Frustrated magnetism on Hollandite lattice

Saptarshi Mandal
(ICTP, Trieste, Italy)

Acknowledgment:
A. Andreanov(MPIKS, Dresden)
Y. Crespo and N. Seriani(ICTP, Italy)

Workshop on Current Trends in Frustrated Magnetism, JNU, New Delhi

February 13, 2015

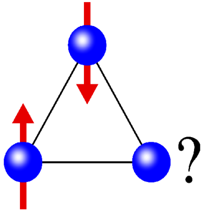
Plan of the Talk

- Introduction
- Hollandite lattice and αMnO$_2$
- Experimental Magnetic properties
- Model
- Phase diagram
- Effect of external magnetic field
- Recent interest

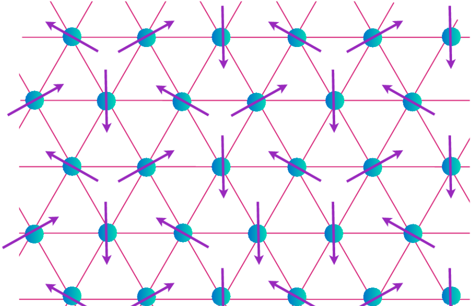
Frustrated Magnetism: AFM interaction or FM + AFM interaction

Geometrical Frustration

- Triangular lattice
- Kagome lattice
- Pyrochlore lattice



Anderson (1973)



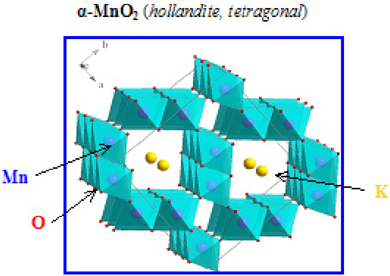
MnO_2 and its various compounds

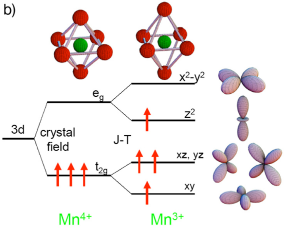
Wide applications

- Catalyst for oxygen reduction reaction. W. Xiao *et al, J. Phys. Chem .C* **114** *1694 (2010)*
- Microbial fuell cell. RSC Adv. **3** 7902 (2013)
- Electrode materials for Li-ion batteries, Lithiam-air batteries.
- Supercapacitor G. -R. Li *et al* Langmuir **26**, 2209 (2010)
- αMnO_2 compounds, ex. $BaMn_8O_{16}$, KMn_8O_{16}. Comes in hollandite and ramsdellite lattice structures.
- βMnO_2 appears in rutile structures.
- γMnO_2 a combination of ramsdellite αMnO_2 and rutile βMnO_2 domains. So far the best material for battary use.

αMnO$_2$ and its properties

- $BaMn_8O_{16}, \quad KMn_8O_{16}, \quad \alpha - Mn0_2\dot{n}H_20$





- $a = 2.86\AA, \quad b = 2.91\AA, \quad c = 3.44\AA$
- Diameters of pores $\sim 4.6\AA$
- Spin moment of Mn is $\frac{3}{2}$

Previous experimental finding.

- AFM state for $K_{<0.7}MnO_2$ (synthesized with hydrothermal technique), N. Yamamoto *et al* Jpn. J. Appl. Phys. **13**, 723 (1974).

- AFM transition for $K_{0.16}MnO_2$ at T$_N$= 18 K Strobel *et al J. Sol. State Chem.* **55**, *67 (1984)*

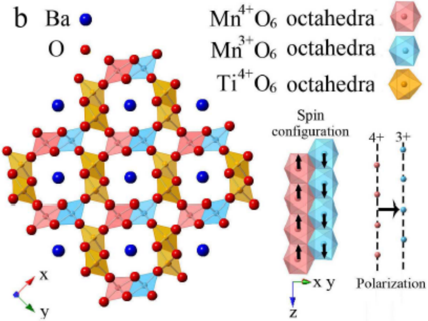
- A helical magnetic structure was also suggested for $K_{0.15}MnO_2$. H. Sato *et al* J. Alloys Comp. **262263**, 443 (1997).

- FM state for 52K to 20K for $K_{1.5}(H_3O)_xMn_8O_{16}$ Below 20 K spatial anisotropic susceptibilities indicate a helical ground state. H. Sato *et al* Phys. Rev. B **59**, 12836 (1999).

- Spin glass behaviour for K_xMnO_2 $(0.087 < x \leq 0.125)$. J. Luo *et al J. Phys. Chem. C* **114**, *8782 (2010). J. Luo et al J. Appl. Phys.* **105**, *093925 (2009), X.-F. Shen et al J. Am. Chem. Soc.* **127**, *6166 (2005).*

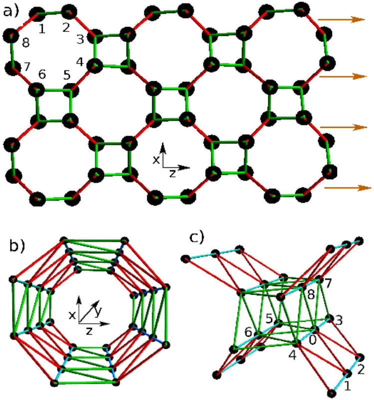
Recent interest

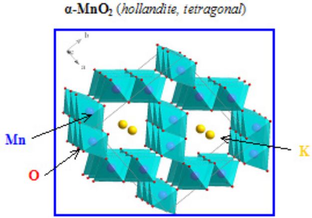
- Spin-glass behaviour with Ising model. Y. Crespo *et al* Phys. Rev. B **88**, 014202 (2013)
- Electronic and magnetic properties..ab initio calculations. Y. Crespo *et al* Phys. Rev. B **88**, 0144428 (2013)
- other works..



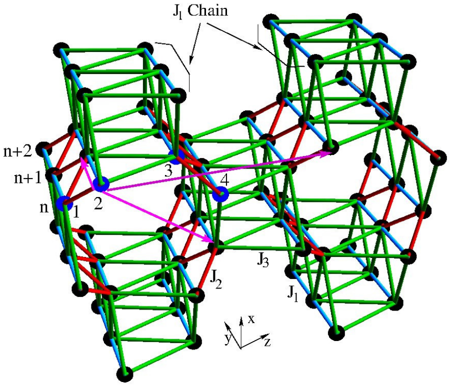
Hollandite as a new class of multiferroics, Scientific Reports 4, 6203 (2014)

Hollandite lattice: lattice of αMnO$_2$





Modelling αMnO$_2$



- Mn-O-Mn angle varies 100° to 130°
- Goodenough-Kanamori-Anderson rule
- DFT insights
- Expeimental insight

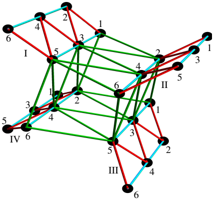
$$\mathcal{H} = J_1 \sum_{\langle ij \rangle} \vec{S}_i . \vec{S}_j + J_2 \sum_{\langle ij \rangle_2} \vec{S}_i . \vec{S}_j + J_3 \sum_{\langle ij \rangle_3} \vec{S}_i . \vec{S}_j \qquad (1)$$

Method..

- Interaction matrix method, $\vec{S}_{i,\alpha} = \sum_k e^{i\vec{K}.\vec{R}_i} \vec{S}_{k,\alpha}$
- $\mathcal{H} = \vec{S}_{k,\alpha} \mathcal{H}_{\alpha,\beta}(k) \vec{S}_{k,\beta}, \qquad \mathcal{H}_{\alpha,\beta}(k) \vec{S}_{k,\beta} = \lambda_{k_{min}} \vec{S}_{k,\beta}$

- Numerical Simulation, inhomogenous meanfield method.
- $\mathcal{H} = \sum_{ij} J_{ij} \vec{S}_i . \vec{S}_j, \ H = \sum_i \vec{h}_i . \vec{S}_j, \qquad \vec{h}_i = \sum_j J_{ij} \vec{S}_j$

- bravais vs non-bravais lattice, $\qquad \lambda_{k_{min}} = E_{site}$



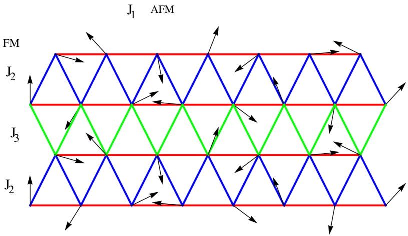
$$\mathcal{H} = \mathcal{H}_{\alpha,\beta}(k) \vec{S}^c_{k,\alpha} \vec{S}^c_{k,\beta}, \qquad \alpha, \ \beta \in 1, 4;$$

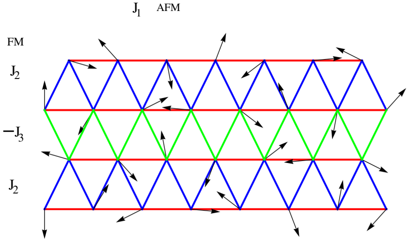
$$E = J_1 \cos 2\phi - (|J_2| + 2|J_3|) \cos\phi$$

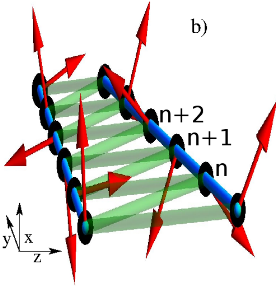
$$E = -J_1 - \frac{(|J_2|+2|J_3|)^2}{8J_1}, \quad \cos\phi = -\frac{|J_2|+2|J_3|}{4J_1}$$

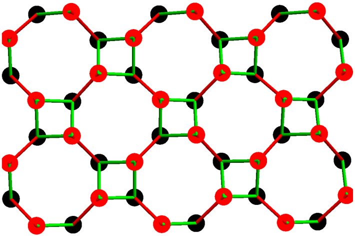
$$E_\phi = -2.125, \qquad \phi = 138.66$$

Ground states of Hollandite lattice (**S.M et. al. Phys. Rev. B 90, 104420, (2014)**

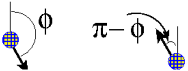


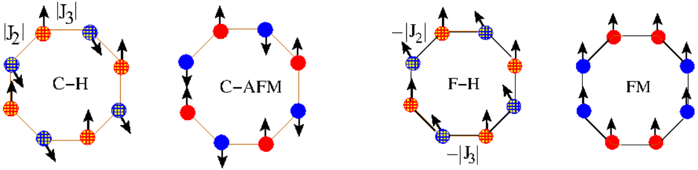


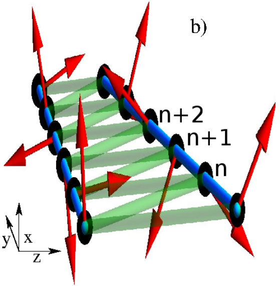


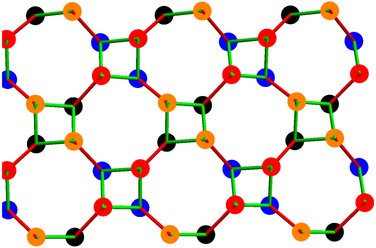


$$\vec{s}_n^{\,\alpha} = \cos(2n\phi)\hat{x} + \sin(2n\phi)\hat{z},$$
$$\vec{s}_n^{\,\beta} = \cos((2n+1)\phi)\hat{x} + \sin((2n+1)\phi)\hat{z}.$$



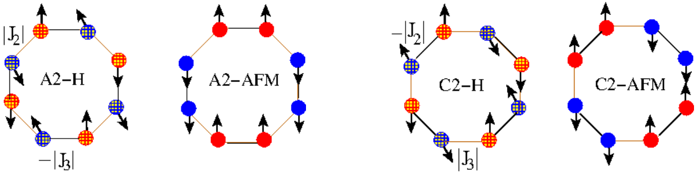




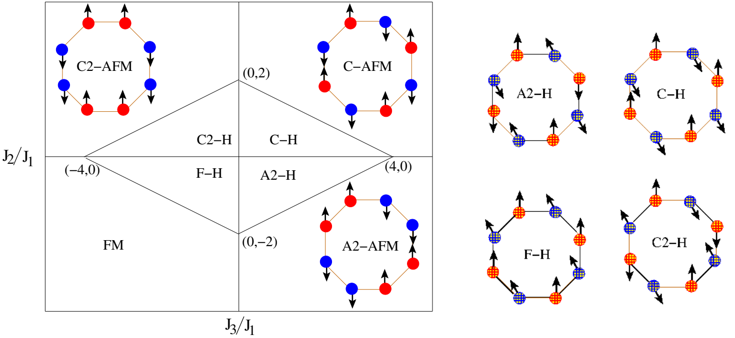


$$\vec{s}_n{}^{\alpha} = \cos(2n\phi)\hat{x} + \sin(2n\phi)\hat{z}, \qquad \vec{s}_n{}^{\alpha_1} = -\vec{s}_n{}^{\alpha}$$

$$\vec{s}_n{}^{\beta} = \cos((2n+1)\phi)\hat{x} + \sin((2n+1)\phi)\hat{z}, \qquad \vec{s}_n{}^{\beta_1} = -\vec{s}_n{}^{\beta}.$$

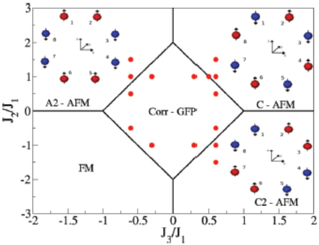


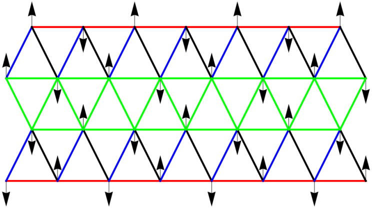
phase diagram-I



- $E_{col} = J_1 - |J_2| - 2|J_3|, \qquad E_{hel} = -J_1 - \frac{(|J_2|+2|J_3|)^2}{8}$
- $\theta = 2\phi$
- Each helical state is continually connected with co-linear phase.

Comparision with Ising model





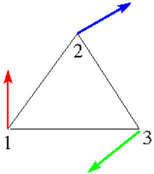
degeneracy!!

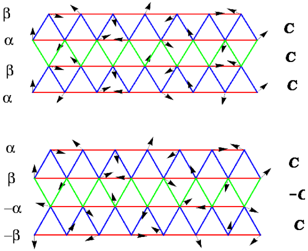
- $E_{GFP} = -J_1$, $E_{hel} = -J_1 - \frac{(|J_2|+2|J_3|)^2}{8J_1}$
- Area of the GFP is smaller than the area of helical phase.
- Boundary between GPF is discontinuous but the boundary between helical and colinear phase is continuous.
- Macroscopic degeneracies of GPF is absent in helical phase.

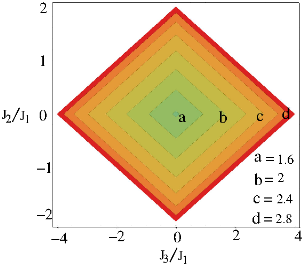
Chirality and degeneracy

Definition:

$$\mathcal{C}_{J_1,J_{2(3)}} = \vec{s}_1 \times \vec{s}_2 + \vec{s}_2 \times \vec{s}_3 + \vec{s}_3 \times \vec{s}_1.$$
$$= \pm(2\sin\phi + \sin 2\phi)\hat{z}$$





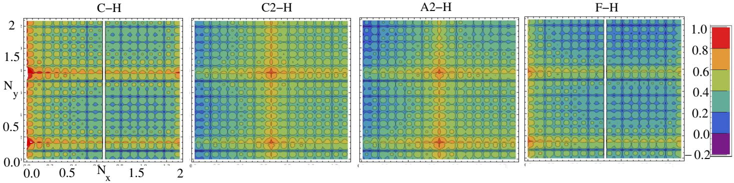


- For J_1 Ferromagnetic the system is not frustrated and simple colinear magnetism is observed.

Neutron diffraction pattarn

Magnetic structure factor $\vec{\mathcal{F}}(\vec{Q}) = \frac{1}{\sqrt{N_t}} \sum_{l=1}^{N_t} e^{i\vec{Q}.\vec{r}_l} \vec{S}(\vec{r}_l)$

$$= \sum_{k=1}^{N_{uc}} \left(\sum_{j\in 1,3}^{5,7} \vec{s}_{k,j} e^{i\vec{Q}.\vec{d}_j} + \sum_{j\in 2,4}^{6,8} \vec{s}_{k,j} e^{i\vec{Q}.\vec{d}_j} \right) e^{i\vec{Q}.\vec{R}_k}.$$



The position of peaks and the value of $|\vec{\mathcal{F}}_M(\vec{Q})|/|\vec{\mathcal{F}}_M(\vec{Q}_{max})|$ is different for each phase.

Ground state magnetisation and susceptibility

$|\vec{\mathcal{F}}_M(\vec{Q})|/|\vec{\mathcal{F}}_M(\vec{Q}_{max})|$

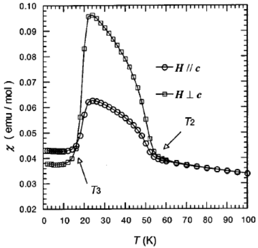
Phase	(0,2ϕ-7)	(1,2ϕ-7)	(2,2ϕ-7)	(0,2ϕ-6)	(1,2ϕ-6)	(2,2ϕ-6)
C-H	0.5618	0	0.0597	1	0	0.1063
C2-H	0	0.5618	0	0	1	0
A2-H	0	1	0	0	0.5933	0
F-H	1	0	0.1063	0.6566	0	0.0698

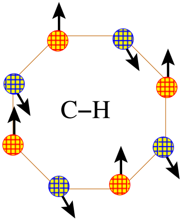
- Magnetisation: $m_\mu = \sum_i s_{i,\mu} = 0$
- Non zero susceptbility tensor:

$$\begin{aligned}\chi_{\mu,\lambda} &= \frac{1}{N}\Big(\sum_{i,j}\langle s_{i,\mu}s_{j,\lambda}\rangle - \langle s_{i,\mu}\rangle\langle s_{j,\lambda}\rangle\Big) = \chi\delta_{\mu,\lambda}, \quad \mu,\lambda \in x,z \\ &= 0.5 \qquad (2)\end{aligned}$$

H. Sato, et. al. J. Alloys Comp. **262263**, 443 (1997).

Effect of magnetic field:





H. Sato et al. Phys. Rev. B **59**, 12836,(1999)

- Unknown FM state between T_2 and T_3
- We consider T=0.
- $H_\perp$ is the magnetic field applied perpendicular to the plane of polarization
- $H_{||}$ is the magnetic field applied along the plane of polarization

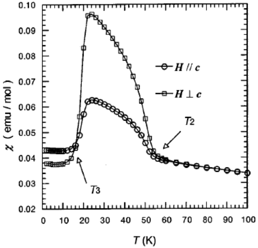
Effect of perpendicular magnetic field

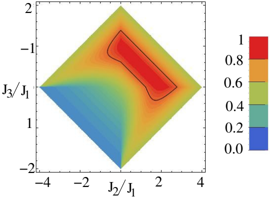
- $H = H_0 + h_\perp \sum_{i=1}^{N_t} s_{y,i}$, $\quad \vec{s}_i = \sqrt{(1-\Delta_i^2)}\vec{s}_{0,i} - \Delta_i \hat{y}$
- self-consistent Eq: $\sum_{j\in i}\Big(- J_{ij}\frac{\sqrt{(1-\Delta_j^2)}}{\sqrt{(1-\Delta_i^2)}}\vec{s}_{0,i}.\vec{s}_{0,j} + J_{ij}\Delta_j\Big) = h_\perp$
- $\vec{s}_i = \sqrt{(1-\Delta^2)}\vec{s}_{0,i} - \Delta\hat{y}$, $\quad \Delta = \frac{h_\perp}{2(J_1+J_2+2J_3-E_{GS})}$
- Ground state energy: $E = E_{GS} - \frac{h_\perp^2}{4(J_1+J_2+2J_3-E_{GS})}$
- $m_\perp = \frac{h_\perp}{2(J_1+J_2+2J_3-E_{GS})}$, $\quad \chi_\perp = \frac{1}{2(J_1+J_2+2J_3-E_{GS})} > 0.$
- Critical Magnetic field $h_y^c = 2(J_1 + J_2 + 2J_3 - E_{GS})$.

Effect of parallel magnetic field, $H = H_0 + h_\parallel \sum_{i=1}^{N_t} s_{x,i}$.

- $\vec{s}_n^\alpha = \cos(\theta_n^\alpha + \delta\theta_n^\alpha)\hat{x} + \sin(\theta_n^\alpha + \delta\theta_n^\alpha)\hat{z}, \quad \alpha \to \beta$.
- $\delta\theta_n^{(\alpha,\beta)} = \frac{h_\parallel \sin\theta_n^{(\alpha,\beta)}}{2\left(J_1\cos^2(2\phi)+(J_2+2J_3)\cos^2\phi - E_{GS}\right)}$.
- $E = E_{GS} - \frac{h_\parallel^2}{8(J_1\cos^2(2\phi)+(J_2+2J_3)\cos^2\phi - E_{GS})}$
- Magnetisation: $m_x = \frac{h_\parallel}{4(J_1\cos^2 2\phi+(J_2+2J_3)\cos^2\phi - E_{GS})}$.
- Susceptibility: $\chi_\parallel = \frac{1}{4(J_1\cos^2(2\phi)+(J_2+2J_3)\cos^2\phi - E_{GS})}$
- No critical field, For strong parallel field, the spins are canted perpenicular to the field.

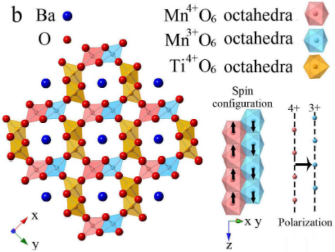
Susceptibility



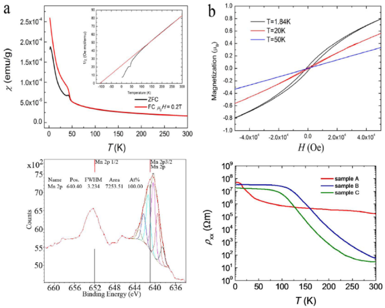


- temperature dependence of Susceptibilities?
- $\chi_\perp > \chi_\parallel, \qquad \frac{\chi_\parallel}{\chi_\perp} = 0.87$
- $\chi_\perp,\ \chi_\parallel\ ,\ \phi$, from neutron diffraction may help to determine J_1, J_2, J_3

Scientific Reports **4**, 6203 (2014)



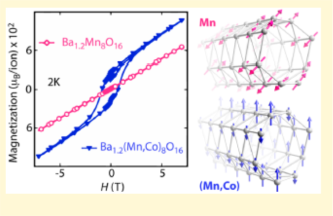
a minimal model includes 4 different nearest neighbour coupling, J_1, J_2, J_3, J_4. Could be frustrating.

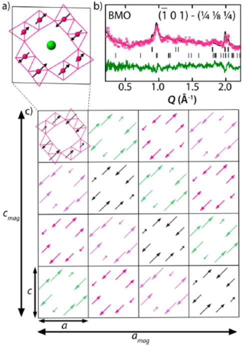


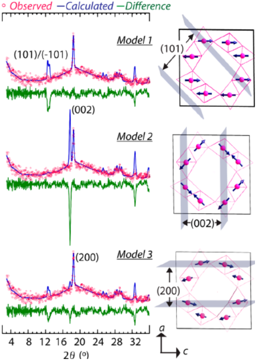
The transition temperature 50^o K is identical to that of α-MnO$_2$, indicating that dynamics along $Mn - Mn$ ladder is the main factor for finite T mechanism.

A. M. Larson et. al, Inducing Ferrimagnetism in Insulating Hollandite $Ba_{1.2}Mn_8O_{16}$,Chem of Mat.

$Ba_xMn_8O_{16}$ from a complex AFM with (T_N) =25 K to a ferrimagnet with Curie temperature (T_C)=180 K via partial Co sustitution for Mn.







Thank you