Crystal and magnetic structures, unconventional superexchange interactions and disorder effects in $A_2MnGaO_{5+\delta}$ (A=Sr,Ca) layered oxides

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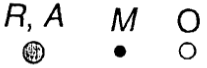
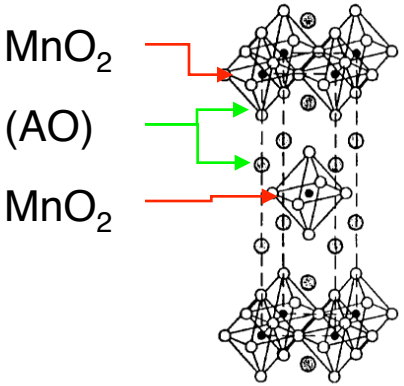
Why A_2MnGaO_{5+x} (A=Sr, Ca)? Manganese oxides with possible CMR

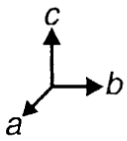
Raddlesden Popper (RP) phases, $(R,A)_{n+1}M_nO_{3n+1}$

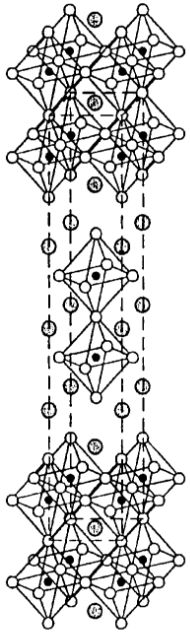
$\ldots(MnO_2)_n-(AO)\ (AO)-(MnO_2)_n\ldots$



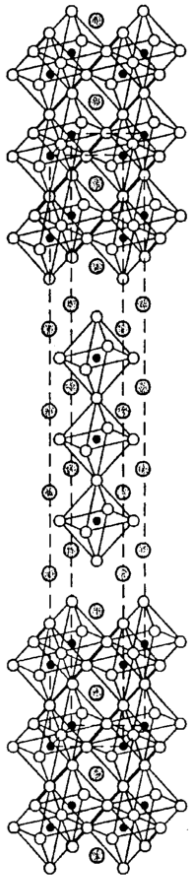


$LaSrMn^{3+}O_4$/
$Sr_2Mn^{4+}O_4$

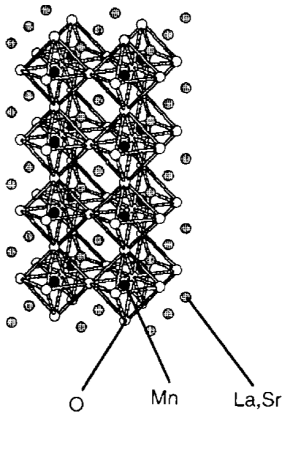




$La_2Sr_1Mn^{3+}{}_2O_7$/
$La_1Sr_2Mn^{4+}{}_2O_7$



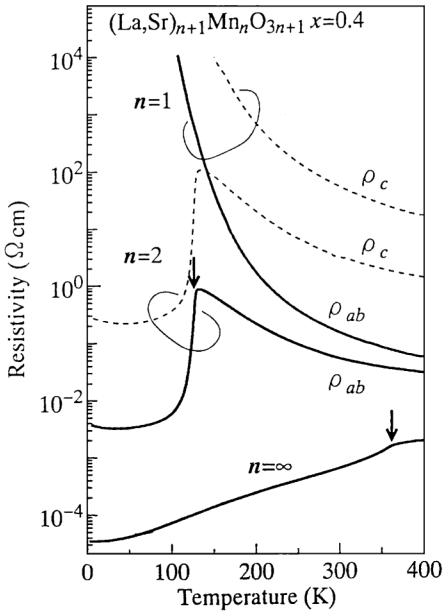
3D Mn-O network

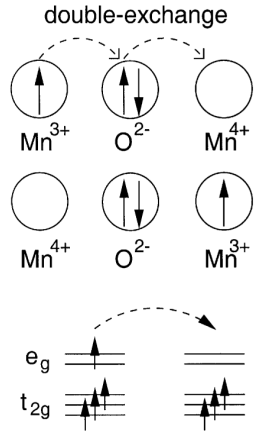


$n=\infty$

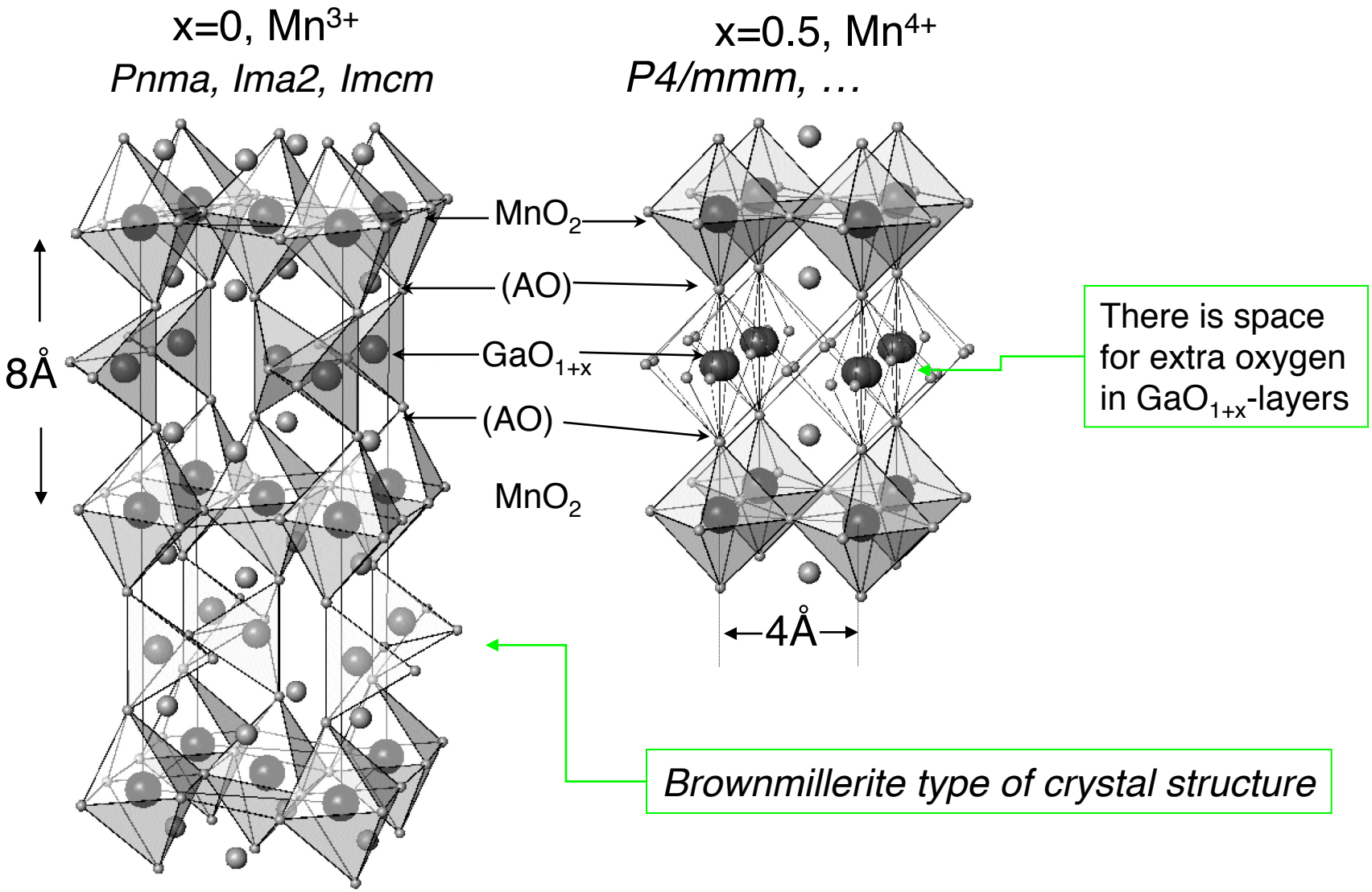
$LaMn^{3+}O_3$/
$SrMn^{4+}O_3$

n=1	n=2	n=3	n=∞
$(R,A)_2MO_4$	$(R,A)_3M_2O_7$	$(R,A)_4M_3O_{10}$	$(R,A)MO_3$





Three buffer (AO) layers: brownmillerite structures of A_2MnGaO_{5+x} (A=Sr, Ca)

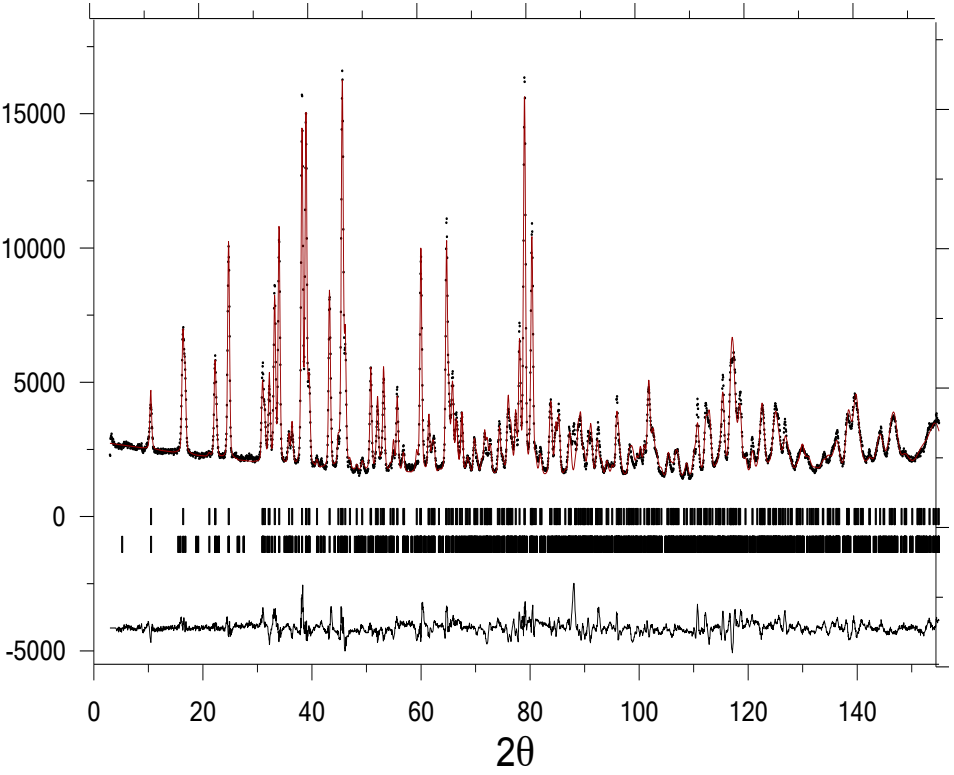


Neutron diffraction. Crystal structure

HRPT/SINQ, λ =1.5 Å, Sr_2MnGaO_{5+x}, T=10K

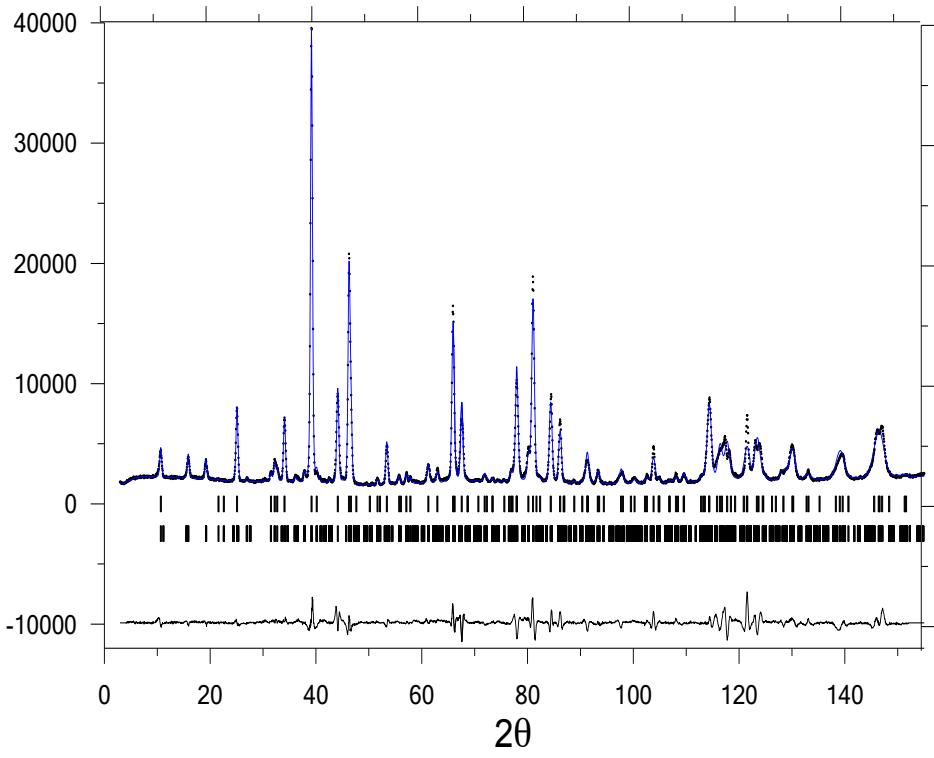
x=0

- *Ima2*
- *Imcm* with disorder in GaO_4 tetrahedra

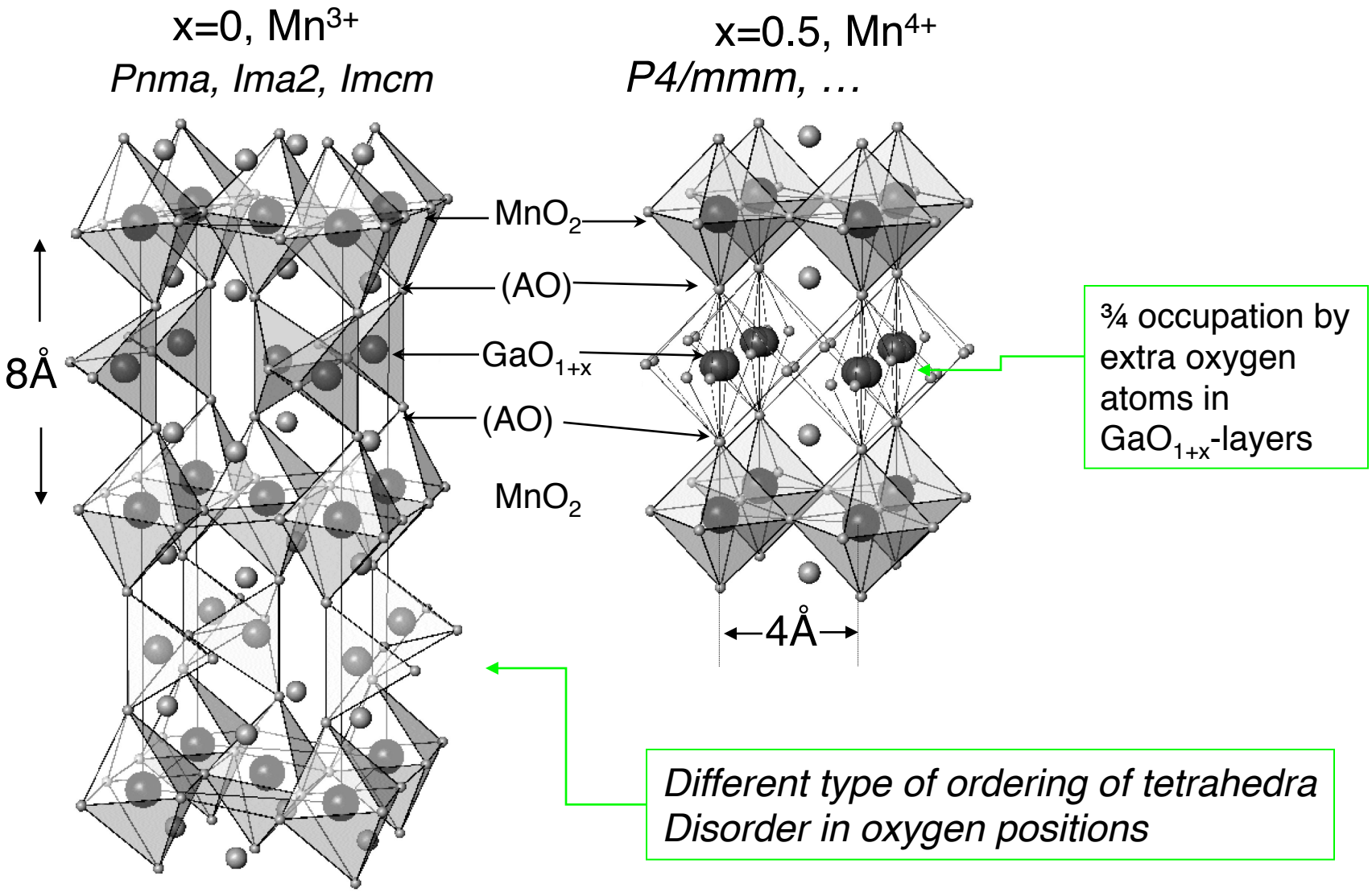


x=0.5

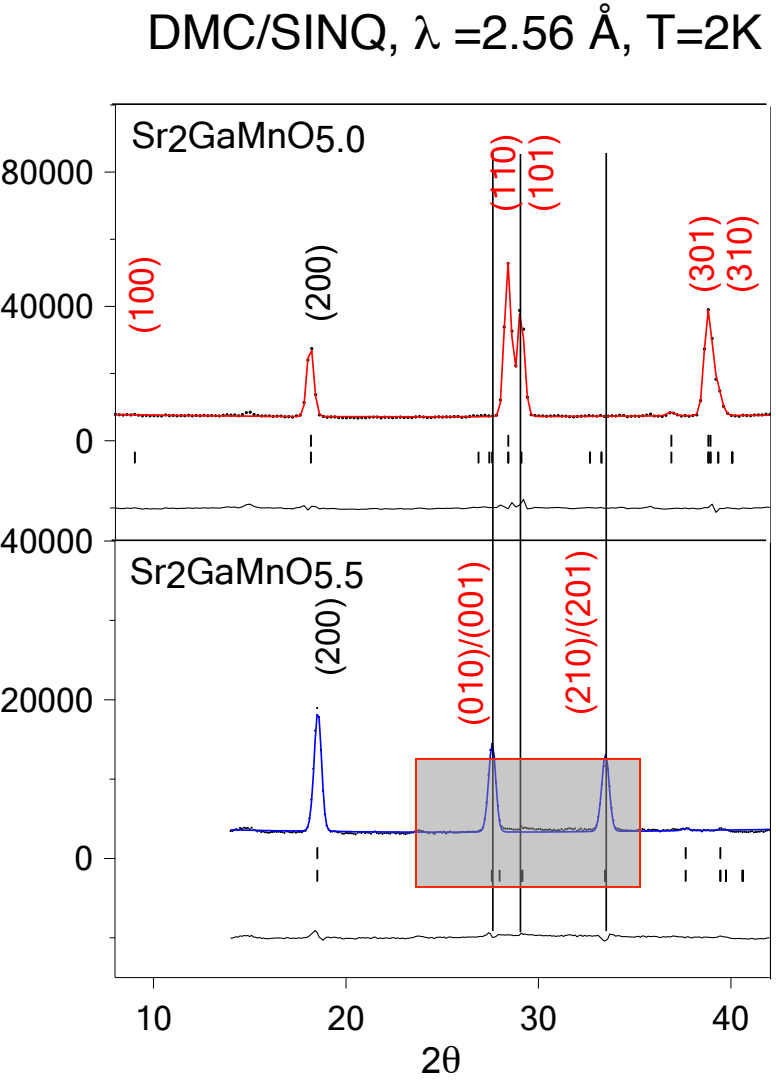
P4/mmm with partially filled GaO_6 octahedra

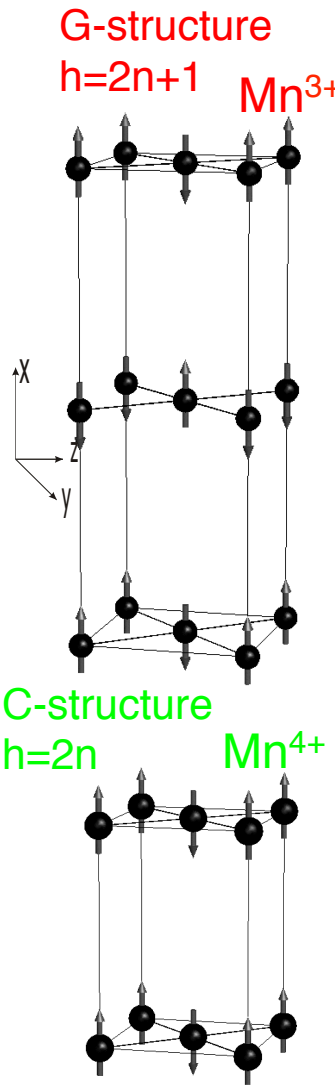


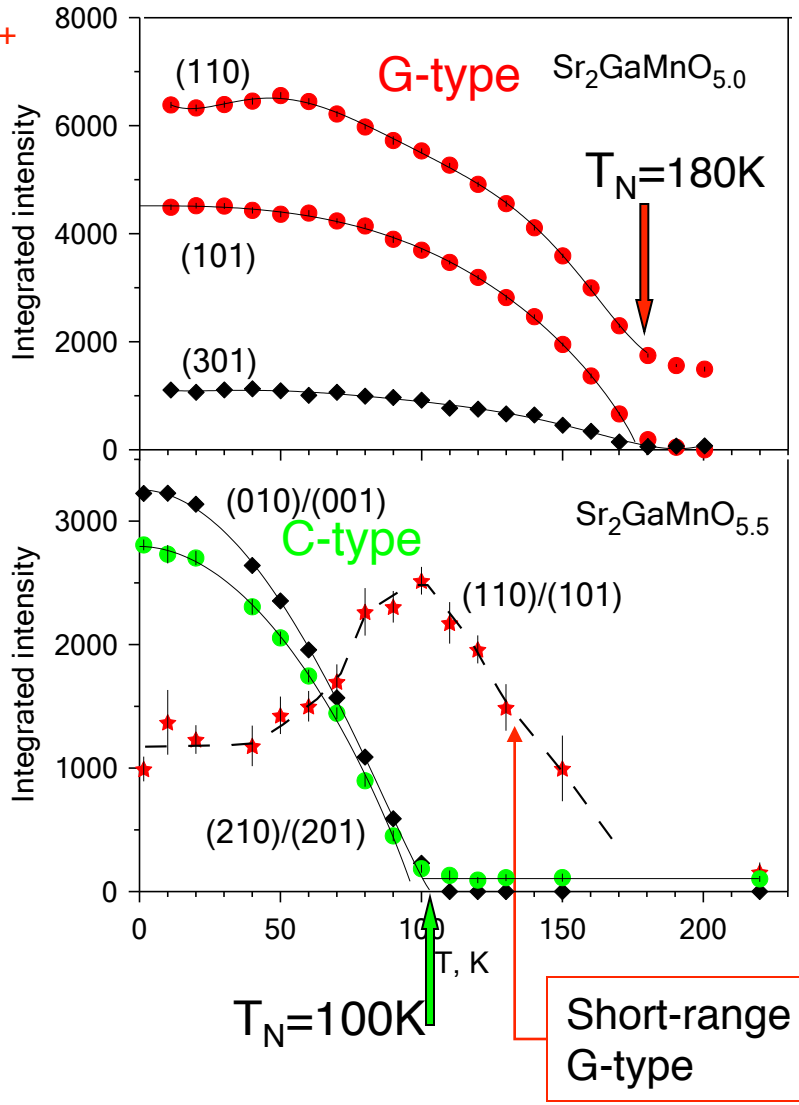
Crystal structures of Sr_2MnGaO_5, Ca_2MnGaO_5 and $Ca_2MnGaO_{5.5}$



Neutron diffraction. Magnetic structure

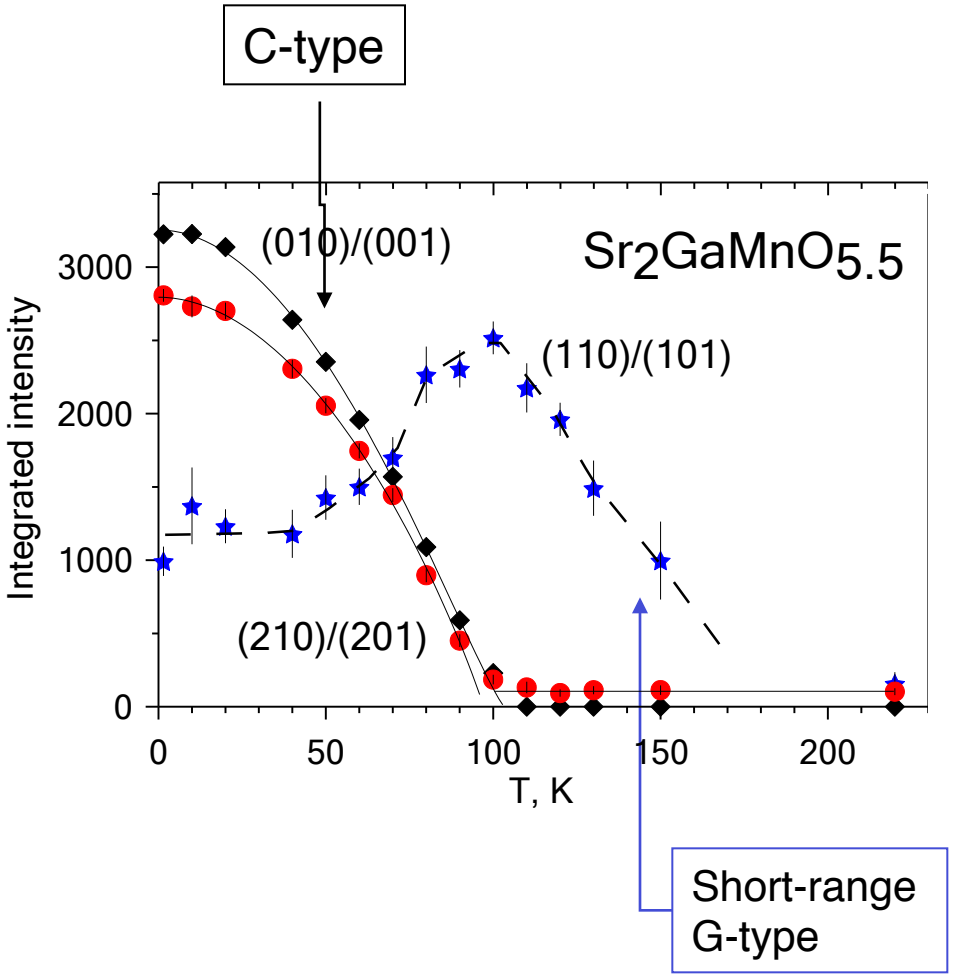


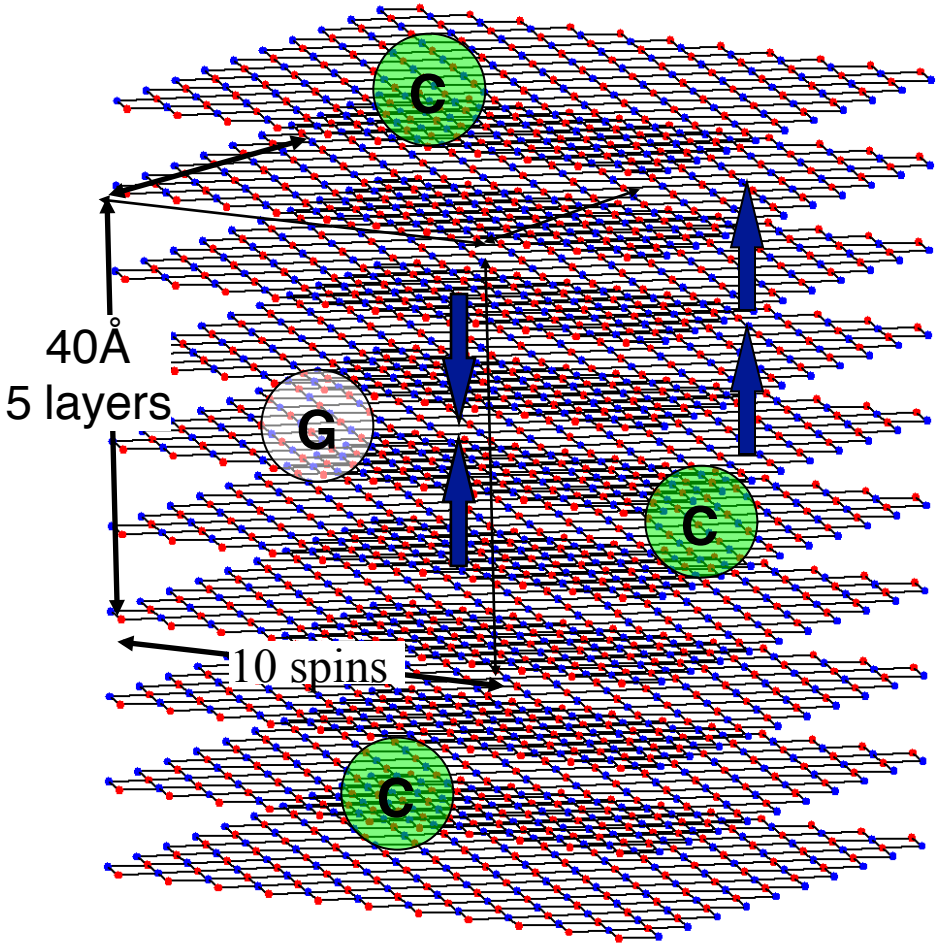




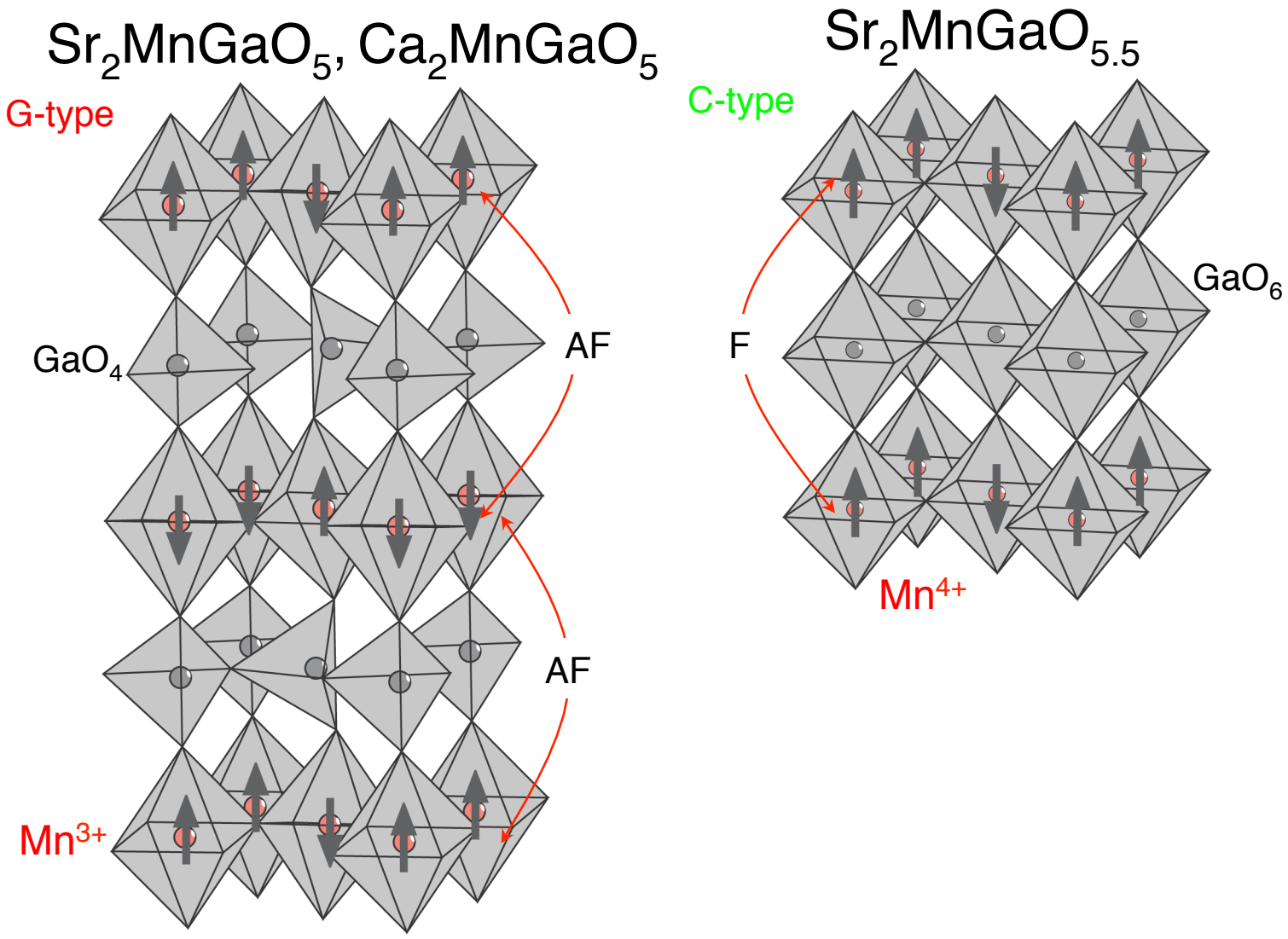
NSCmr2002, PSI, Villigen

Short range ordering effects



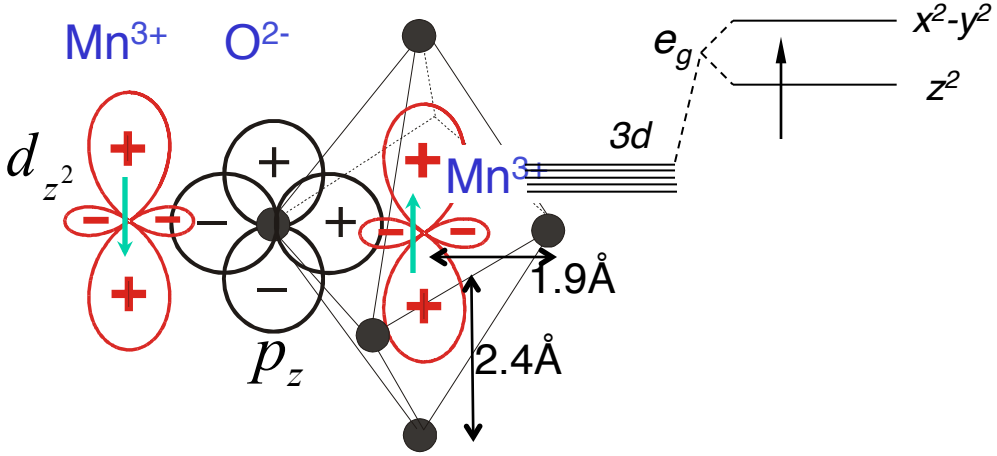


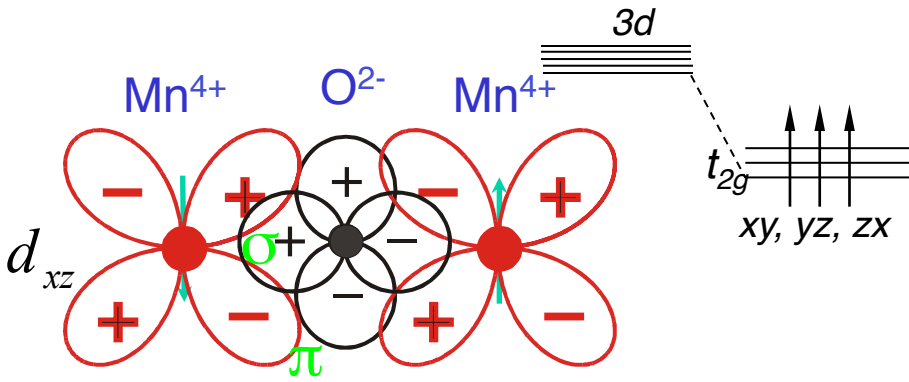
Magnetic and crystal structures



AF in-plane superexchange (SE)

Antiferromagnetic MnO_2 planes both for Mn^{3+} and Mn^{4+} in accord with standard SE.

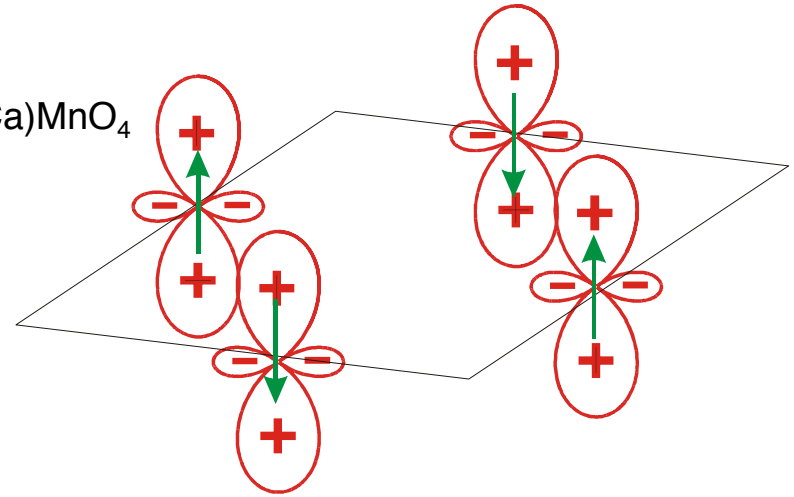


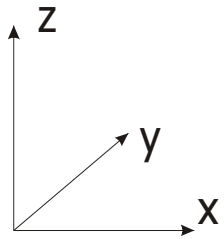


Similar to $CaMnO_3$

Similar to RP phase (n=1) (SrCa)MnO_4

$Mn^{3+}O_2$ plane

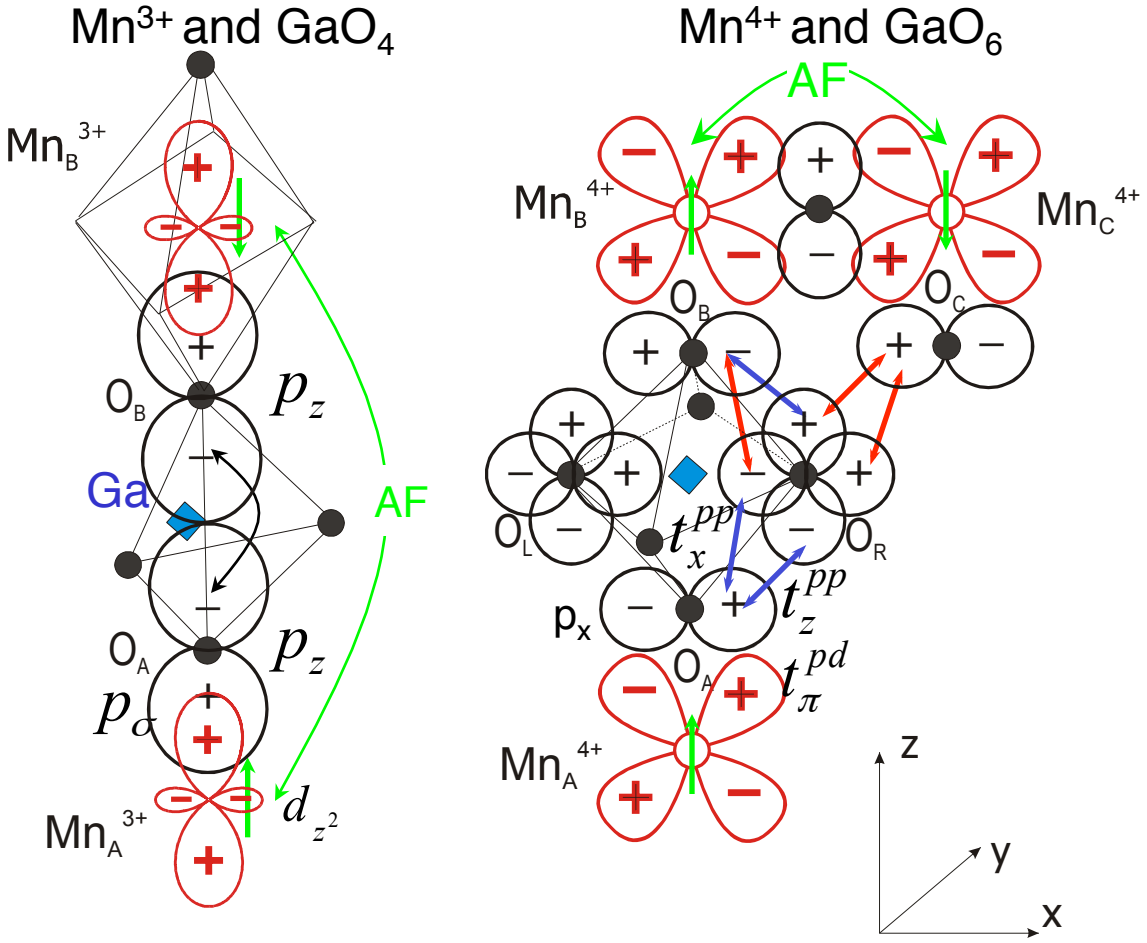




Interplane Mn-O-O-(O)-Mn superexchange

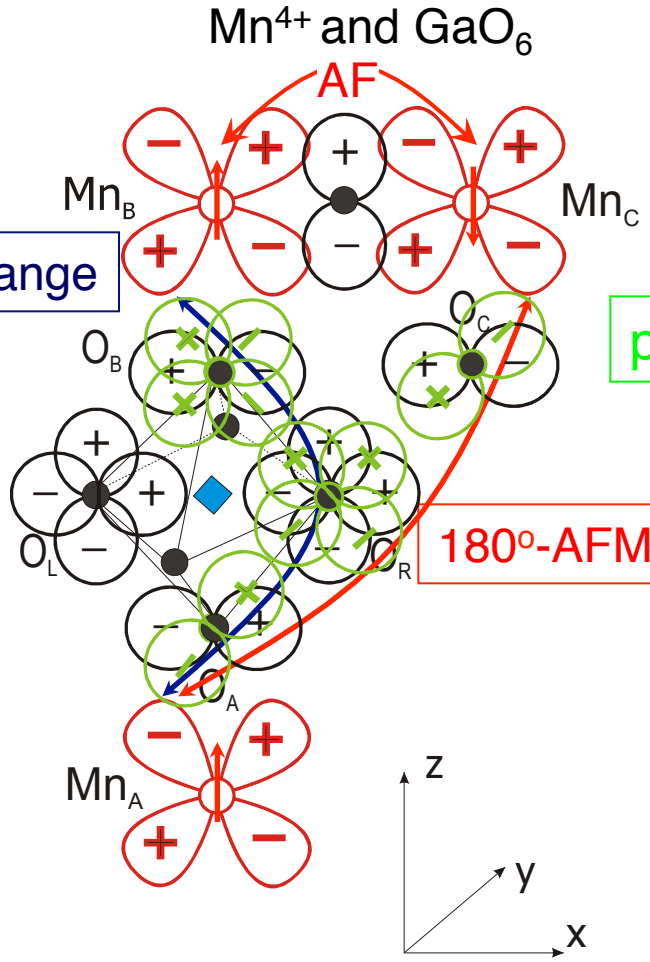
180°-AFM superexchange

Unconventional "diagonal" superexchange



Interplane Mn-O-O-(O)-Mn superexchange

Unconventional “diagonal” superexchange



90° weak FM superexchange

p_x, p_z orbitals rotated by 45°

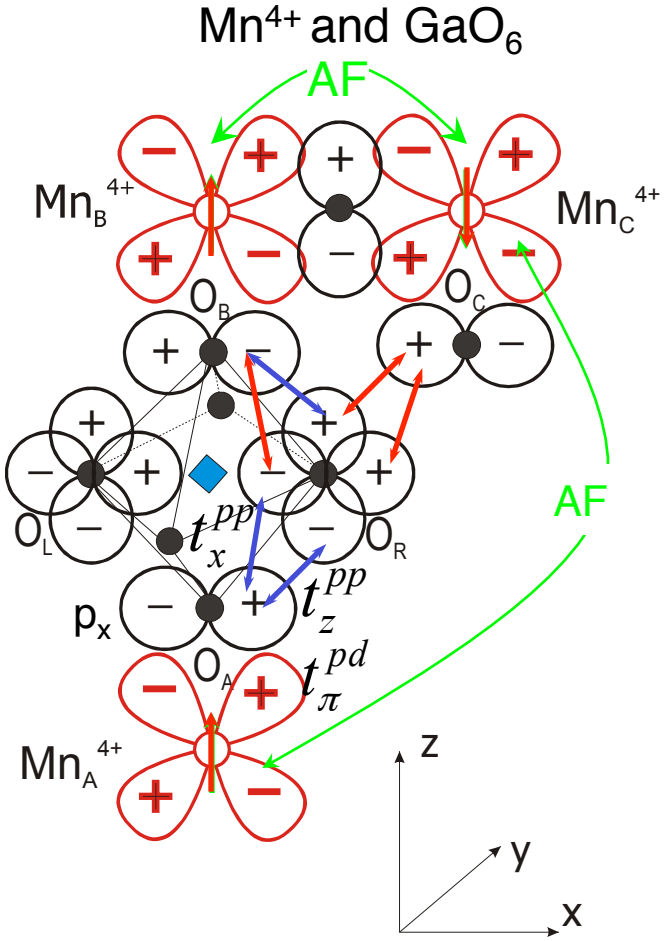
180°-AFM superexchange

Interplane Mn-O-O-(O)-Mn superexchange

Unconventional “diagonal” superexchange

$$t_x = t_\pi^{pd} t_x^{pp} / \Delta$$

$$\delta t = (t_x - t_z)/2$$



Vertical SE Mn_A–Mn_B

weak FM $\sim \frac{2J_p}{2\Delta+U_p}$

weak AFM $\sim \left(\frac{\delta t}{t}\right)^2$

Diagonal SE Mn_A–Mn_C

weak FM $\sim \frac{2J_p}{2\Delta+U_p}\left(\frac{\delta t}{t}\right)^2$

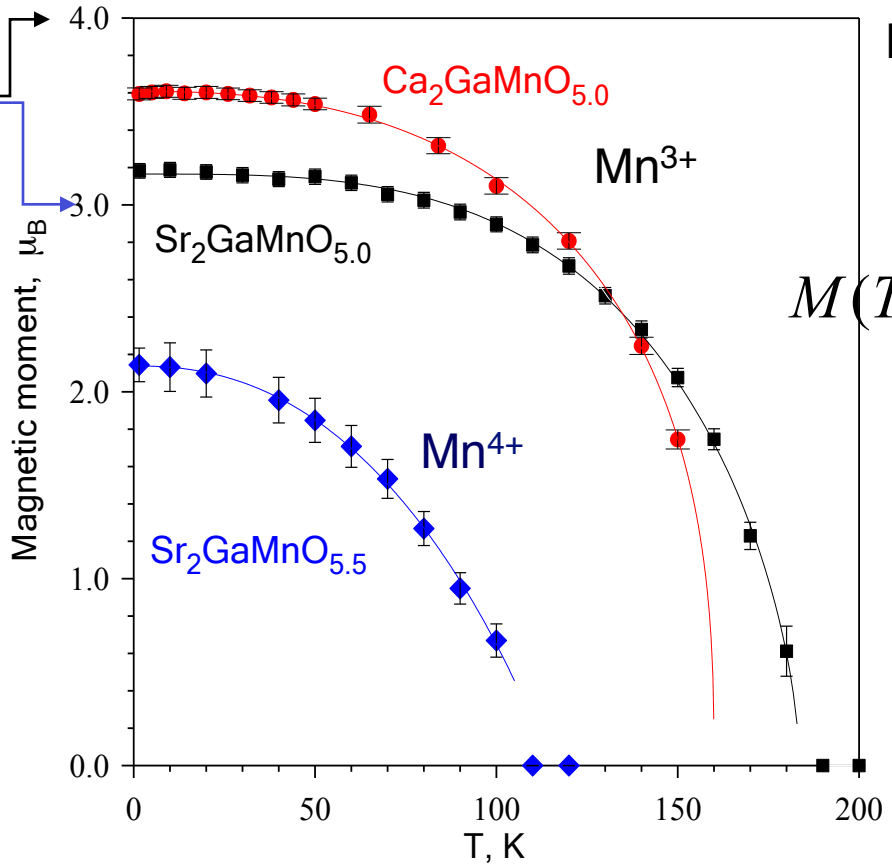
AFM $\sim \frac{(2t)^4}{\Delta^2}\left(\frac{2}{2\Delta+U_p}+\frac{1}{U_d}\right)$

Magnetic moments of Mn^{3+} and Mn^{4+}

Spin-only values

Mn^{3+}

Mn^{4+}



DMC/SINQ

$$M(T) = M_0(1-(T/T_N)^{\alpha})^{\beta}$$

Magnetic moment seen by neutron diffraction is appreciably reduced -- local disorder, hybridization?

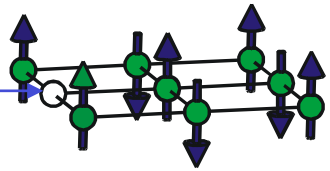
M_{eff} accessed by neutron diffraction

Effective magnetic moment $M_{eff} = M_0 \xi \sqrt{v}$

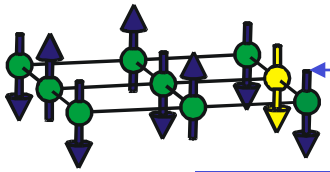
real moment

volume fraction

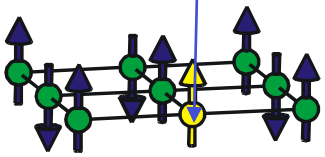
effective occupancy



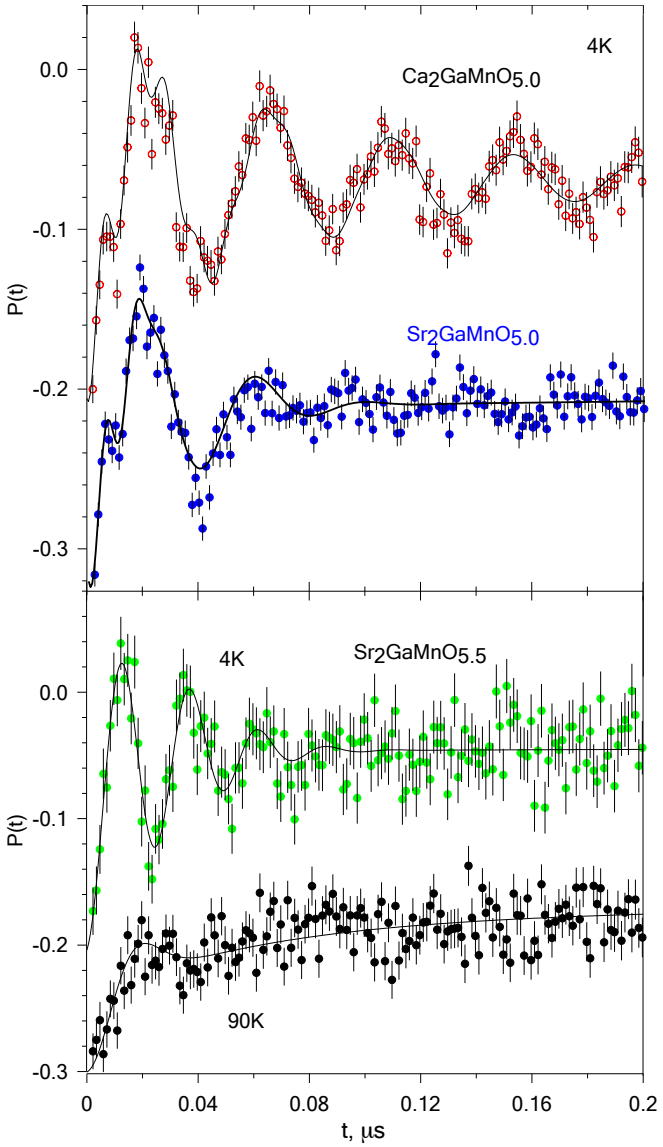
Spin vacancy



Spin flips: $M=M_0(1-2c)$



Local magnetic field distribution seen by μSR



Muon spin polarization P(t) below T_N

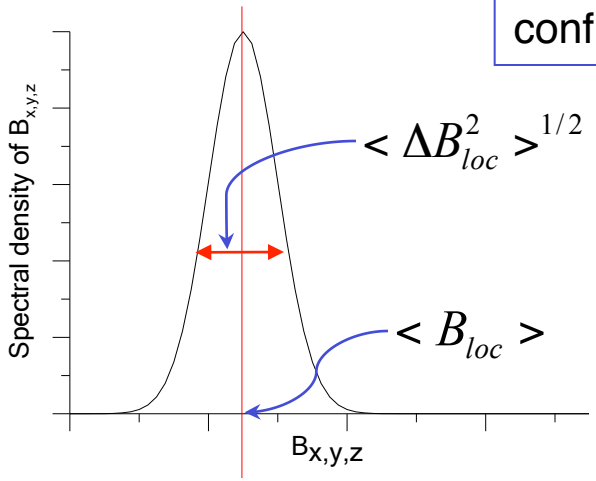
$$P(t) = \sum_{i=1}^{2} a_i G(t, f_i, \sigma_i)$$

$$G(t) = \frac{1}{3} + \frac{2}{3} e^{(\sigma t)^2/2} (\cos \varpi t - \sigma^2 t / \varpi \sin \varpi t)$$

$\varpi = 2\pi f \sim < B_{loc} >$ — Coherent precession – long range ordering of Mn-spins

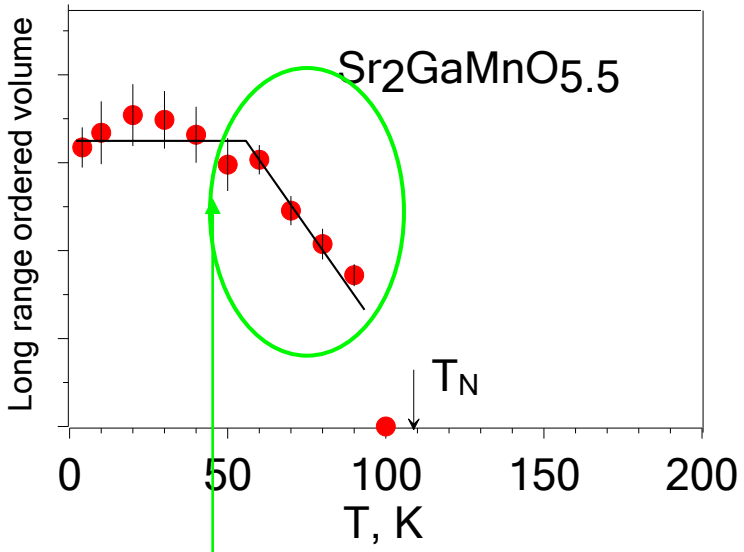
$\sigma \sim < \Delta B_{loc}^2 >^{1/2}$ — Muon spin relaxation – disorder of Mn-spin configuration/value/direction

$a \sim$ ordered fraction

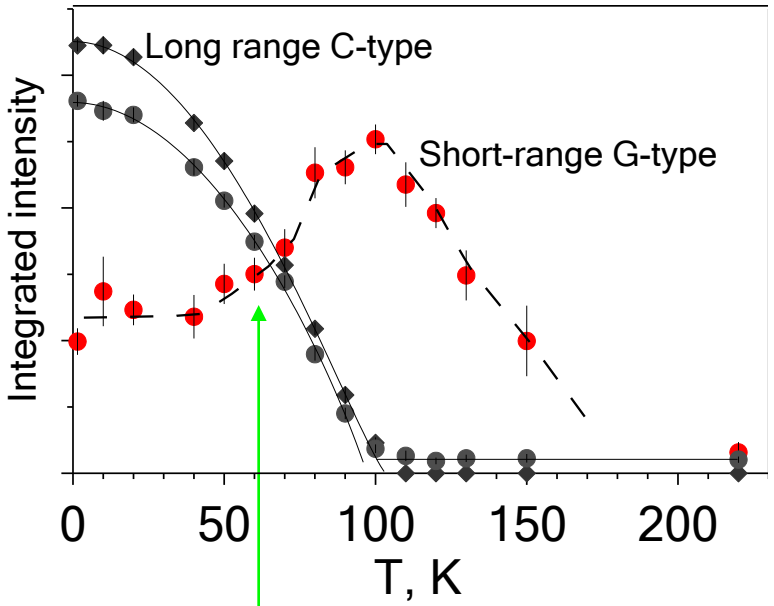


Short range magnetic ordering in $Sr_2MnGaO_{5.5}$

From ZF μSR-precession amplitude



ND integrated intensities

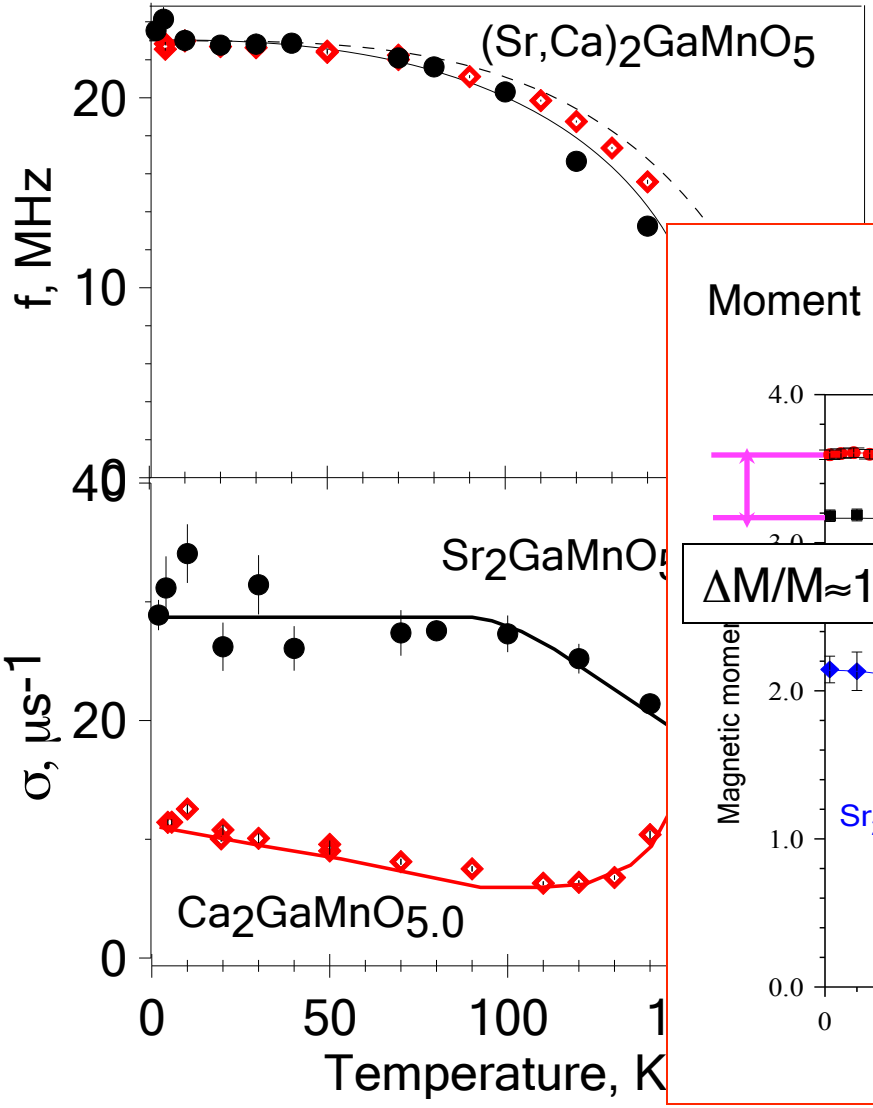


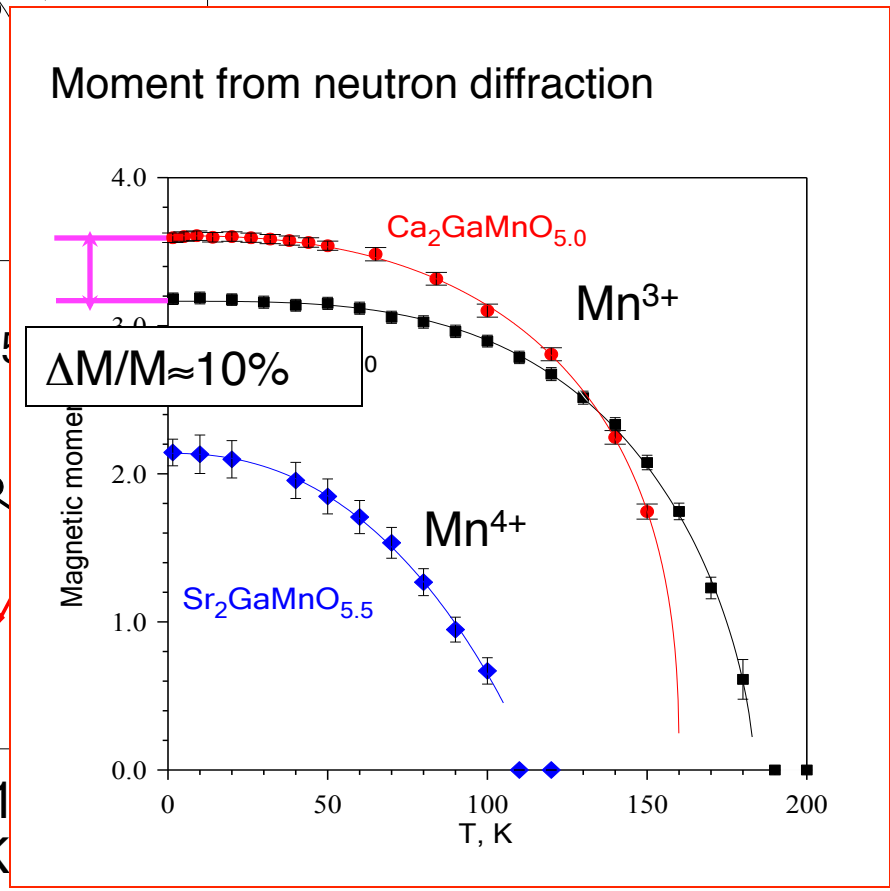
Volume fraction decreased – second phase develops spatially separated

Local field distribution in Sr_2MnGaO_5 and Ca_2MnGaO_5

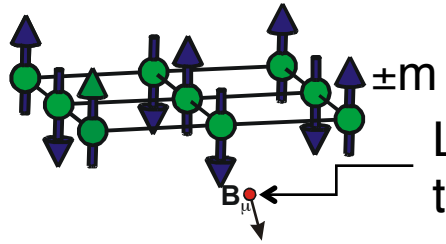
Frequency

Relaxation rate





Configurational disorder



Local field at the muon

Convergence radius of the dipole sum

$$\mathbf{B}_{\text{loc}} = \sum_{\mathbf{m}(\mathbf{r})}^{r<r_L} \mathbf{B}_{\text{dip}}$$

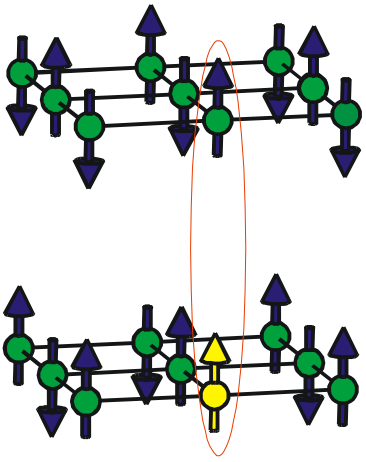
$$\mathbf{B}_{dip} = 3\frac{(\mathbf{mr})\mathbf{r}}{r^5} - \frac{\mathbf{m}}{r^3}$$

1. If $c^{-1/3} \gg r_L$ then: $< B_{loc} > \propto m$

2. Disordered field from the flipped spin

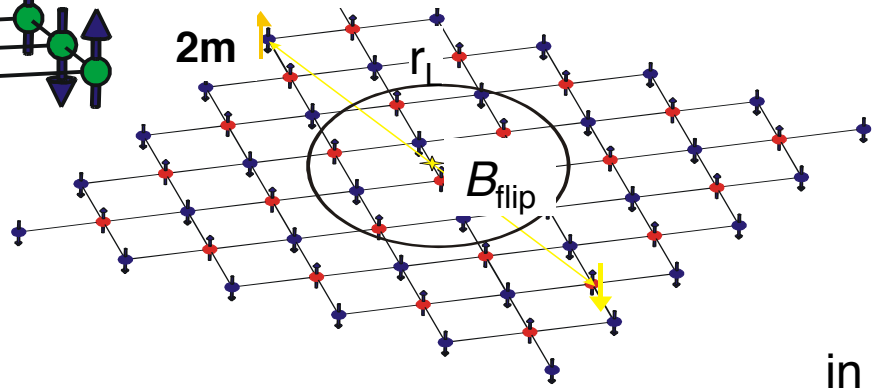
$$B_{flip} \sim \frac{2m}{r^3}$$

c<<1



Disorder of spin-configuration:

Spin-flips with concentration *c*



Lorentzian field distribution

$$\Delta B_{loc} = \sigma \sim \frac{m}{r_{flip}^3} = \alpha \cdot (c/100) \cdot m$$

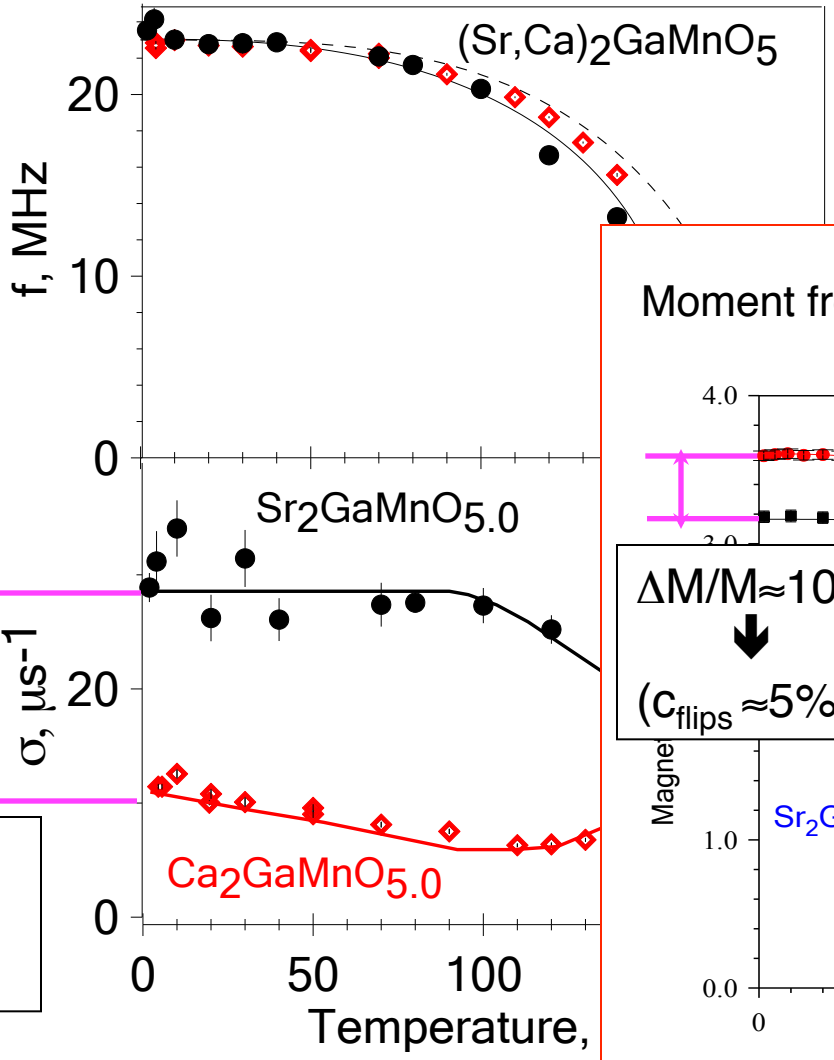
Independent on muon site

in $(Ca,Sr)_2MnGaO_5$: $\alpha \approx 7$ G/μ_B ($c \leq 5\%$)

Local spin-flips in Sr_2MnGaO_5 and Ca_2MnGaO_5

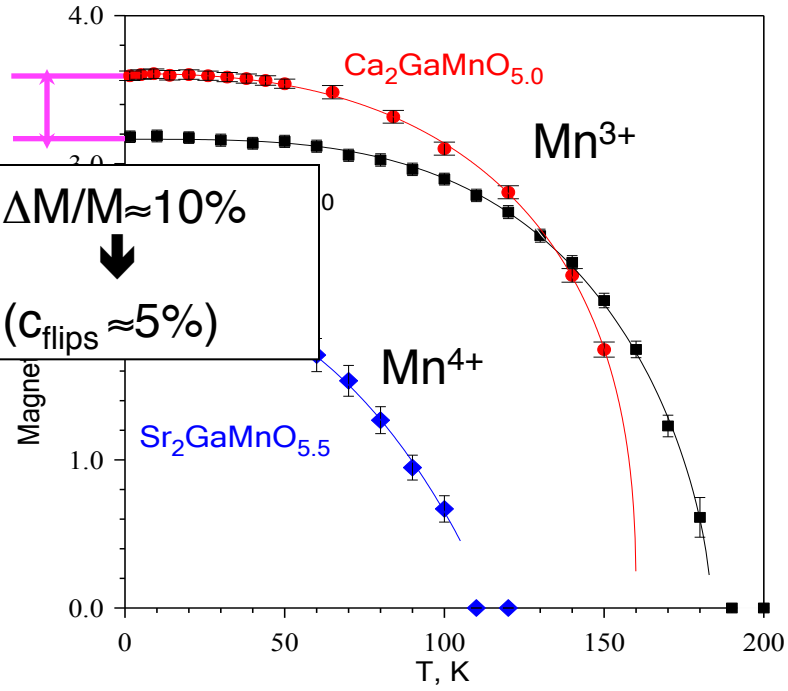
Frequency

Relaxation rate



$\Delta\sigma \approx 230G$ ⬇ $c_{flips} \approx 8\%$

Moment from neutron diffraction



$\Delta M/M \approx 10\%$ ⬇ $(c_{flips} \approx 5\%)$

Summary

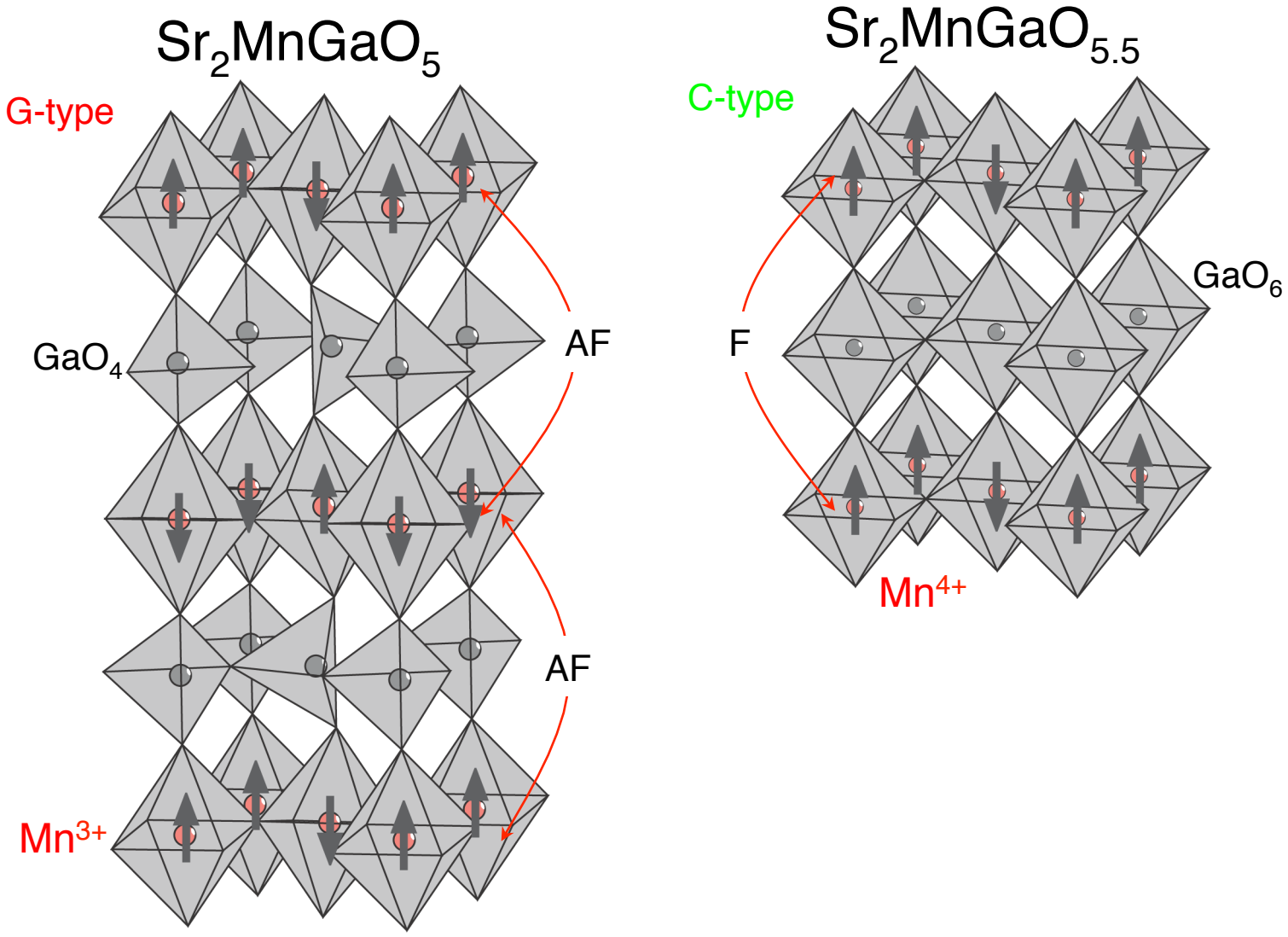
- Novel manganese layered oxides $A_2MnGaO_{5+\delta}$ (A=Sr,Ca) with adjustable Mn^{3+}/Mn^{4+}-valence: synthesis and structure.

- The principal structure difference between the $\delta\approx0$ (Mn^{3+}) and $\delta\approx0.5$ (Mn^{4+}) is $GaO_{1+\delta}$ buffer layer, which is formed by tetrahedra or partially filled octahedra

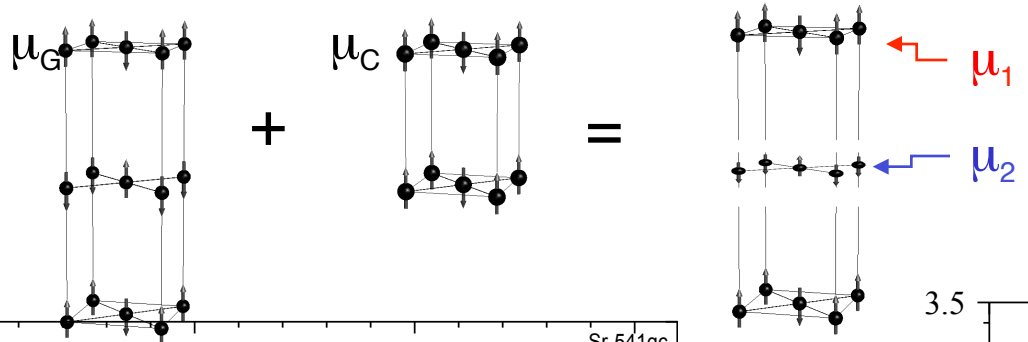
- AFM ($\delta\approx0$) --> FM ($\delta\approx0.5$) coupling between the AFM ordered MnO_2-layers. Unconventional diagonal superexchange Mn^{4+}-O-O-O-Mn^{4+}

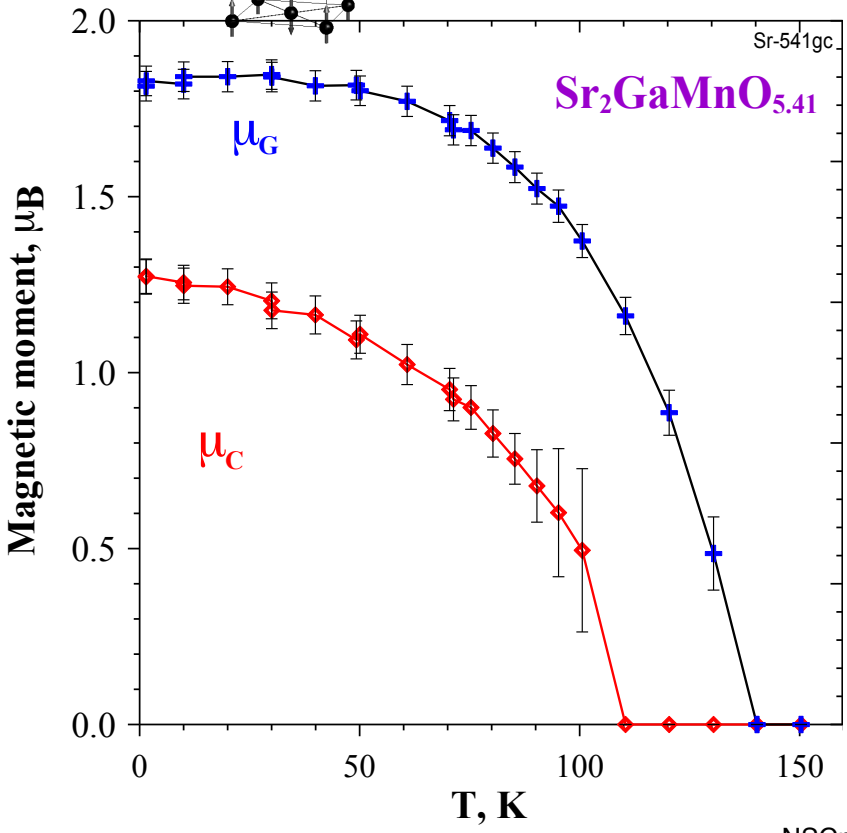
- Disorder effects in magnetic ordering - spin flips and short range phase separation. The magnetic disorder can be caused by the disorder in oxygen positions in $GaO_{1+\delta}$ -layer.

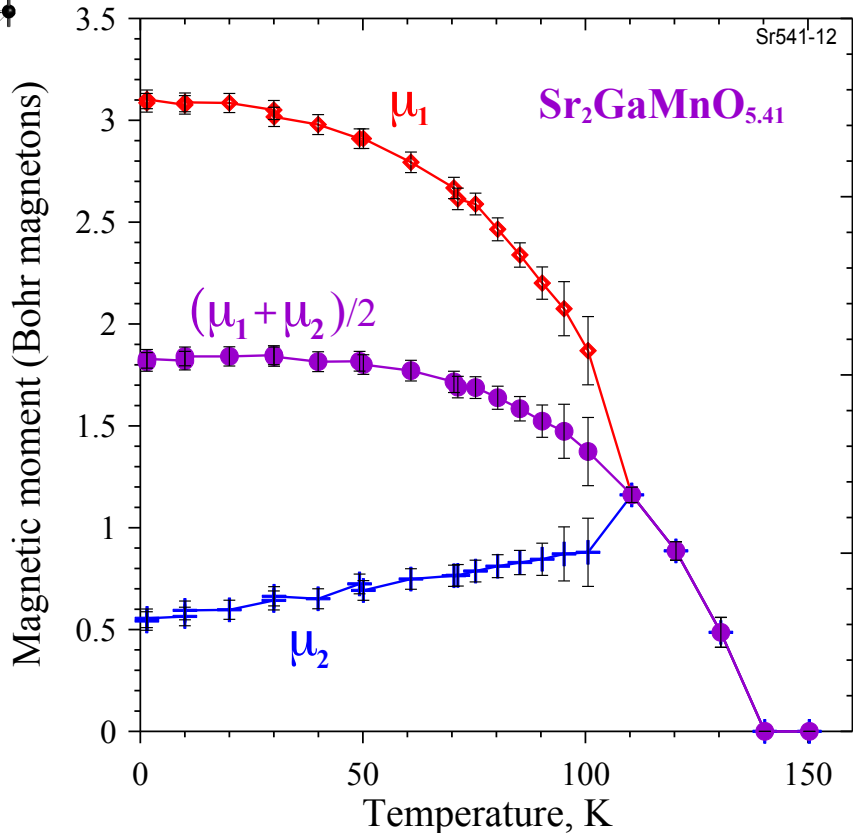
The end



Intermediate Mn-valence in $Sr_2MnGaO_{5+\delta}$. δ=0.13, δ=0.41





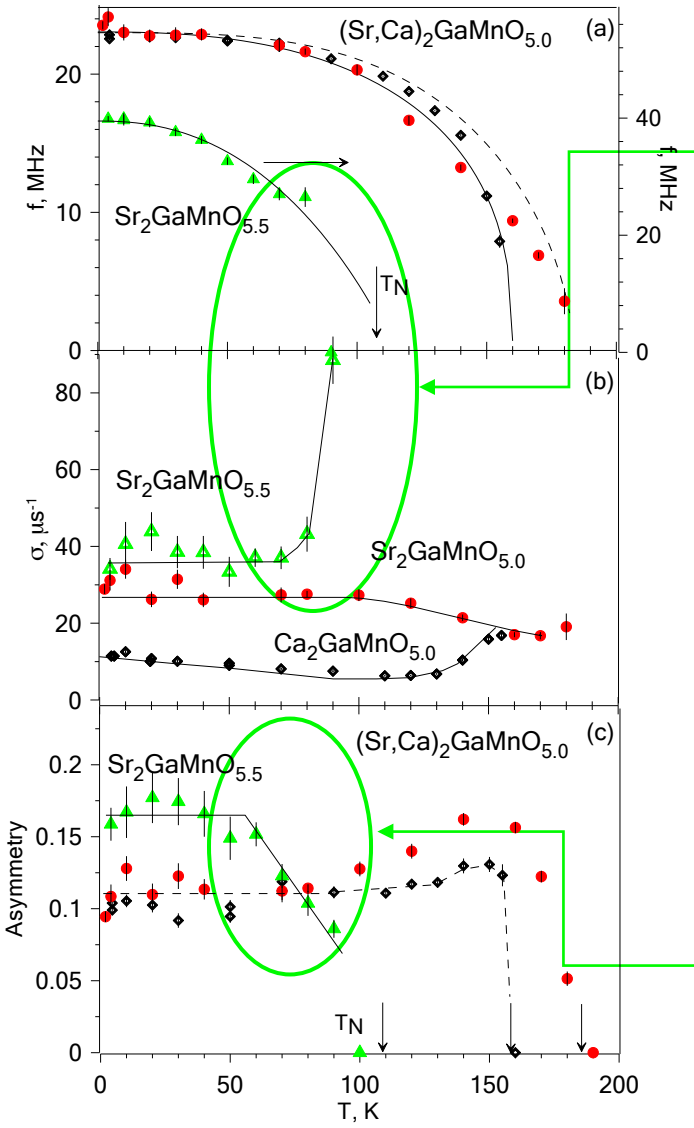


ND-μSR: Short-range order in $Sr_2MnGaO_{5.5}$

Frequency

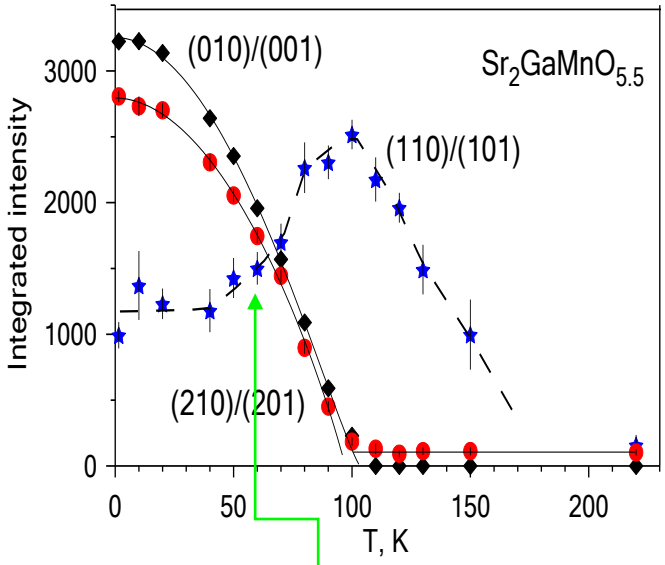
Relaxation rate

Precession amplitude



$Sr_2MnGaO_{5.5}$ (C-type)

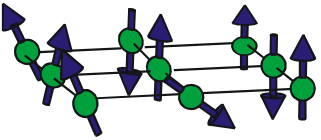
Local spin fluctuations (spin-flips)



Volume fraction decreased – second phase develops spatially separated

Configurational disorder

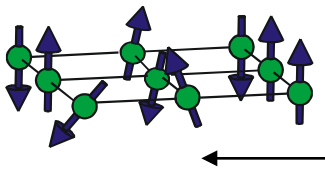
Disordered component of moment



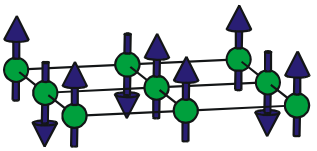
$$\mathbf{m} = \mathbf{m}_0 + \mathbf{m}_1$$

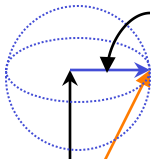
$$\mathbf{m}_0 = <\mathbf{m}>$$

$$m_1 = <(\mathbf{m} - \mathbf{m}_0)^2>^{1/2}$$



Local field $\mathbf{B}_{loc} = \sum_{\mathbf{m}} \mathbf{B}_{dip}$





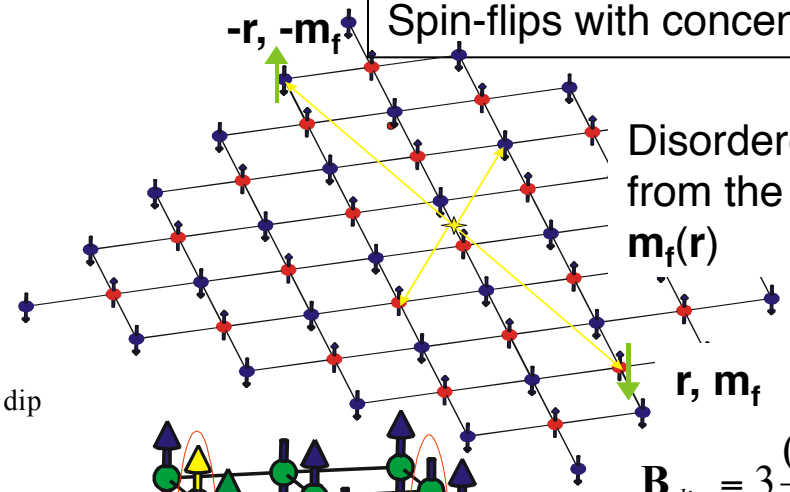
$$< \Delta B_{loc}^2 >^{1/2} \propto m_1$$

$$< B_{loc} > \propto m_0$$

$\mathbf{B}_{loc}$

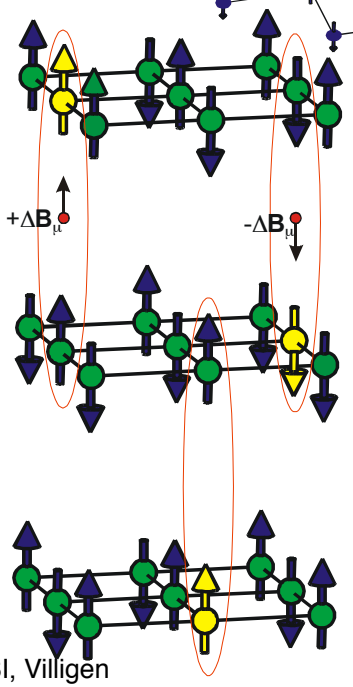
μSR frequency $f \sim m_0$
ND magnetic moment $M \sim m_0$

Disorder of spin-configuration:
Spin-flips with concentration c<<1



Disordered field from the flipped spin $\mathbf{m}_f(\mathbf{r})$

$$\mathbf{B}_{dip} = 3\frac{(\mathbf{m}_f\mathbf{r})\mathbf{r}}{r^5} - \frac{\mathbf{m}_f}{r^3}$$



$$< B_{loc} > \propto m$$

$$< \Delta B_{loc}^2 >^{1/2} \propto c$$

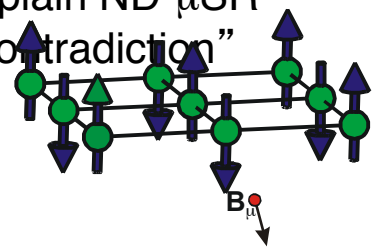
f~ *m*, while
M ~ *m*(1-2*c*)

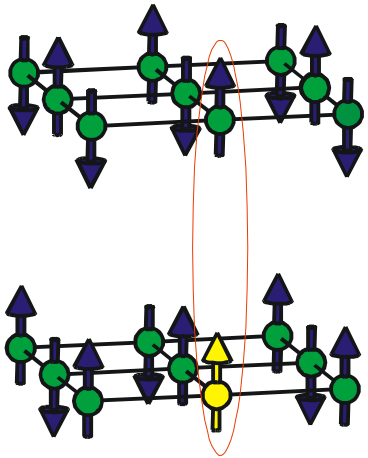
ND-μSR: Local magnetic disorder

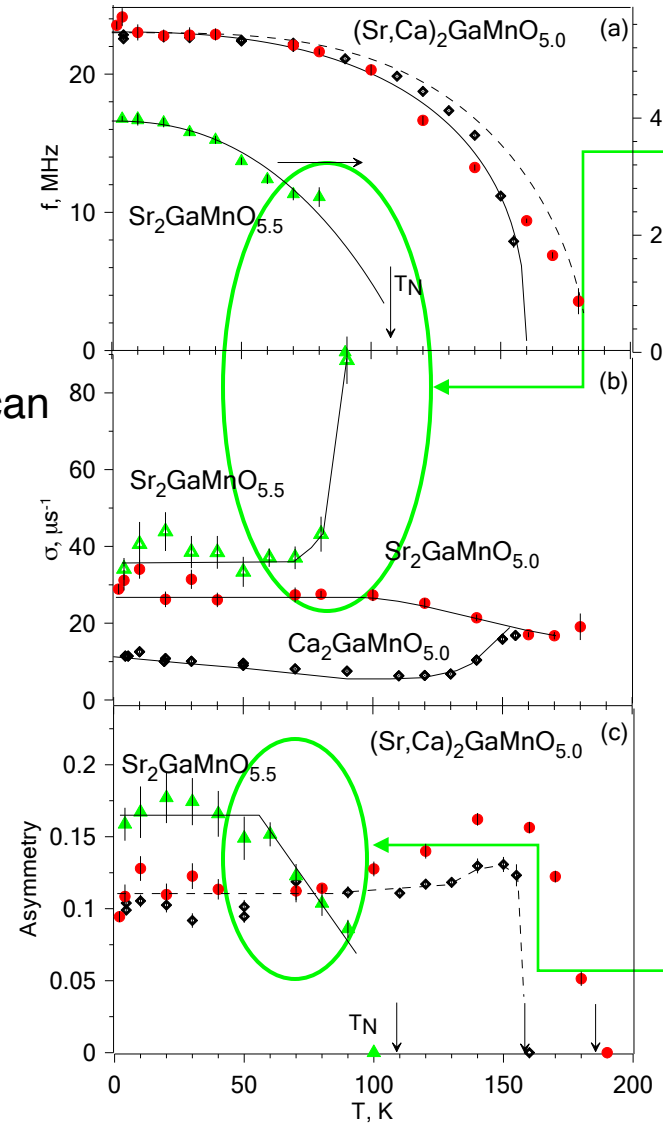
$Ca_2MnGaO_{5.0}$
$Sr_2MnGaO_{5.0}$ (G-type)

- $f_{Sr}=f_{Ca}$, while $\Delta M/M \approx 10\%$ ($c_{flips} \approx 5\%$)
- $\Delta\sigma \approx 230G \rightarrow c_{flips} \approx 8\%$

Spin flips (concentration<<1) can explain ND-μSR "contradiction"

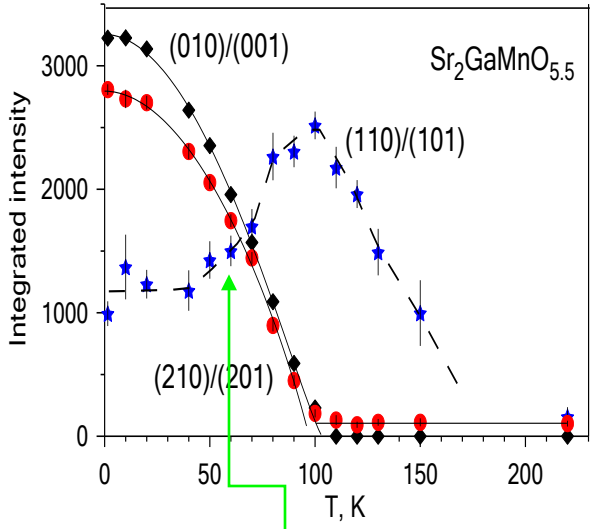






$Sr_2MnGaO_{5.5}$ (C-type)

Local spin fluctuations (spin-flips)



Volume fraction decreased – second phase develops spatially separated

NSCmr2002, PSI, Villigen

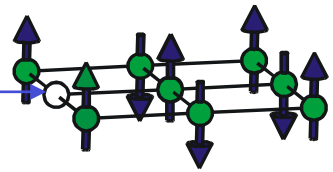
M_{eff} accessed by neutron diffraction

Effective magnetic moment $M_{eff} = M_0 \xi \sqrt{v}$

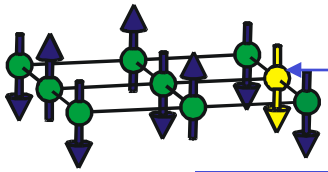
real moment

volume fraction

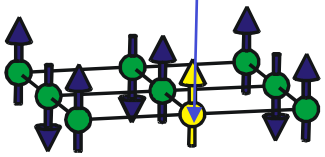
effective occupancy



Spin vacancy



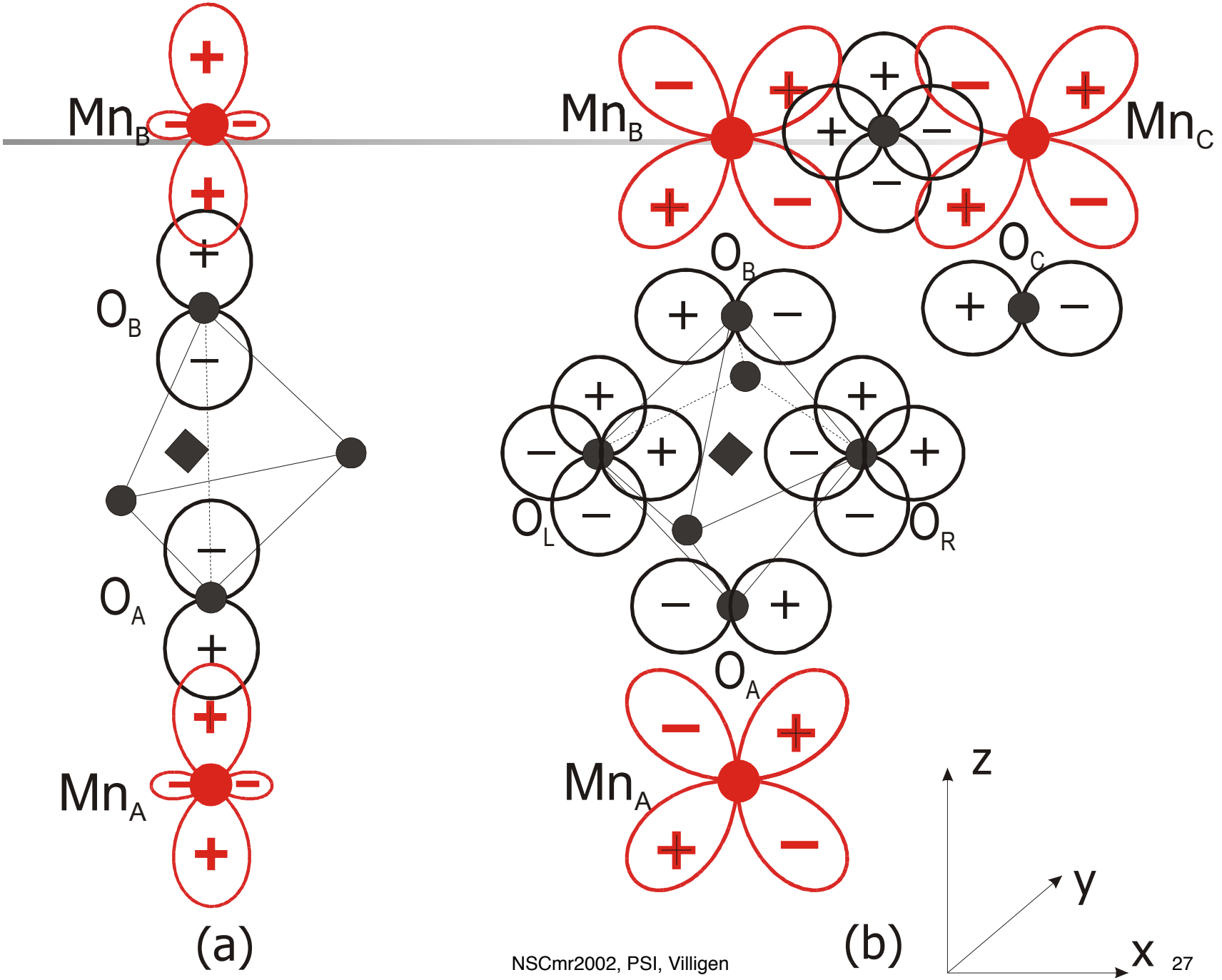
Spin flip δM/M=-2c



Magnetic structure factor

$$\mathbf{F(H)} \propto \sum_j P(\mathbf{H}) \xi_j \mathbf{M}_j e^{2\pi i (\mathbf{r}_j \mathbf{H})}$$

$$\frac{I_{mag}}{I_{nucl}} \propto \frac{N_{mag} (\xi M_0)^2}{N_{nucl} F^2}$$


Mn_B
O_B
O_A
Mn_A
(a)
Mn_B
Mn_C
O_B
O_C
O_L
O_R
O_A
Mn_A
(b)
z
y
x

Mn^{3+}/ Mn^{4+} in octahedral site