. 7: the oscillations of the muon spin polarization P(t) at T = 90 K are strongly damped (the precession frequency f was fixed to zero). In addition, the asymmetry of the main oscillating signal starts to decrease above 60 K [see Fig. 8(c)], and a nonoscillating exponentially relaxing component develops, implying that the volume occupied by the main C-type phase is decreased with the temperature. This temperature behavior correlates with the increase in the intensity

of the G-type diffuse peak (Fig. 4) above 60 K observed in the ND experiment. The fact that the muon spin precession signal becomes strongly damped above 70 K means that the G-type fluctuations are also present locally as spin-flips inside the main C-type phase. Otherwise if the G-type phase would develop only in completely spatially separated regions then the muons localized in the C-type phase would preserve their coherent oscillations with the frequency proportional to the magnetic moment until the ordered moment of the C-type structure is seen in the ND experiment (i.e., up to the Néel temperature). One should keep in mind that in this transient temperature region, the magnetic moment M determined in the ND experiment is decreased by a factor proportional to the fraction of the Mn spins which are not ordered in the C-type structure. This provides an explanation of the unusual temperature dependence of the magnetic moment M(T) discussed in Sec. II. Above the Néel temperature, the ZF muon spin polarization P(t) has no relaxation (except from a small nuclear dipole contribution) and full asymmetry, implying the absence of magnetic correlations, which are static on the muon lifetime scale (10^{-6} s) . Hence the diffuse Bragg peak which is still well seen in the paramagnetic region (Fig. 5) originates from the short-ranged (40 Å as shown above) and dynamical G-type fluctuations. From the relaxation rate (λ $<0.1\mu s^{-1}$) above T_N one can estimate the low limit of the fluctuation frequency as $\nu > 10^{11}$ Hz, according to the formula for the fast field fluctuations¹⁶ $\nu \simeq 2(2 \pi f)^2 / \lambda$ (it is assumed that the width of the internal magnetic field distribution is approximately given by the muon spin precession frequency f, as $\langle \Delta B^2 \rangle^{1/2} = 2 \pi f / \gamma_{\mu}$.

IV. THEORY AND DISCUSSION OF THE MAGNETIC ORDERING TYPE

In this section we propose a theoretical model, which explains the transition from anti- to ferromagnetically coupled AF ordered MnO₂ planes by oxygen doping. In the reduced composition with $\delta \simeq 0.0$, the MnO₆ octahedra have longer distances between Mn ion and the apical oxygen ions as compared to that in the basal plane (Table I). Thus the orbital e_g doublet is split and the ground state configuration of Mn^{3+} ion is $(d_z t_{2g}^3)$. Though t_{2g} orbitals are also weakly split, in our semiquantitative analysis we avoid introducing new symmetry notation and retain the old one throughout the paper, i.e. t_{2g} , for this group of low-lying d orbitals of Mn ions. In the oxidized composition with $\delta \simeq 0.5$, the MnO₆ octahedra are only slightly distorted (Table I), implying very small splitting of the t_{2g} orbitals within the ground state configuration (t_{2g}^3) of Mn⁴⁺ ions. When varying δ , strong changes both in the Mn ion oxidation state and the structure of the nonmagnetic $GaO_{1+\delta}$ buffer layers lead to strong modifications in the basic magnetic interactions between Mn ions belonging to adjacent MnO₂ layers. The superexchange theory provides a firm basis for considering these modifications and explaining the observed magnetic ordering type.

A. Sr₂MnGaO₅, Ca₂MnGaO₅

Short-distant Mn-O-Mn superexchange (SE) hoppings of both e_g and t_{2g} electrons produce a strong in-plane antifer-



FIG. 10. Schematic representation of the exchange interactions in the Sr_2MnGaO_5 (a) and $Sr_2MnGaO_{5.5}$ (b). Only relevant orbitals for Mn^{3+} , Mn^{4+} , and O^{2-} ions are shown. Manganese and oxygen ions are shown as circles. Ga ions are shown as diamonds.

romagnetic (AFM) interaction of neighboring Mn ions. Though several more distant SE paths contribute to a magnetic exchange between Mn ions in the adjacent magnetic layers, only one apparently dominates. The relevant d_{z^2} orbitals for Mn^{3+} ions and $2p_7$ orbitals for oxygen ions are shown in Fig. 10(a). In this figure we use the following notation for the axes: x and y are the directions along Mn-O-Mn bonds in the MnO_2 layers, and z is the perpendicular direction. This dominant AFM exchange is due to σ overlaps of d_{z^2} orbitals of Mn_A and Mn_B ions with p_z orbitals of corresponding oxygens designated as O_A and O_B in Fig. 10(a). Orbitals of spatially close Ga ion can contribute to this SE process or provide paths, however; their inclusion would enhance the resulting total AFM exchange along the "vertical" bond because the Ga³⁺ ion has completely filled shells. The interlayer AFM coupling, together with ordinary AFM exchange in the basal MnO_2 plane, stabilize the observed G-type magnetic structure.

B. Sr₂MnGaO_{5.5}

There are two significant modifications induced by oxidation, both of which are important in explaining the observed magnetic structure in this compound. First, nearly all Mn ions are now $Mn^{4+}(t_{2g}^3 \text{ configuration})$, i.e., they have no e_g electrons with strong σ overlap with oxygen. The exchange interaction in the basal MnO₂ planes changes only quantitatively: it may become somewhat weaker because of the absence of $d_{z^2-p}(O) \cdot d_{z^2}$ exchange channel, but remains strongly AFM due to the short-distant t_{2g} -p(O)- t_{2g} overlaps. Second, a structure of the nonmagnetic buffer GaO layers is changed substantially: as shown in Fig. 2, the consecutive magnetic MnO₂ layers are now linked by GaO₆ octahedra, whereas some of these octahedra have missing oxygens in the GaO planes. Therefore, the magnetic interlayer interactions are expected to be changed drastically as well.

Let us examine a SE coupling between Mn ions belonging to adjacent magnetic layers. First we consider a connection through regular GaO₆ octahedra which occurs, at least locally, in the real material. In Fig. 10(b) a configuration for relevant d_{xz} orbitals of Mn and p_x and p_z orbitals of O ions is shown, which allows us to compare SE coupling along the "vertical" (Mn_A-O_A)-(O_R+O_L)-(O_B-Mn_B) bond with that for a shortest "diagonal" (Mn_A-O_A)-O_R-(O_C-Mn_C) one. We apply the perturbation SE theory to a minimal model including the relevant orbitals of intervening oxygens (O_R and O_L), and ignoring Ga orbitals. Possible effects of the latter will be discussed shortly later.

Taking into account the signs of the orbital lobes in Fig. 10(b) we define the following hopping parameters between neighboring oxygen *p*-orbitals: $t(p_x^A, p_z^L) = -t(p_x^A, p_z^R) = t(p_x^B, p_z^R) = t(p_$

$$H_{t}^{eff} = -t_{z}(d_{A}^{\dagger} + d_{B}^{\dagger})(p_{z}^{R} - p_{z}^{L}) - t_{x}(d_{A}^{\dagger} - d_{B}^{\dagger})(p_{x}^{R} + p_{x}^{L}) + d_{C}^{\dagger}(t_{z}p_{z}^{R} + t_{x}p_{x}^{R}) + \text{H.c.},$$
(1)

where the effective second-order hopping amplitudes $t_{z,x} = t_{\pi}^{pd} t_{z,x}^{pp} / \Delta$ are of the same sign. Here t_{π}^{pd} is a standard parameter for a hopping of an electron (hole) between the d_{xz} orbital of Mn and the p_x orbital of the nearest O ion (in the notation of Fig. 10), and $\Delta = |\epsilon_p - \epsilon_d|$ is the corresponding (insulating) charge-transfer energy. Energy levels of crystal-lographically different p-orbitals of oxygen ions in the cluster [Fig. 10(b)], are split due to the crystal field effects. This splitting is of minor importance and, hence, dropped in our minimal model. We introduce also Coulomb integrals U_d and U_p , and Hund's exchange constant $J_p > 0$ describing on-site electron (hole) interactions on d and p orbitals, respectively.

One can see from Fig. 10(b) that the "vertical" and "diagonal" magnetic coupling, for instance, through O_R -ion are determined by similar SE paths. However, these paths interfere in different way, destructively (for a "vertical" bond) or constructively (for a "diagonal" bond), which is controlled by a sequence of the hopping amplitude signs along particular paths. This results in a large difference between exchange constants J_{AB} and J_{AC} for the "vertical" and "diagonal" bonds, respectively. The problem can be viewed in another way. Actually, if one rotates both orbitals p_x^R and p_z^R , by an angle 45° about the y direction, approximately 90° and 180° bond geometries can be easily recognized for the "vertical" $Mn_A \ldots -O_R \ldots -Mn_B$ and "diagonal" Mn_A -... O_R ...- Mn_C bonds, respectively. Hence one can expect that the "diagonal" coupling is AFM and dominates the "vertical" coupling (which can be even a weak FM one).

To make the statement more explicit, let us first define the hopping difference $\delta t = (t_z - t_x)/2$ and their average $t = (t_z + t_x)/2$. Then by collecting all the SE paths contributing to the "vertical" coupling one obtains an expression for the isotropic exchange constant J_{AB} with two distinct terms, $J_{AB} = J_{AB}^{afm} + J_{AB}^{fm}$. The AFM term reads

$$J_{AB}^{afm} = \frac{16}{9} \frac{(2t)^4}{\Delta^2} \left[\frac{1}{\Delta} + \frac{1}{2\Delta + U_p} + \frac{2}{U_d} \right] \left(\frac{\delta t}{t} \right)^2, \quad (2)$$

while the FM one is

$$J_{AB}^{fm} = -\frac{2}{9} \frac{(2t)^4}{\Delta^2 (2\Delta + U_p)} \frac{2J_p}{2\Delta + U_p} \left[1 + \left(\frac{\delta t}{t}\right)^4 \right].$$
 (3)

Note that SE processes through the orbitals lying in (yz) plane lead to doubling of strength of Mn_A-Mn_B coupling, which is taken into account in Eqs. (2) and (3).

When $(\delta t/t) \rightarrow 0$, only the FM contribution [Eq. (3)] survives and the result strongly resembles that for 90°-bond geometry. As seen from Eq. (3), FM coupling is controlled by a small factor $2J_p/(2\Delta + U_p)$. This is the ratio of the energy of the singlet-triplet splitting for two electrons (holes) occupying orthogonal p orbitals of the same O ion to the energy of two electrons (holes) occupying the same p-orbital. In the real material under consideration, $Mn_A \dots -O_{R,L} \dots -Mn_B$ bonds deviate from the pure 90°-bond geometry. In our theory, this deviation is described by a small parameter $(\delta t/t)^2$ that controls the strength of the AFM contribution [Eq. (2)] to J_{AB} . In the present consideration, competition between AFM and FM contributions can formally result in exchange constant J_{AB} of any sign. To decide about a sign and a value of J_{AB} both the quantitative estimates within the present model and an inclusion into consideration of the relevant Ga orbitals are required. We expect, however, that Ga orbitals are energetically strongly separated from the oxygen p levels. In this case, their inclusion would give a rather weak AFM contribution in favor of the total AFM "vertical" coupling. In any case, the total exchange J_{AB} , even if AFM, will be strongly reduced.

As far as the "diagonal" bond is concerned, similar calculations lead to the following expression for exchange constant $J_{AC} = J_{AC}^{afm} + J_{AC}^{fm}$:

$$J_{AC}^{afm} = \frac{1}{9} \frac{(2t)^4}{\Delta^2} \left[\frac{2}{2\Delta + U_p} + \frac{1}{U_d} \right] \left[1 + \left(\frac{\delta t}{t} \right)^2 \right]^2, \quad (4)$$

$$J_{AC}^{fm} = -\frac{2}{9} \frac{(2t)^4}{\Delta^2 (2\Delta + U_p)} \frac{2J_p}{2\Delta + U_p} \left(\frac{\delta t}{t}\right)^2.$$
 (5)

In the limit $(\delta t/t) \rightarrow 0$, the expression for J_{AC} takes on the form well known for 180°-bond geometry with strong AFM exchange. Even if the parameter $\delta t/t$ is finite, the FM term [Eq. (5)] gives a small correction to this exchange. Like in the case of the "vertical" bond, an inclusion of Ga orbitals would lead to an additional weak AFM contribution, thus enhancing the total AFM exchange along the "diagonal" bond.

The experimentally observed magnetic structure is of *C* type (i.e. FM ordering along z-direction). In view of apparently strong AFM interaction in the MnO₂ plane, this structure becomes evident for the AFM "diagonal" coupling and the FM "vertical" bond. In the case of the weak AFM "vertical" bond, one has to compare the stabilization energy $z_d J_{AC}$ (z_d is a number of operating "diagonal" bonds per

site) with the frustration energy J_{AB} per site. If the GaO₆ octahedra (Fig. 2) are regular, $z_d = 4$, and the ratio of the two energies is given by $4J_{AC}/J_{AB}$: hence the dominant exchange J_{AC} stabilizes the *C*-type magnetic state. A random oxygen vacancy in GaO layer, first, breaks a "diagonal" bond, $z_d \rightarrow 3$ and, second, reduces a "vertical" exchange constant $J_{AB} \rightarrow 5J_{AB}/8$. Therefore for the given J_{AC} and J_{AB} the above mentioned ratio even increases and our arguments in favor of the stability of the *C*-type state remains valid for the real structure with the oxygen vacancies in GaO layers.

V. SUMMARY

Crystal and magnetic structures of new complex manganese oxides $Sr_2GaMnO_{5+\delta}$ $(\delta \approx 0.01, 0.52)$ and Ca₂GaMnO_{5+ δ} ($\delta \approx 0.05$) were studied by neutron powder diffraction (ND) and μ SR technique. The crystal structures belong to a brownmillerite type and consist of alternating SrO, MnO₂, SrO, and GaO_{1+ δ} layers. The compounds have orthorhombic (Ima2 or Imcm, Pnma space groups) and tetragonal (P4/mmm) crystal lattices for oxygen reduced and the oxidized compositions respectively. The principal difference between the $\delta \simeq 0(Mn^{3+})$ and $\delta \simeq 0.5(Mn^{4+})$ compounds is structure of $(GaO_{1+\delta})$ buffer layer, which is formed by tetrahedra or partially filled octahedra. The space group choice for the oxygen reduced composition is mainly determined by the ordering type of the GaO₄ tetrahedra. In both oxygen reduced and the oxidized composition a certain disorder in the oxygen positions in the $GaO_{1+\delta}$ -layer is very well seen from the neutron diffraction data.

The Mn-Mn distance between the MnO_2 planes is about 8 Å, which is more than two times larger than interplane Mn-Mn distances. In spite of the layered crystal structure the magnetic ordering is 3-dimentional with the Néel temperatures $T_N = 183$ and 160 K for the Sr- and Ca-based oxygen reduced compositions, respectively. The lower T_N in the Cabased sample can be caused by the different oxygen content and slightly different interatomic distances. In the oxidized Sr₂GaMnO_{5.5} composition the Néel temperature amounts to $T_N \simeq 110$ K. The magnetic moments of Mn are coupled antiferromagnetically in MnO₂ plane, but antiferromagnetically (G type) or ferromagnetically (C type) between the planes in the reduced and oxidized compositions respectively. The notations for the magnetic structures are in accordance with the classification used in the 3D perovskitelike manganese oxides. On the basis of superexchange theory we show that the transition from the antiferro- to ferro-coupled MnO₂ planes by the oxygen doping is driven by the strong diagonal 180° superexchange AFM interaction between Mn⁴⁺ ions (t_{2g}^3) in the adjacent layers through additional (octahedrally coordinated around the Ga ion) oxygen atoms in the GaO buffer

layer: more distant ("diagonal") interlayer antiferromagnetic superexchange dominates the shortest ("vertical") one. This is mainly caused by a constructive or destructive interference of superexchange paths through a specially arranged lattice of oxygen ions within the nonmagnetic buffer $(GaO_{1+\delta})$ layers. Numerous interlayer "diagonal" bonds stabilize the resulting *C*-type magnetic structure, and suppress frustration effects which may arise due to weaker (presumably antiferromagnetic) "vertical" bonds.

The low temperature saturated magnetic moments are $M(0) = 3.61(5)\mu_B$ for Ca₂GaMnO₅, $3.16(6)\mu_B$ for Sr_2GaMnO_5 , and 2.1(1) μ_B for $Sr_2GaMnO_{5.5}$. The magnetic moments in Sr-based samples are appreciably reduced in comparison with the spin-only values of the corresponding Mn ion. By using complementary information on local magnetic field distribution from μ SR we quantitatively show that the reduced value of the long range ordered magnetic moment seen by ND in Sr₂GaMnO₅ is caused by the presence of magnetic disorder due to locally flipped Mn-spins in the neighboring MnO₂ planes. From both ND and μ SR data we also show that in Sr_2GaMnO_{55} , the Néel state of C type has a temperature dependent contribution from short-ranged $(\sim 40 \text{ Å})$ antiferromagnetic correlations preserving the G-type magnetic structure of the reduced ($\delta = 0$) composition. The reduction of the C-type ordered magnetic moment is caused by the presence of these short-ranged G-type fluctuations, which effectively reduce the number of C-type ordered Mn spins. The contribution of the short-ranged G-type fluctuations appears below $\simeq 180$ K and then decreases near 100 K, suggesting that the C-type magnetic ordering suppresses the G-type AFM fluctuations developed at higher temperatures. The spin flips and the short-ranged magnetic phase can be caused by the disorder observed in the oxygen positions of the GaO_{1+ δ} layer, because the coupling between the MnO₂ layers is mediated by the geometry of the superexchange path through these oxygen atoms.

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