The superexchange interaction in overdoped manganites

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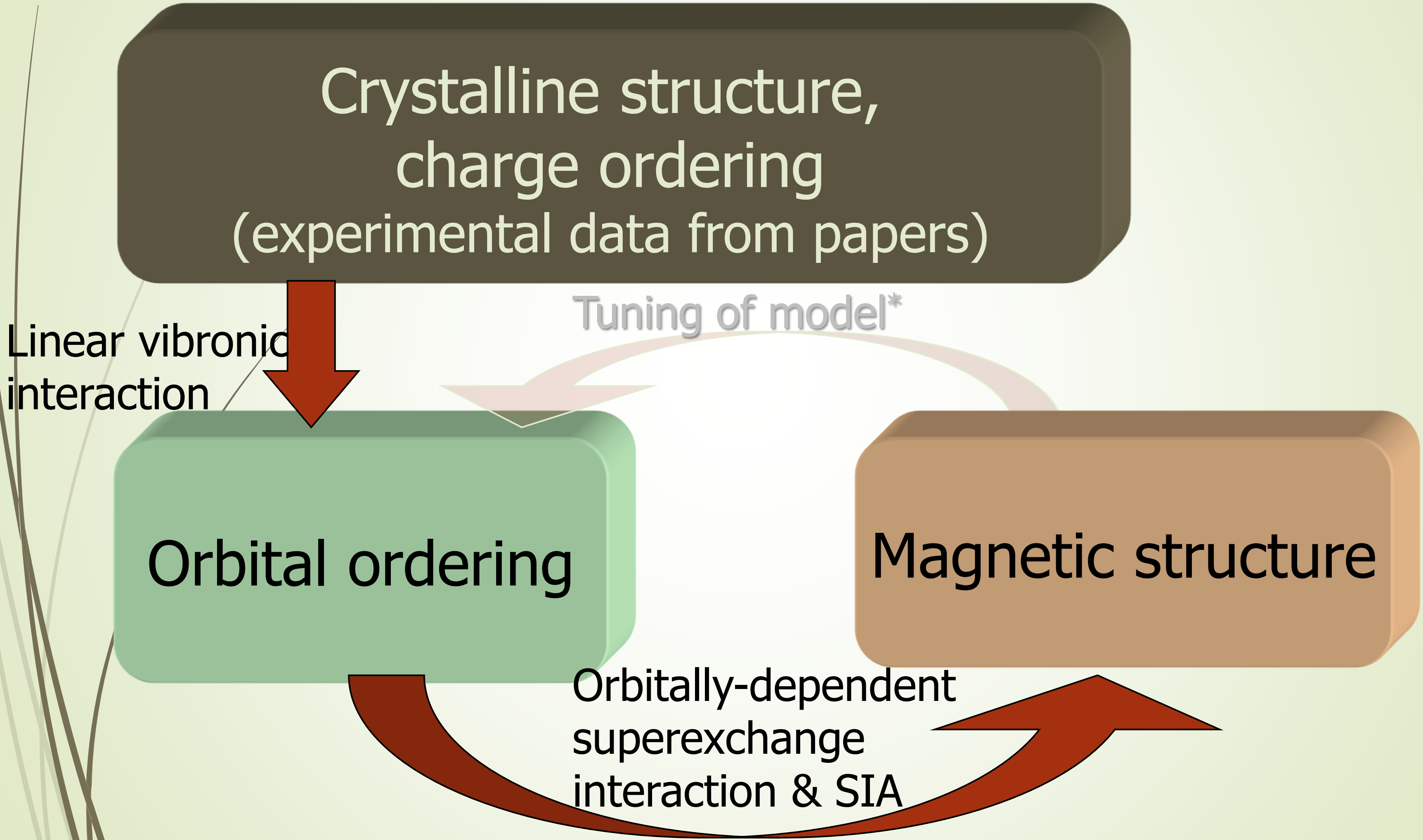
Model of the JT magnetic crystal



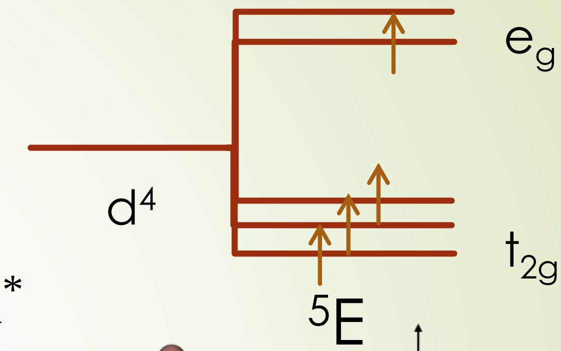
*If necessary, the non-linear and non-local parts could be added to the model. These part are not used in current investigation,

Orbital subsystem model

Mn^{3+} –d^4,

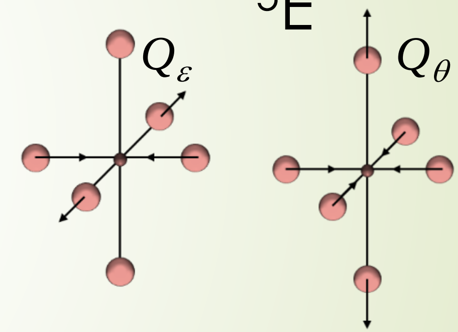
in the crystal field of octahedron ^5E,

eigenfunctions: $|\theta\rangle \sim 2z^2-x^2-y^2$, $|\varepsilon\rangle \sim x^2-y^2$



$$H_{JT}=V_e(Q_\theta X_\theta+Q_\varepsilon X_\varepsilon)$$

$V_e = -1{,}29$ эВ/Å*



$$X_\theta=\begin{array}{cc}\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix} & \begin{array}{c}\theta\\ \varepsilon\end{array}\end{array};\quad X_\varepsilon=\begin{array}{cc}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} & \begin{array}{c}\theta\\ \varepsilon\end{array}\end{array}.$$

Θ–angle parameter characterizing the orbital state of Mn^{3+} - the main in the work

$$\Psi=\begin{cases}\left|\cos\frac{\Theta}{2}\right||\theta\rangle-\left|\sin\frac{\Theta}{2}\right||\varepsilon\rangle,\ Q_\varepsilon<0,\\ \left|\cos\frac{\Theta}{2}\right||\theta\rangle+\left|\sin\frac{\Theta}{2}\right||\varepsilon\rangle,\ Q_\varepsilon>0.\end{cases}$$

* A.E. Nikiforov, S.E. Popov Appl. Phys. A 74, S1743 (2002)

$$\sin\Theta_n=-\frac{Q_{\varepsilon n}}{\sqrt{Q_{\theta n}^2+Q_{\varepsilon n}^2}},\quad \cos\Theta_n=-\frac{Q_{\theta n}}{\sqrt{Q_{\theta n}^2+Q_{\varepsilon n}^2}}$$

Symmetrized e_g-distortions and orbital structures

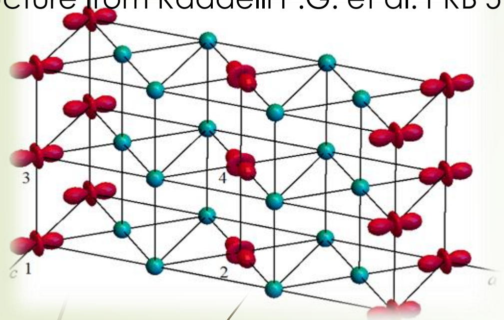
Mn^{3+}–^5E $\quad \Psi_n = \left|\cos\frac{\Theta_n}{2}\right| |\theta\rangle_n \pm \left|\sin\frac{\Theta_n}{2}\right| |\varepsilon\rangle_n$

$\Theta_1 = \Theta_3 \approx 2\pi - \Theta_2 = 2\pi - \Theta_4 = \Theta$

Mn^{4+} –$^4A_2$

$La_{1/3}Ca_{2/3}MnO_3$, Pnma×3

structure from Radaelli P.G. et al. PRB 59,14440 (1999)



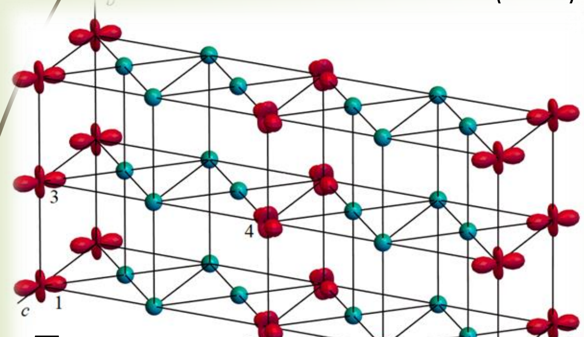
$$Q_\varepsilon = \sqrt{2}\left[\frac{(v_{x1}+v_{x2})}{2}a + \frac{(v_{z1}+v_{z2})}{2}c\right],$$

$$Q_\theta = \frac{1}{\sqrt{12}}\left(b - \frac{\frac{1}{3}a + c}{\sqrt{2}}\right) - \frac{1}{\sqrt{6}}\left((v_{x1}-v_{x2})a + (v_{z1}-v_{z2})c\right),$$

$$\Theta = \arctan\left(Q_\varepsilon / Q_\theta\right) \approx \frac{5\pi}{3}$$

$La_{1/4}Ca_{3/4}MnO_3$, $P2_1/m$

structure from M. Pissas et al. PRB 72, 064426 (2005)



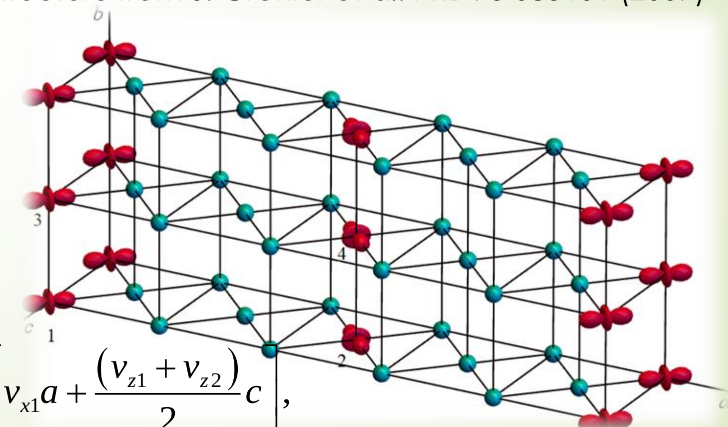
$$Q_{\varepsilon a,b} = \sqrt{2}\left[v_x a + v_{z1,2}c\right] \; (v_{x1} = v_{x2}),$$

$$Q_\theta = \frac{1}{\sqrt{12}}\left(b - \frac{\frac{1}{4}a + c}{\sqrt{2}}\right),$$

$$\Theta = \arctan\left(Q_\varepsilon / Q_\theta\right) \approx 1.58\pi$$

$Bi_{1/5}Ca_{4/5}MnO_3$, Pnma×5

structure from S. Grenier et al. PRB 75 085101 (2007)



$$Q_\varepsilon = \sqrt{2}\left[v_{x1}a + \frac{(v_{z1}+v_{z2})}{2}c\right],$$

$$Q_\theta = \frac{1}{\sqrt{12}}\left(b - \frac{\frac{1}{5}a + c}{\sqrt{2}}\right) - \frac{1}{\sqrt{6}}(v_{z1}-v_{z2})c,$$

$$\Theta = \arctan\left(Q_\varepsilon / Q_\theta\right) \approx 1.66\pi$$

Magnetic subsystem model

$$\hat{H}_{mag} = \sum_{i>j} J_{ij}(\Theta_i, \Theta_j)\left(\mathbf{S}_i \cdot \mathbf{S}_j\right) + \sum_i \hat{H}_{an}^{(i)}$$

$$J_{ij}(\Theta_i, \Theta_j) = \frac{J_{0,k} \cos^2 \varphi_{ij}}{r_{ij}^{10}} F_{ij}(\Theta_i, \Theta_j)$$

$$\hat{H}_{an}^{(i)} = D_i S_{iz_\ell}^2 + E_i \left(S_{ix_\ell}^2 - S_{iy_\ell}^2\right)$$

$$D_i = -3P\cos\Theta_i \quad E_i = -\sqrt{3}P\sin\Theta_i$$

+ transformation of the reference frame from local axes of octahedron to general system

Orbitally-dependent exchange interaction

$$J_{ij}^{\gamma} = \frac{J_0^{1,2,3}\cos^2\varphi_{ij}}{r_{ij}^{10}} \boxed{F(\Theta_i,\Theta_j)}.$$

1) Mn^{3+} – Mn^{3+} (*x*, *y*, *z*)

$$J_{ij}^{z} = \frac{J_0^{1}\cos^2\varphi_{ij}}{r_{ij}^{10}} \boxed{(1-\alpha(\cos\Theta_i+\cos\Theta_j)+\beta\cos\Theta_i\cos\Theta_j),}$$

$$J_{ij}^{x,y} = \frac{J_0^{1}\cos^2\varphi_{ij}}{r_{ij}^{10}} \boxed{\left(1+\frac{\alpha}{2}(\cos\Theta_i \pm \sqrt{3}\sin\Theta_i + \cos\Theta_j \pm \sqrt{3}\sin\Theta_j) + \frac{\beta}{4}(\cos\Theta_i \pm \sqrt{3}\sin\Theta_i)(\cos\Theta_j \pm \sqrt{3}\sin\Theta_j)\right).}$$

2) Mn^{3+} – Mn^{4+} (*x*, *y*, *z*)

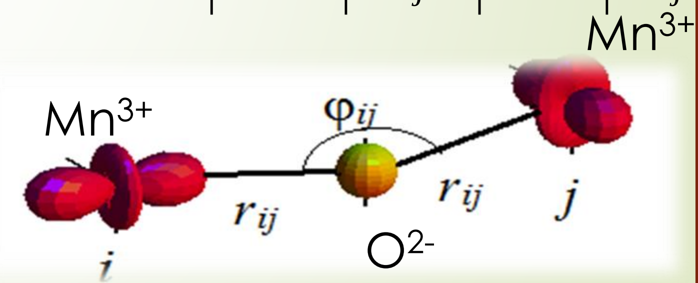
$$J_{ij}^{z} = \frac{J_0^{2}\cos^2\varphi_{ij}}{r_{ij}^{10}} \boxed{(1-\alpha'\cos\Theta_i),}$$

$$J_{ij}^{x,y} = \frac{J_0^{2}\cos^2\varphi_{ij}}{r_{ij}^{10}} \boxed{\left(1+\alpha'/_2\left(\cos\Theta_i \pm \sqrt{3}\sin\Theta_i\right)\right),}$$

3) Mn^{4+} – Mn^{4}+

$$J_{ij} = \frac{J_0^{3}\cos^2\varphi_{ij}}{r_{ij}^{10}}.$$

$$\psi_j = \left|\cos\frac{\Theta_j}{2}\right| |\theta\rangle_j \pm \left|\sin\frac{\Theta_j}{2}\right| |\varepsilon\rangle_j$$

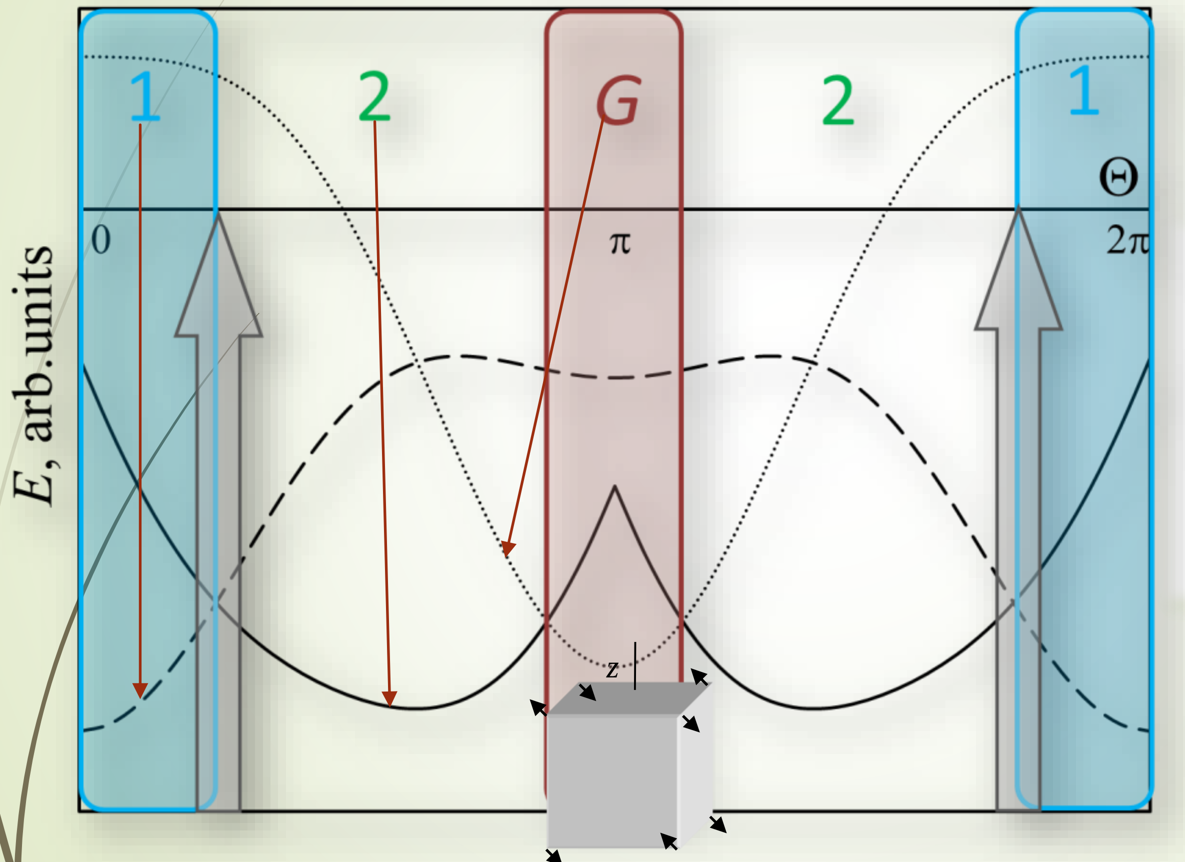


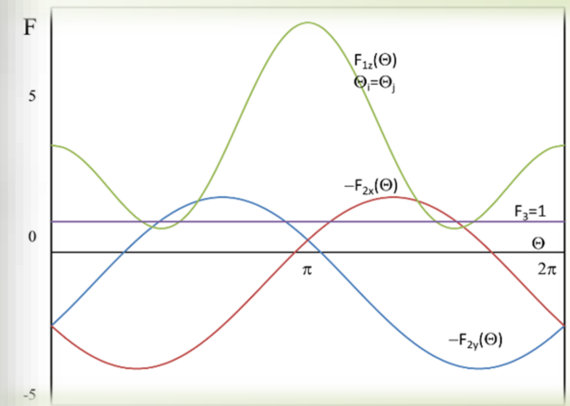
$$\psi_i = \left|\cos\frac{\Theta_i}{2}\right| |\theta\rangle_i \pm \left|\sin\frac{\Theta_i}{2}\right| |\varepsilon\rangle_i$$

Parameters of interactions

Compound	Parameters, meV
$La_{1/3}Ca_{2/3}MnO_3$ ($\Theta=5\pi/3$)	$J_3^{ac}=1.0$, $J_2^{ac,1}=2.2$, $J_2^{ac,2}=$ **-9.1**, $J_3^{b}=1.3$, $J_1^{b}=2.4$ $D=0.15$, $E=\pm0.15$
$La_{1/4}Ca_{3/4}MnO_3$ ($\Theta=1.58\pi$)	$J_3^{ac}=1.0$, $J_2^{ac,1}=2.6$, $J_2^{ac,2}=$ **-9.7**, $J_3^{b}=1.3$, $J_1^{b}=1.4$ $D=0.08$, $E=\pm0.17$
$Bi_{1/5}Ca_{4/5}MnO_3$ ($\Theta=1.66\pi$)	$J_3^{ac}=1.2$, $J_2^{ac,1}=3.4$, $J_2^{ac,2}=$ **-9.0**, $J_3^{b}=1.3$, $J_1^{b}=1.3$ $D=0.14$, $E=\pm0.15$

Orbital dependence of superxchange interaction and exchange energy

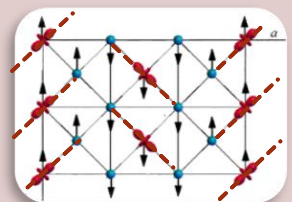
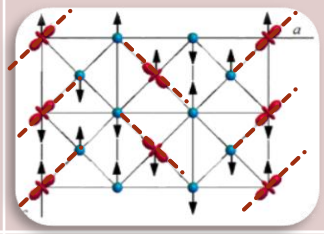
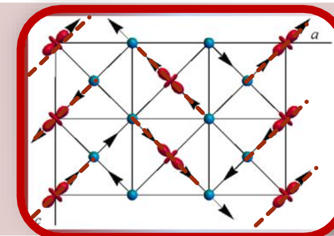
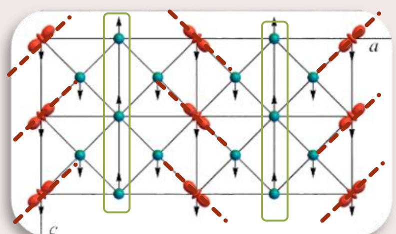
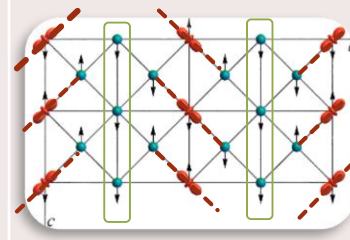
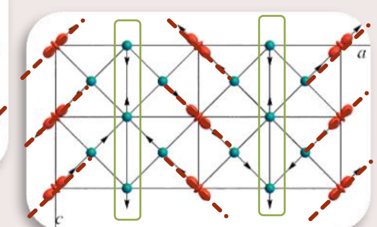
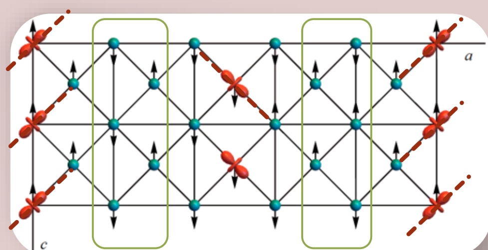
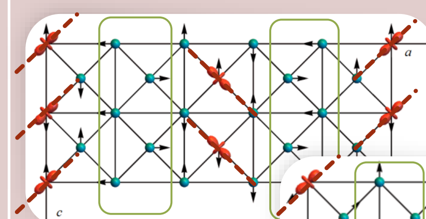
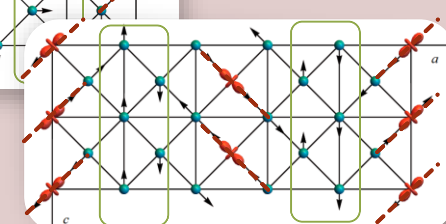




Wide arrows show the orbital mixture angles of the experimental structures [Radaelli P.G. et al. PRB 59,14440 (1999), M. Pissas et al. PRB 72, 064426 (2005), S. Grenier et al. PRB 75 085101 (2007)]

Magnetic structures of types 1 and 2 are complicated. They are drawn in slide 9.

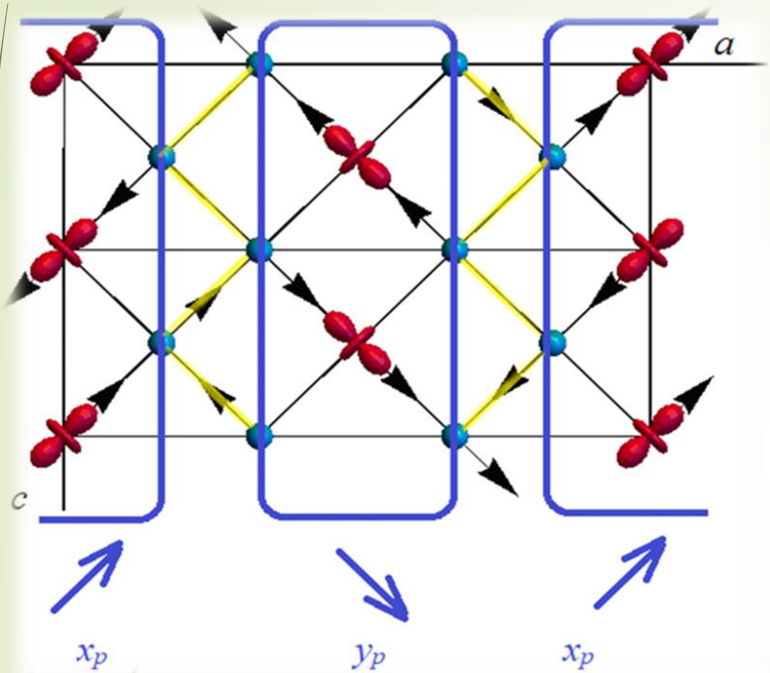
Magnetic structures (next pane –opposite directions)

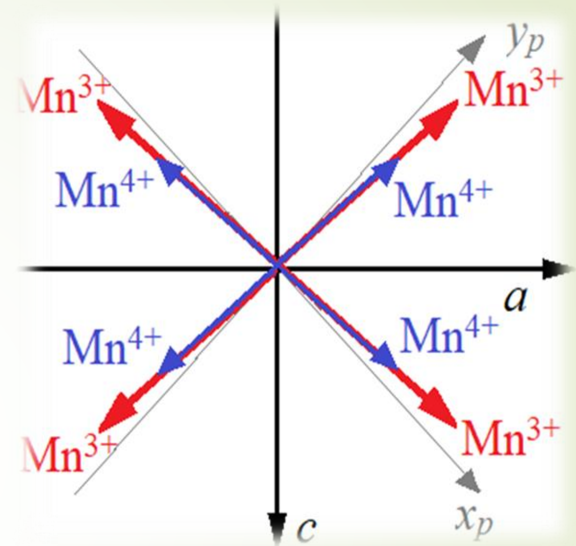
Compound	**1- k_c=0**	**2 - k_c={0,0,1/2}**	
	$\|\|$	$\|\|$	$\perp$
$La_{1/3}Ca_{2/3}MnO_3$ FM trimers - - - -			
$La_{1/4}Ca_{3/4}MnO_3$ FM trimers - - - - FM stripes (AFM stripes)			and some others 
$Bi_{1/5}Ca_{4/5}MnO_3$ FM trimers - - - - AFM stripes			and some others 

Magnetic structure: comments

- The main differences between *1* and 2 magnetic structures are:
  1. the propagation wave vector of magnetic structure in c direction
     - $\mathbf{k_c}$=0 for *1* structure;
     - $\mathbf{k_c}$={0, 0, ½} for 2 structure;
  2. the AFM frustrated bonds (Mn^{3+} S_1=2, Mn^{4+} $S_2 = \frac{3}{2}$)
     - Mn^{3+} –Mn^{4+} for *1* structure $\left(\frac{2J^{ac,1} \cdot S_1}{J^{ac,3} \cdot S_2} < 1\right)$;
     - Mn^{4+} –Mn^{4+} for 2 structure $\left(\frac{2J^{ac,1} \cdot S_1}{J^{ac,3} \cdot S_2} > 1\right)$;
- The regions of Θ are (approximately, due to *orbital part* only):
  1. 0–π/3, 5π/3–2π for *1* structure;
  2. π/3–0.69π, 1.31π–5π/3 for 2 structure;
  3. 0.69π–1.31π for G structure.
- There are lots of non-collinear structures in 2 orbital-mixing-angles region, a choice could be made using single-ion anisotropy with tilting account.

Magnetic structure: $La_{1/3}Ca_{2/3}MnO_3$





Comparing with experiments

(Radaelli, PRB59 14440, Fernández-Díaz, PRB59 1277(1999)) :

- Wave vector of MS
- Magnetic trimers, angle between trimers 80^0 (56^o –Radaelli, 80^o- Fernández-Díaz)

Conclusions

- Model describes various magnetic structures of JT insulating manganites
- Magnetic subsystem is dependent upon orbital one
- Orbital dependence afford to describe both general ordering and non-collinear components of magnetic structure
- The main feature of magnetic structure: FM trimers with Mn^{4+} - Mn^{4+} planar bond frustration
- NO C-structure

Thank you for attention!

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Model is published in…

- J.Magn.Magn.Mater. **465**, 661 (2018)
- Physics of the Solid State **61**, 728 (2019)
- J.Magn.Magn.Mater. **513**, 167248 (2020)
- Low Temp.Phys. **48**, 37 (2022)
- Phys. Met. Met. **123**, 268 (2022)
- Appl Magn. Reson. **54**, 503–511 (2023)