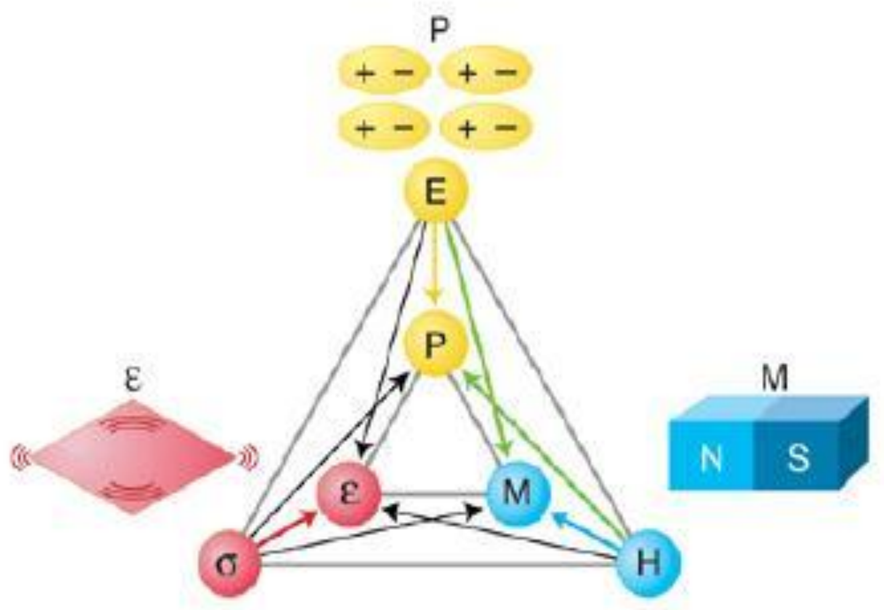
Multiferroics – Combining Magnetism with Ferroelectricity



Amnon Aharony, BGU and TAU

M. Sc. Thesis of **Shlomi Matityahu**

Work with **Ora Entin-Wholman (**earlier also **A Brooks Harris)**

Multiferroics

- **Type I multiferroics** – ferroelectricity and magnetism have different sources and are independent

  Weak coupling, different transition temperatures

- **Type II multiferroics** – ferroelectricity and magnetism are strongly coupled → Magnetic order **causes** ferroelectricity and therefore **giant magnetoelectric** effect ; **can change magnetic (electric) moment by electric (magnetic) field**

SPINTRONICS

Symmetry considerations in multiferroics

	T	I
Magnetic moment	-	+
Electric moment	+	-
Strain	+	+

- Multiferroic state requires **both** broken symmetries!

Landau theory:

(1) Use **symmetry group theory** to identify **order parameters,** then incorporate **inversion symmetry** and analyze **general Landau expansion.**

(2) Start from **microscopic Hamiltonian,** “derive” **Landau expansion in spins.**

Landau Theory for magnetic part

- **Energy** –

$$H = -\frac{1}{2}\sum_{\vec{R},\vec{R}'}\sum_{\tau,\tau'=1}^{n_\tau}\sum_{\alpha,\beta=1}^{3} J_{\alpha\beta}\left(\vec{R}+\vec{\tau},\vec{R}'+\vec{\tau}'\right)S_\alpha\left(\vec{R}+\vec{\tau}\right)S_\beta\left(\vec{R}'+\vec{\tau}'\right)$$

- **Entropy** –

$$S = -\frac{1}{2}a\sum_{\vec{R}}\sum_{\tau=1}^{n_\tau}\vec{S}^2\left(\vec{R}+\vec{\tau}\right)-b\sum_{\vec{R}}\sum_{\tau=1}^{n_\tau}\vec{S}^4\left(\vec{R}+\vec{\tau}\right)$$

- **Magnetic free energy** –

$$F_{mag} = \frac{1}{2}\sum_{\vec{R},\vec{R}'}\sum_{\tau,\tau'=1}^{n_\tau}\sum_{\alpha,\beta=1}^{3} \chi^{-1}_{\alpha\beta}\left(\vec{R}+\vec{\tau},\vec{R}'+\vec{\tau}'\right)S_\alpha\left(\vec{R}+\vec{\tau}\right)S_\beta\left(\vec{R}'+\vec{\tau}'\right)+O\left(S^4\right)$$

Inverse susceptibility matrix -

$$\chi^{-1}_{\alpha\beta}\left(\vec{R}+\vec{\tau},\vec{R}'+\vec{\tau}'\right)=aT\delta_{\vec{R},\vec{R}'}\delta_{\tau,\tau'}\delta_{\alpha,\beta}-J_{\alpha\beta}\left(\vec{R}+\vec{\tau},\vec{R}'+\vec{\tau}'\right)$$

- **Magnetic free energy per unit cell** –

$$f_{mag} = \frac{1}{2} \sum_{\tau,\tau'=1}^{n_\tau} \sum_{\alpha,\beta=1}^{3} \sum_{\vec{q}} \chi_{\alpha\beta}^{-1}(\vec{q};\tau,\tau') S_\alpha^{*}(\vec{q},\tau) S_\beta(\vec{q},\tau') + O(S^4)$$

- **Fourier transform of the inverse susceptibility matrix** –

$$\chi_{\alpha\beta}^{-1}(\vec{q};\tau,\tau') \equiv \sum_{\vec{r}} \chi_{\alpha\beta}^{-1}(\vec{\tau},\vec{r}+\vec{\tau}') e^{-i\vec{q}\cdot(\vec{r}+\vec{\tau}'-\vec{\tau})} \rightarrow 3n_\tau \times 3n_\tau \; Hermitian\, Matrix$$

- For each $\vec{q}$, The inverse susceptibility matrix has N= $3n_\tau$ eigenvalues $\left\{\chi_i(\vec{q},T)\right\}_{i=1}^{3n_\tau}$ which depend on temperature and $3n_\tau$ eigenvectors $\left\{\vec{S}_i(\vec{q})\right\}_{i=1}^{3n_\tau}$

$$F_{M,2} = \frac{1}{2} \sum_{\mathbf{q},\alpha,\beta;\tau,\tau'} \chi^{-1}_{\alpha\beta}(\mathbf{q};\tau,\tau') S_\alpha(\mathbf{q},\tau)^* S_\beta(\mathbf{q},\tau') + \ldots$$

Diagonalize $\chi^{-1}_{\alpha\beta}(\mathbf{q};\tau,\tau')$; Eigenvalues correspond to **irreducible representations (irreps)** of symmetry group of paramagnetic phase, **incorporate inversion**

Landau: Coming down from paramagnetic phase – **only one irrep orders**

Dimension of irrep determines the degeneracy of the eigenvalues and the # of coefficients of degenerate eigenvectors in N-component spin structure vector

Components of normalized eigenvectors related by symmetry: (N-1) ratios

Higher order terms in *F* determine actual order parameters

Interesting **critical phenomena** with a large number of order parameter components, N

Coupling to ferroelectric mode

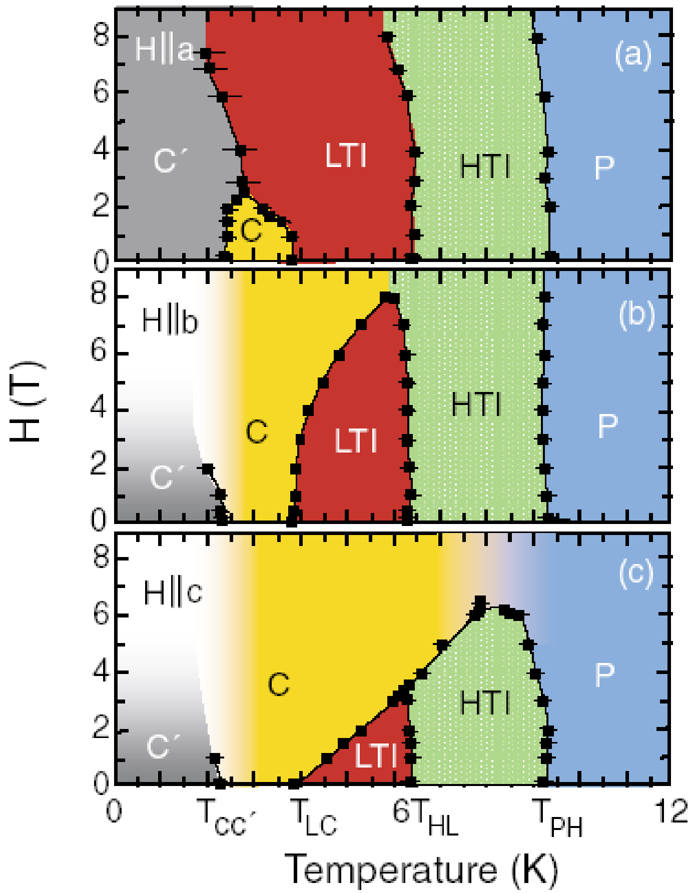
$$f_{ele} = V_{cell} \sum_{\alpha=1}^{3} \frac{P_\alpha^{\ 2}}{2\chi_{E,\alpha}^{0}}$$

$$f_{int} = \frac{1}{2} \sum_{\tau,\tau'=1}^{n_\tau} \sum_{\alpha,\beta=1}^{3} \sum_{\gamma=1}^{3} \sum_{\vec{q}} A_{\alpha\beta\gamma}\left(\vec{q};\tau,\tau'\right) S_\alpha^{\ *}\left(\vec{q},\tau\right) S_\beta\left(\vec{q},\tau'\right) P_\gamma$$

- Some of the coefficients in the magnetoelectric term vanish due to symmetry considerations
- Minimization with respect to P_α gives the induced polarization in a magnetically ordered state

1^{st} approach: use **symmetry, group theory and Landau theory**, emphasizing the role of inversion.

$Ni_3V_2O_8$



This approach was first used to explain multiferroicity in multiferroic NVO, G. Lawes *et al.*, PRL **95,** 087205 (2005)

P ➡ HTI ➡ LTI ➡ C

LTI is ferroelectric

Approach reviewed with many examples:
A. B. Harris, PRB **76,** 054447 (2007)

For group theory, see also
P. G. Radaelli and L. C. Chapon, PRB **76,** 054428 (2007)

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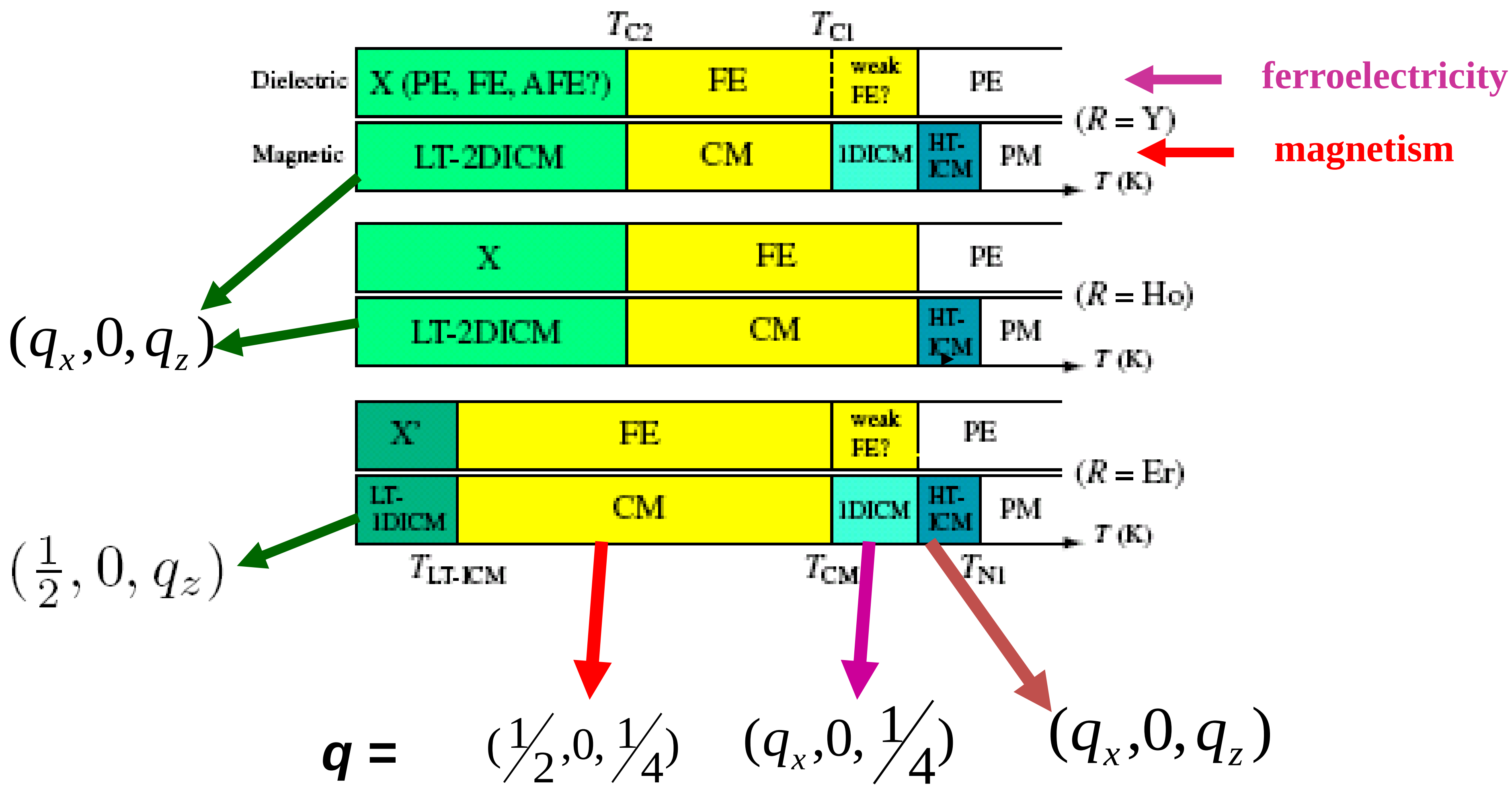
R=Y, Ho, Tb, Er, Tm

Spiral Spin Structure in the Commensurate Magnetic Phase of Multiferroic RMn_2O_5

Hiroyuki KIMURA*, Satoru KOBAYASHI[1], Yoshikazu FUKUDA, Toshihiro OSAWA, Youichi KAMADA, Yukio NODA, Isao KAGOMIYA[2], and Kay KOHN[3]

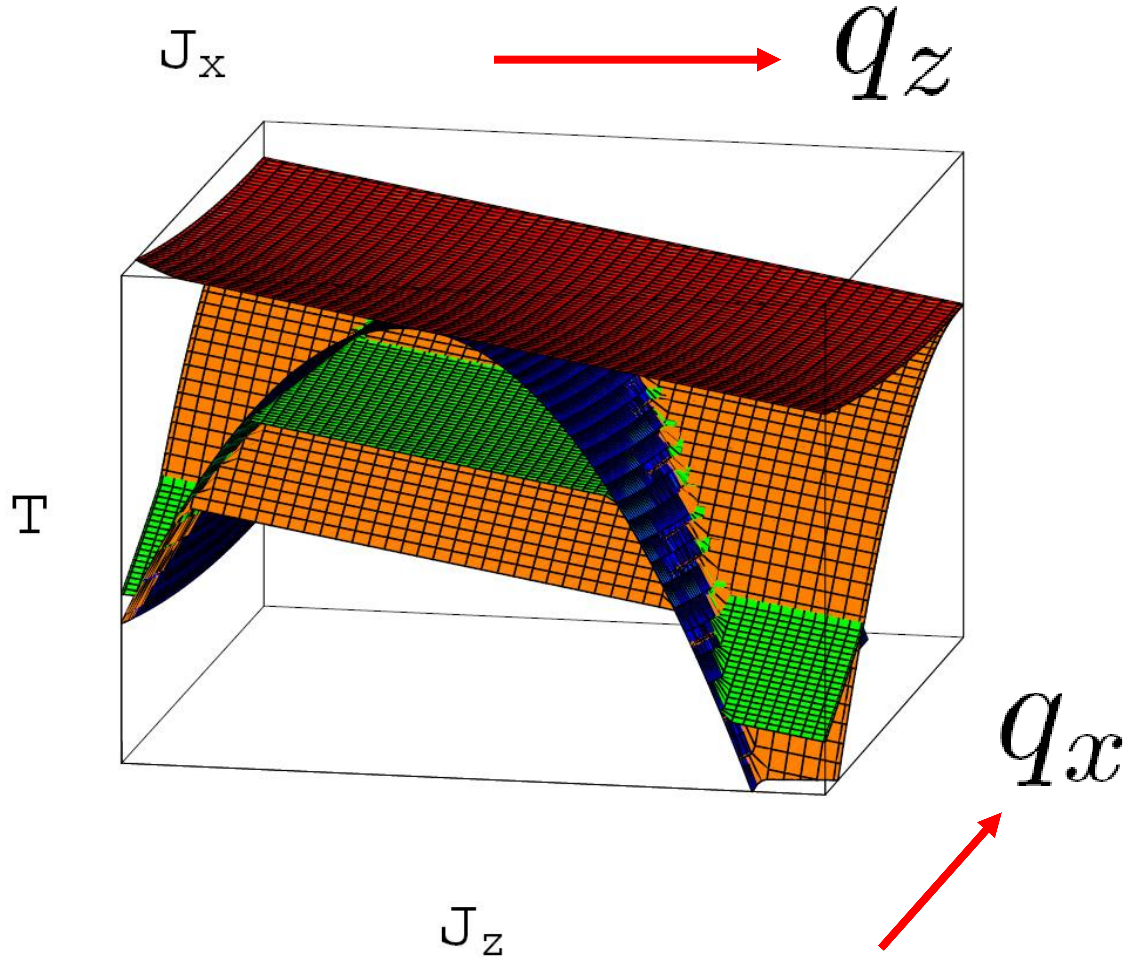


PRL **100,** 217202 (2008) PHYSICAL REVIEW LETTERS week ending 30 MAY 2008

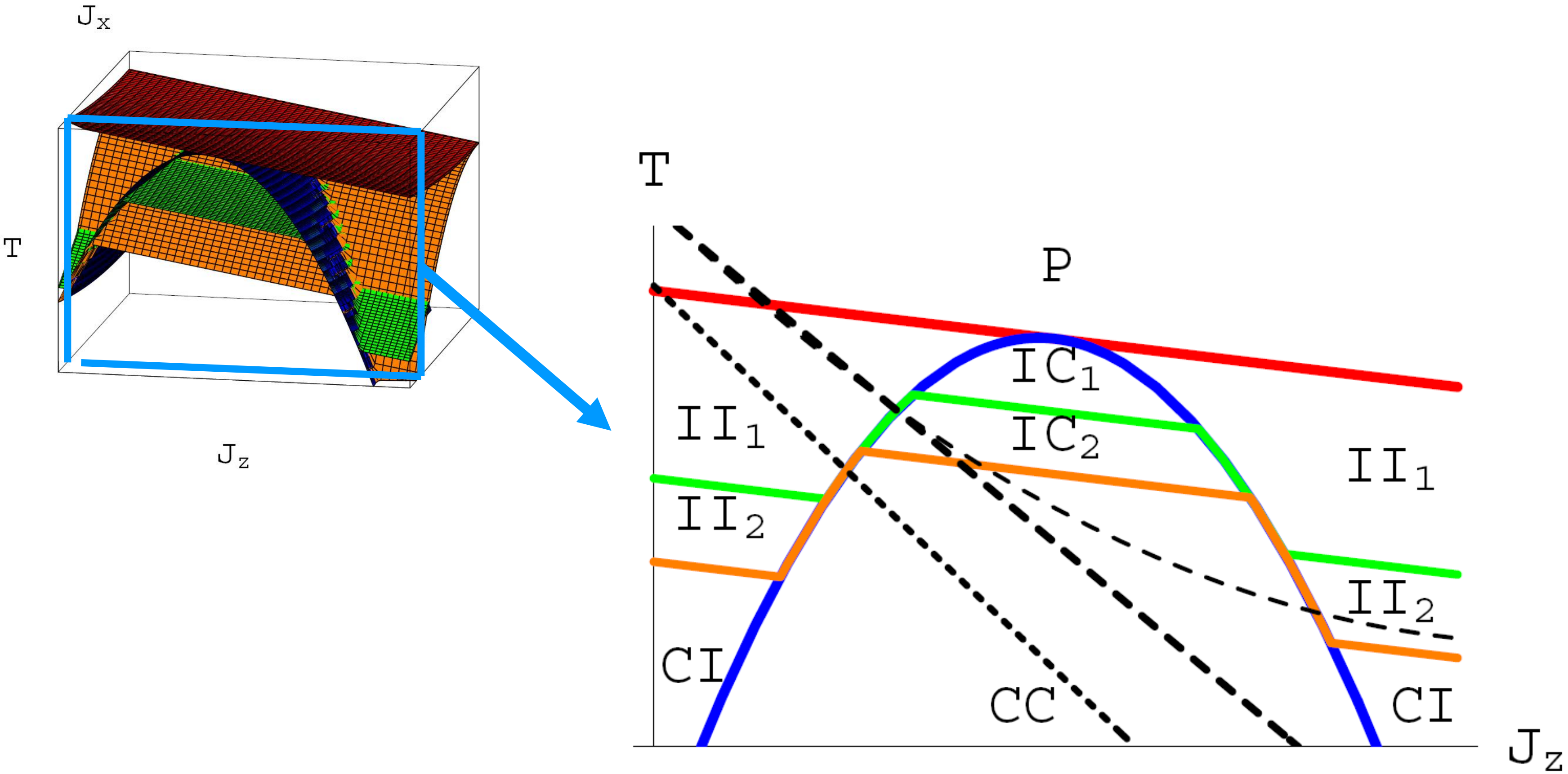
Order Parameters and Phase Diagram of Multiferroic RMn_2O_5

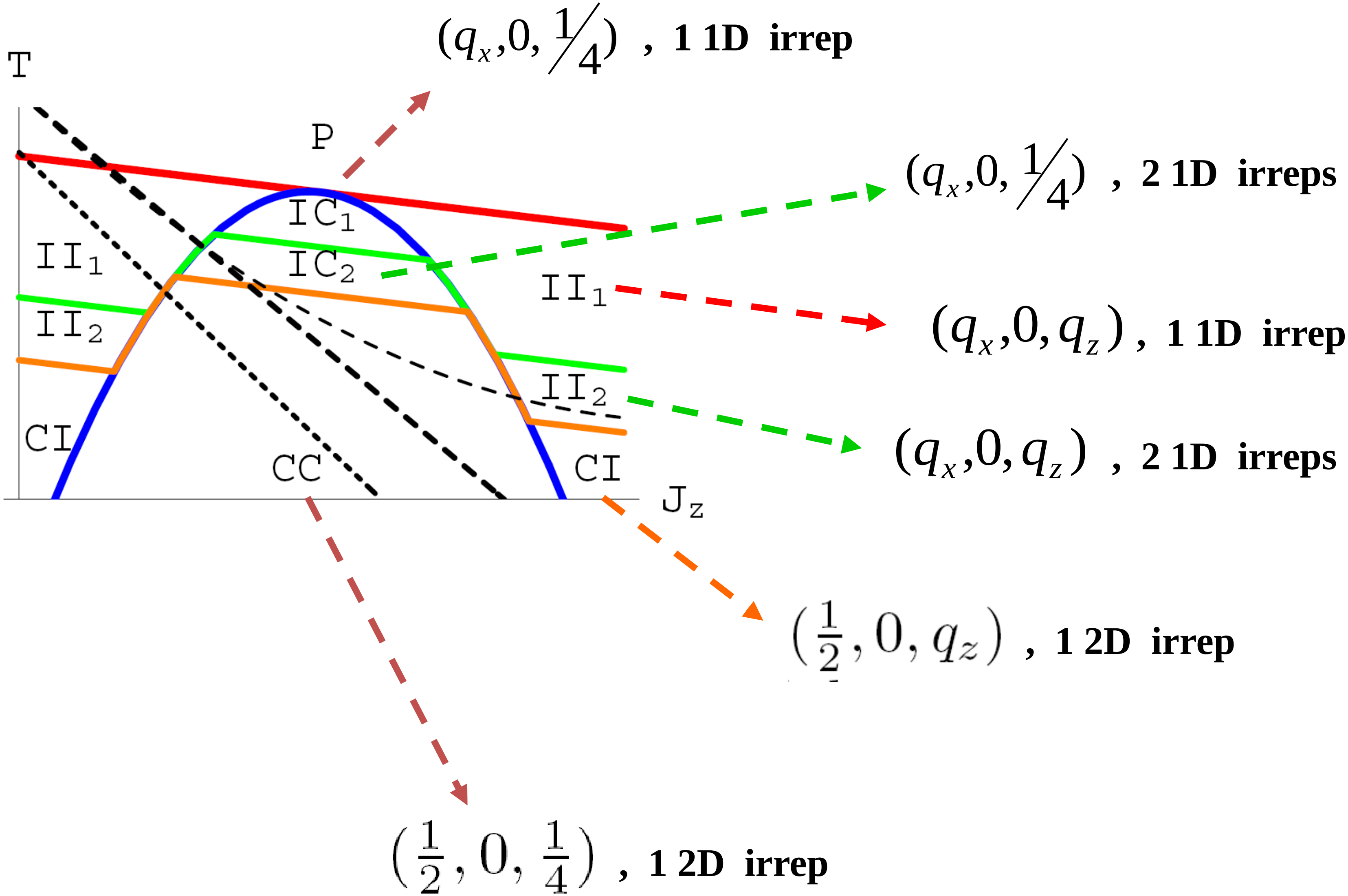
A. B. Harris,[1] Amnon Aharony,[2,*] and Ora Entin-Wohlman[2,*]

Our results: Generic phase diagram, *T* versus control parameters



RMn_2O_5 Generic phase diagram

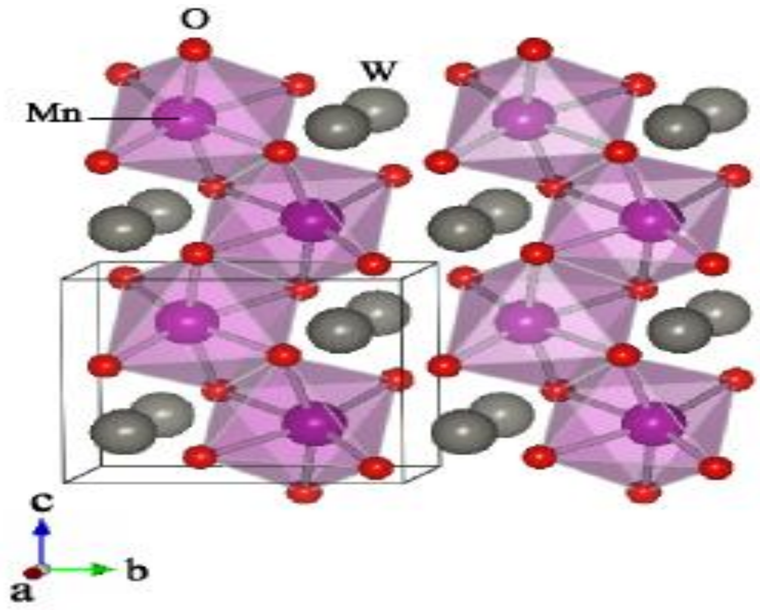




$(q_x, 0, \frac{1}{4})$, 1 1D irrep
T
P
$(q_x, 0, \frac{1}{4})$, 2 1D irreps
IC_1
II_1
IC_2
II_1
$(q_x, 0, q_z)$, 1 1D irrep
II_2
II_2
$(q_x, 0, q_z)$, 2 1D irreps
CI
CC
CI
J_z
$(\frac{1}{2}, 0, q_z)$, 1 2D irrep
$(\frac{1}{2}, 0, \frac{1}{4})$, 1 2D irrep

Shlomi Matityahu: Multiferroic $MnWO_4$

- Crystal structure – monoclinic with alternate zigzag chains of Mn^{2+}, W^{6+}
- Two magnetic ions $Mn^{2+}\left(S=\frac{5}{2}, L=0\right)$ per unit cell $\Rightarrow$ N=4

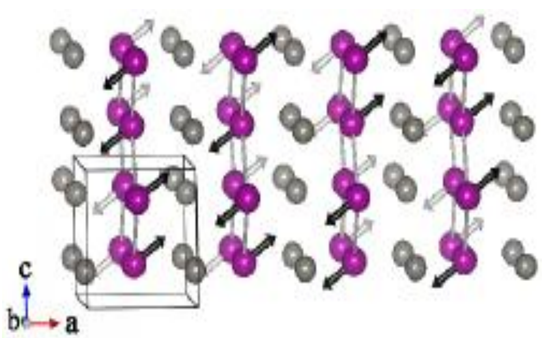


Taniguchi *et al.*, PRB **77**, 064408 (2008)

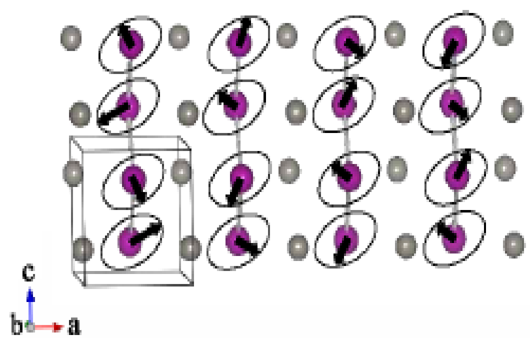
Multiferroic $MnWO_4$

- Three magnetic phase transitions –

	Temperature	Wave vector	Structure
AF3	13.5K	$\vec{q}_{IC} = (-0.214, 0.5, 0.457)$	Sinusoidal
AF2	12.3-12.7K	$\vec{q}_{IC} = (-0.214, 0.5, 0.457)$	Spiral elliptical
AF1	7-8K	$\vec{q}_{C1,2} = (\pm 0.25, 0.5, 0.5)$	↑↑↓↓



AF1

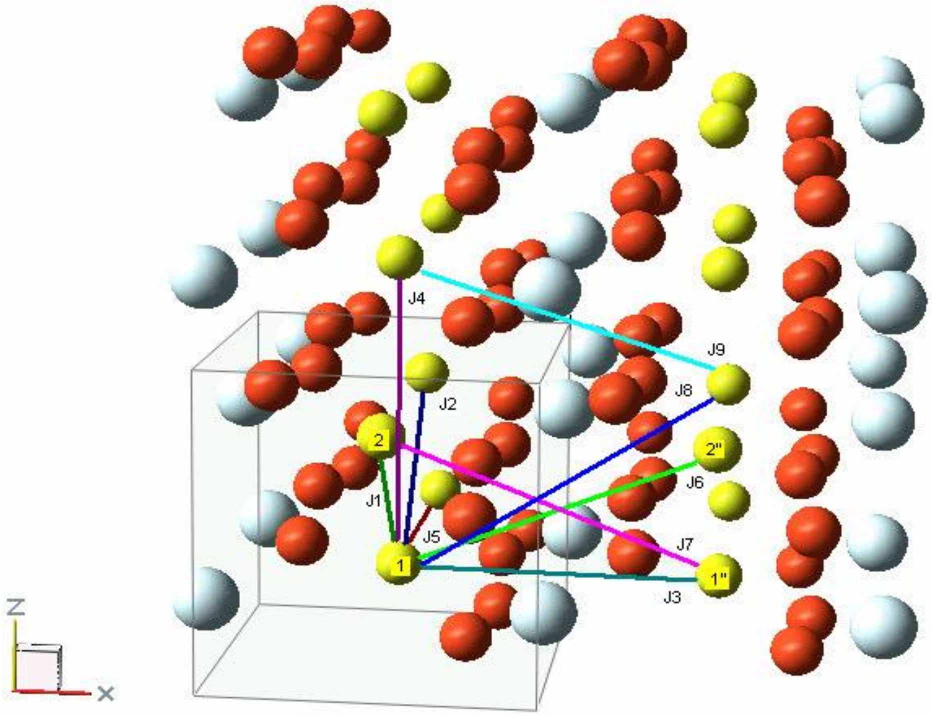


AF2

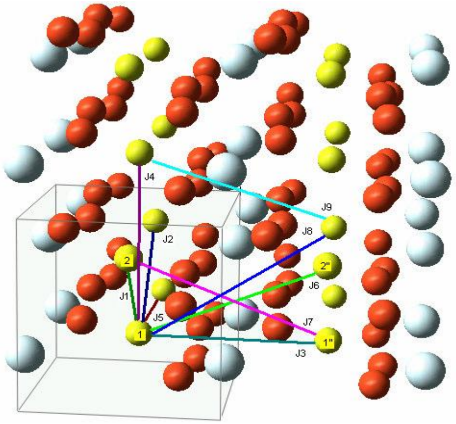
Taniguchi *et al.*, PRB **77**, 064408 (2008)

The model – use 2nd approach

- **Heisenberg model** with nine exchange couplings
- **Single ion anisotropy** which favor the **easy axis**
- We will omit the hard axis



Ehrenberg *et al.*, J. Phys. Condens. Matter **11**, 2649 (1999)



Frustration

Table 1. Indirect exchange couplings for the Mn ion at $(\frac{1}{2}, y, \frac{1}{4})$ via one or two oxygens of a common octahedron, $y = 0.6853$, together with the values determined and the observed relative orientations of the two corresponding spin pairs. The anisotropy parameter is refined to $J_{anis} = 0.284\ k_B$ K.

Position of neighbour	Distance (Å)	Exchange coupling	Value (k_B K)	Spin alignment
$(\frac{1}{2}, 1-y, \frac{3}{4})$ $(\frac{1}{2}, 1-y, -\frac{1}{4})$	3.283	J_1	−0.195	↑↓, ↑↑
$(\frac{1}{2}, 2-y, \frac{3}{4})$ $(\frac{1}{2}, 2-y, -\frac{1}{4})$	4.398	J_2	−0.135	↑↓, ↑↑
$(\frac{3}{2}, y, \frac{1}{4})$ $(-\frac{1}{2}, y, \frac{1}{4})$	4.823	J_3	−0.423	↑↓, ↑↑
$(\frac{1}{2}, y, \frac{5}{4})$ $(\frac{1}{2}, y, -\frac{3}{4})$	4.992	J_4	0.414	↑↓, ↑↓
$(\frac{1}{2}, y+1, \frac{1}{4})$ $(\frac{1}{2}, y-1, \frac{1}{4})$	5.753	J_5	0.021	↑↓, ↑↓
$(\frac{3}{2}, 1-y, \frac{3}{4})$ $(-\frac{1}{2}, 1-y, -\frac{1}{4})$	5.795	J_6	−0.509	↑↓, ↑↓
$(-\frac{1}{2}, 1-y, \frac{3}{4})$ $(\frac{3}{2}, 1-y, -\frac{1}{4})$	5.873	J_7	0.023	↑↑, ↑↑
$(\frac{3}{2}, 2-y, \frac{3}{4})$ $(-\frac{1}{2}, 2-y, -\frac{1}{4})$	6.492	J_8	0.491	↑↑, ↑↑
$(-\frac{1}{2}, 2-y, \frac{3}{4})$ $(\frac{3}{2}, 2-y, -\frac{1}{4})$	6.561	J_9	−1.273	↑↓, ↑↓

- **Fourier transform of the inverse susceptibility matrix** –

$$\chi^{-1}(\vec{q}) = \begin{pmatrix} aT - J(\vec{q};1,1) & -J(\vec{q};1,2) & 0 & 0 \\ -J^{*}(\vec{q};1,2) & aT - J(\vec{q};1,1) & 0 & 0 \\ 0 & 0 & aT + D - J(\vec{q};1,1) & -J(\vec{q};1,2) \\ 0 & 0 & -J^{*}(\vec{q};1,2) & aT + D - J(\vec{q};1,1) \end{pmatrix}$$

- $J(\vec{q};1,1), J(\vec{q};1,2)$ are determined by the superexchange interaction couplings

- Eigenvalues and eigenvectors of the $\chi^{-1}(\vec{q})$ matrix:

$$\zeta_{+,x}(\vec{q},T) = aT - \lambda_{+}(\vec{q}) \quad ; \quad \zeta_{-,x}(\vec{q},T) = aT - \lambda_{-}(\vec{q})$$

$$\zeta_{+,b}(\vec{q},T) = aT + D - \lambda_{+}(\vec{q}) \quad ; \quad \zeta_{-,b}(\vec{q},T) = aT + D - \lambda_{-}(\vec{q})$$

$$\vec{S}_{+,x}(\vec{q}) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{-i\varphi(\vec{q})} \\ 0 \\ 0 \end{pmatrix} \; ; \; \vec{S}_{-,x}(\vec{q}) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -e^{-i\varphi(\vec{q})} \\ 0 \\ 0 \end{pmatrix}$$

$$\vec{S}_{+,b}(\vec{q}) = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 0 \\ 1 \\ e^{-i\varphi(\vec{q})} \end{pmatrix} \; ; \; \vec{S}_{-,b}(\vec{q}) = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 0 \\ 1 \\ -e^{-i\varphi(\vec{q})} \end{pmatrix}$$

$$\lambda_{\pm}(\vec{q}) \equiv J(\vec{q};1,1) \pm \left| J(\vec{q};1,2) \right|$$

$$e^{i\varphi(\vec{q})} \equiv \frac{J(\vec{q};1,2)}{\left| J(\vec{q};1,2) \right|}$$

Magnetic field

$$\chi(T) = \frac{\frac{(g\mu_B)^2 J(J+1)}{3k_B}}{T-\theta}$$

$$a = \frac{3}{J(J+1)} k_B .$$

- The critical wave vector $\vec{q}_{IC}$ of the first transition is determined by maximizing $\lambda_{+}(\vec{q})$
- Order parameters for the **first two transitions**:

$$\begin{pmatrix} S_x(\vec{q}_{IC},\tau_1) \\ S_x(\vec{q}_{IC},\tau_2) \\ S_b(\vec{q}_{IC},\tau_1) \\ S_b(\vec{q}_{IC},\tau_2) \end{pmatrix} = \sigma_x(\vec{q}_{IC})\vec{S}_{+,x}(\vec{q}_{IC}) + \sigma_b(\vec{q}_{IC})\vec{S}_{+,b}(\vec{q}_{IC})$$

- Order parameters for the **third transition lock-in at commensurate wave vector**:

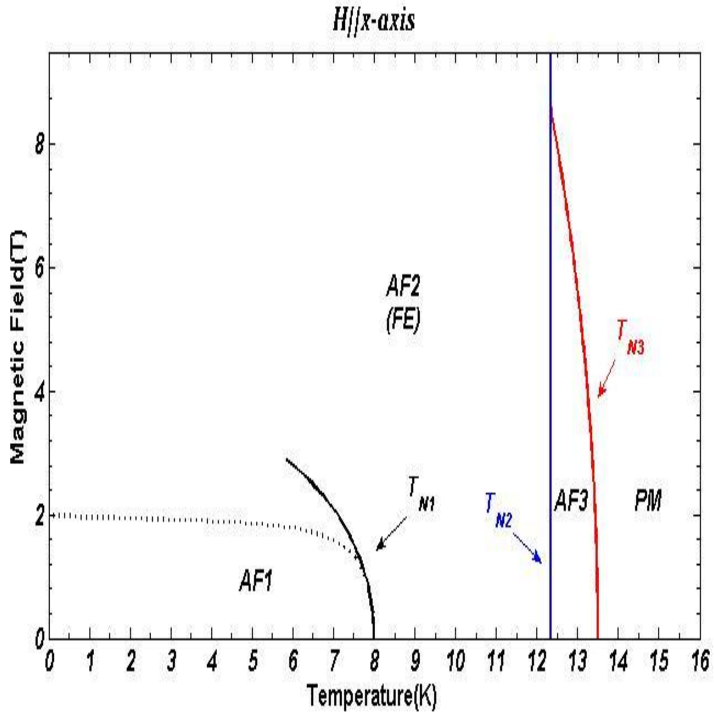
$$\begin{pmatrix} S_x(\vec{q}_C,\tau_1) \\ S_x(\vec{q}_C,\tau_2) \\ S_b(\vec{q}_C,\tau_1) \\ S_b(\vec{q}_C,\tau_2) \end{pmatrix} = \sigma_x(\vec{q}_C)\vec{S}_{+,x}(\vec{q}_C)$$

$$
\begin{aligned}
f = \; & \left(aT - \lambda_+(\overrightarrow{q}_{IC})\right)\left|\sigma_x(\overrightarrow{q}_{IC})\right|^2 + 3bT\left|\sigma_x(\overrightarrow{q}_{IC})\right|^4 + \left(aT + D - \lambda_+(\overrightarrow{q}_{IC})\right)\left|\sigma_b(\overrightarrow{q}_{IC})\right|^2 \\
& + 3bT\left|\sigma_b(\overrightarrow{q}_{IC})\right|^4 + 2bT\left|\sigma_x(\overrightarrow{q}_{IC})\right|^2\left|\sigma_b(\overrightarrow{q}_{IC})\right|^2\left[2 + \cos(2\varphi_x - 2\varphi_b)\right] \\
& + V_{cell}\sum_{\alpha=1}^{3}\frac{{P_\alpha}^2}{2\chi^0_{E,\alpha}} + r\left|\sigma_x(\overrightarrow{q}_{IC})\right|\left|\sigma_b(\overrightarrow{q}_{IC})\right|\sin(\varphi_x - \varphi_b)P_b
\end{aligned}
$$

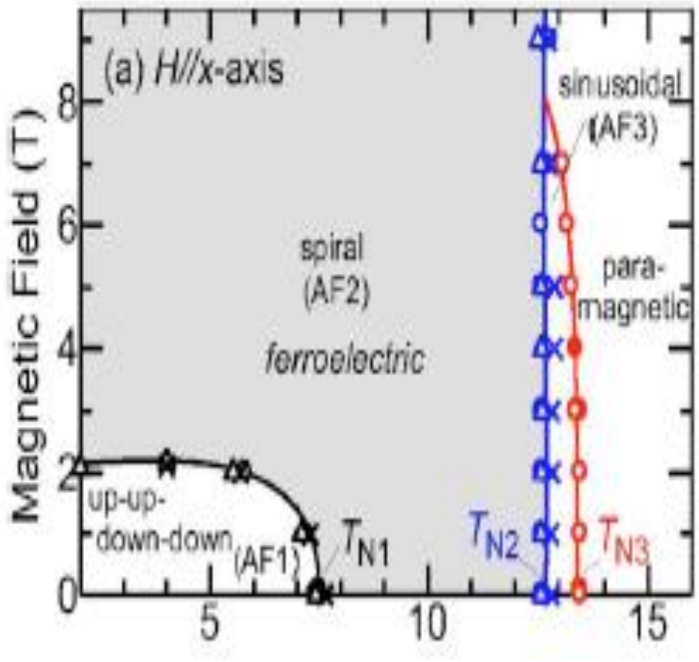
$$
\begin{aligned}
f = \; & \left(aT - \lambda_+(\overrightarrow{q}_{IC})\right)\left|\sigma_x(\overrightarrow{q}_{IC})\right|^2 + 3bT\left|\sigma_x(\overrightarrow{q}_{IC})\right|^4 \\
& + \left(aT + D - \lambda_+(\overrightarrow{q}_{IC})\right)\left|\sigma_b(\overrightarrow{q}_{IC})\right|^2 + 3bT\left|\sigma_b(\overrightarrow{q}_{IC})\right|^4 \\
& + 2bT\left|\sigma_x(\overrightarrow{q}_{IC})\right|^2\left|\sigma_b(\overrightarrow{q}_{IC})\right|^2\left[2 + \cos(2\varphi_x - 2\varphi_b) - \frac{\chi^0_{E,b}r^2}{4V_{cell}bT}sin^2(\varphi_x - \varphi_b)\right]
\end{aligned}
$$

Results - Phase diagram of $MnWO_4$

Theory



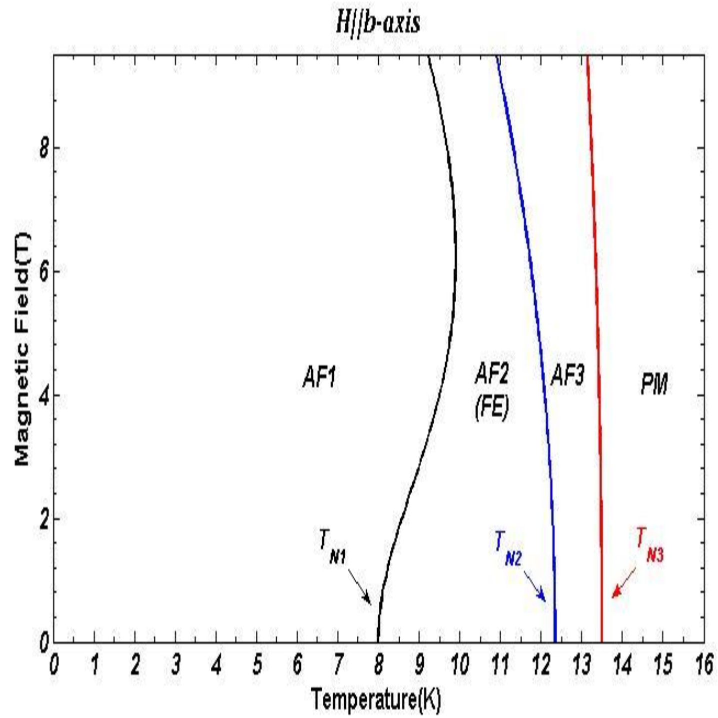
Experiment



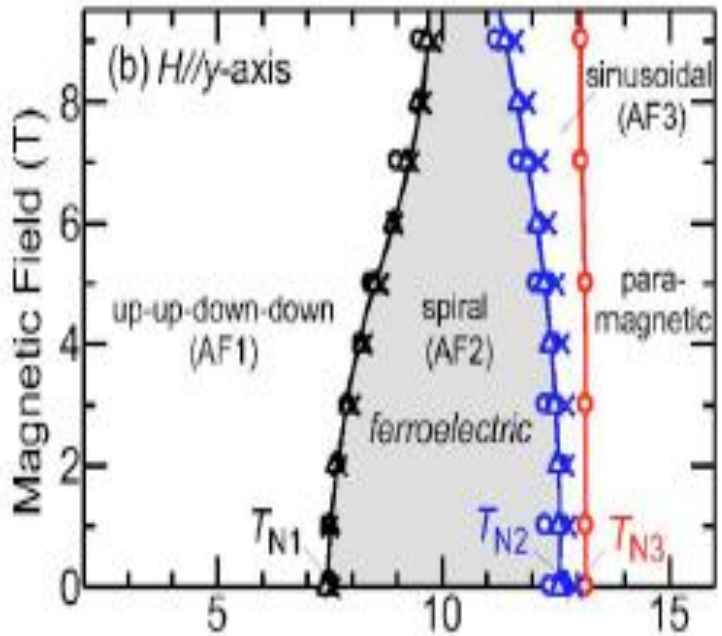
Arkenbout *et al.*, PRB **74**, 184431 (2006)

Results - Phase diagram of $MnWO_4$

Theory



Experiment



Arkenbout *et al.*, PRB **74**, 184431 (2006)

Dilution

$$a(x) = a_{Mn}x + a_{Fe}(1-x)$$

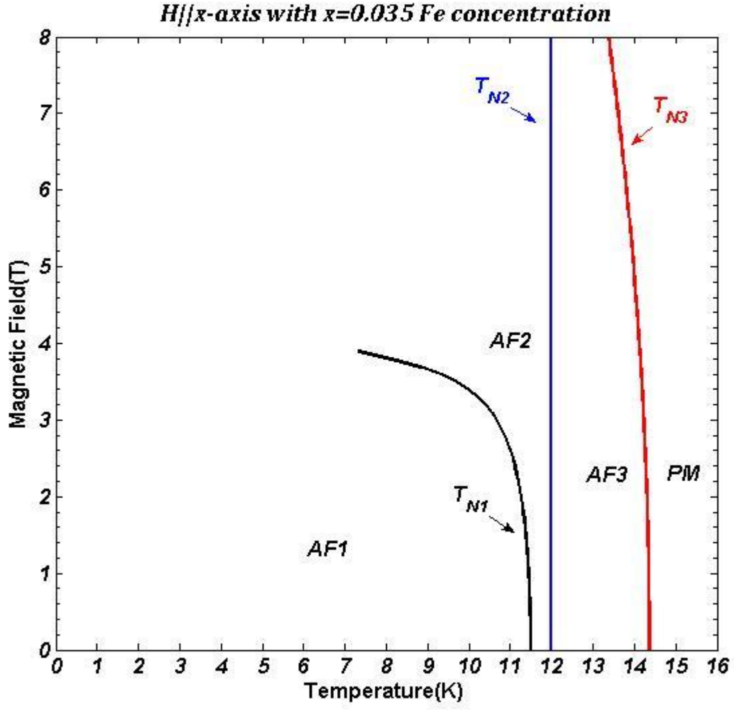
$$\lambda_+(\overrightarrow{q}_{IC}(x), x) = \lambda_{+,IC}(0) + c_1 x$$

$$D(x) = D(0) + c_2 x$$

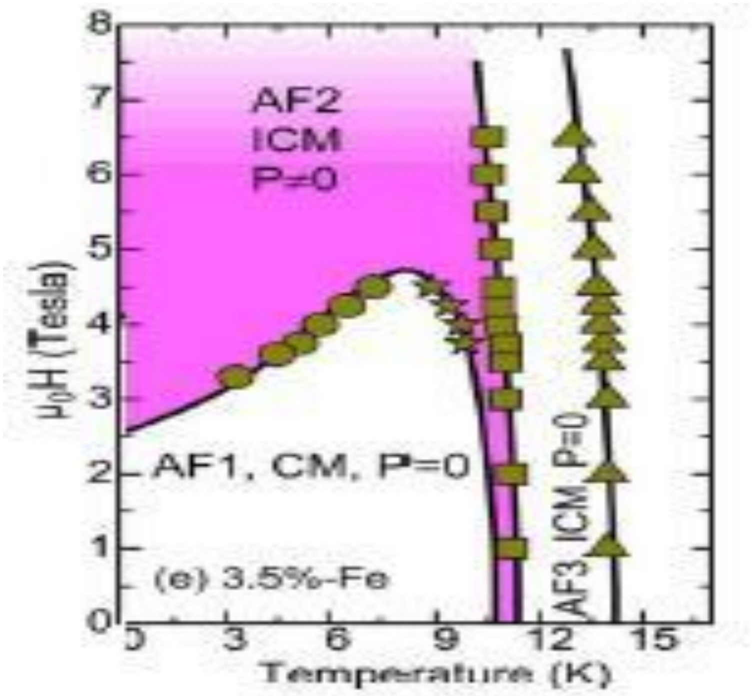
$$\eta(x) = \eta(0) + c_3 x \qquad \eta \equiv \frac{\lambda_+(\overrightarrow{q}_C)}{\lambda_+(\overrightarrow{q}_{IC})}$$

Results - Phase diagram of $Mn_{0.965}Fe_{0.035}WO_4$

Theory



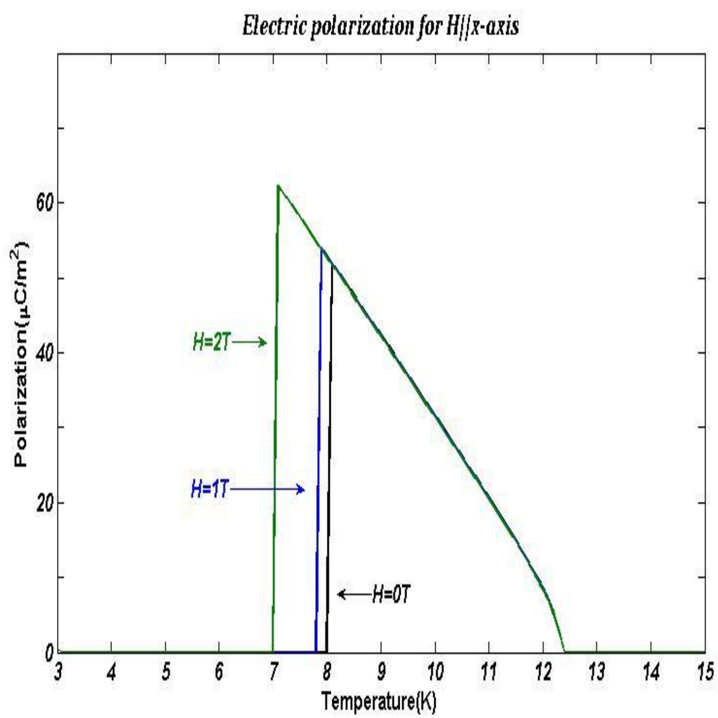
Experiment



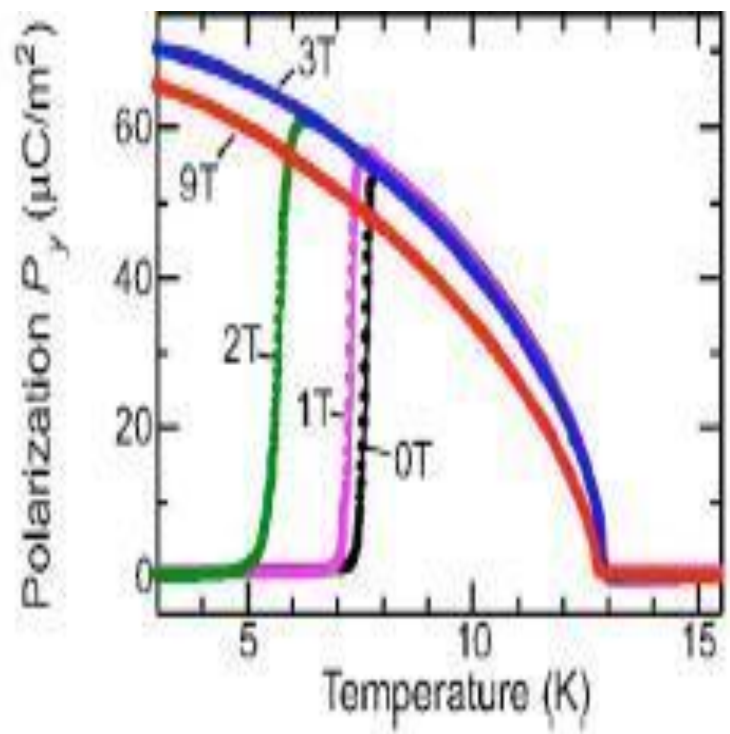
Ye *et al.*, PRB **78**, 193101 (2008)

Results– Electric polarization of MnWO4

Theory



Experiment

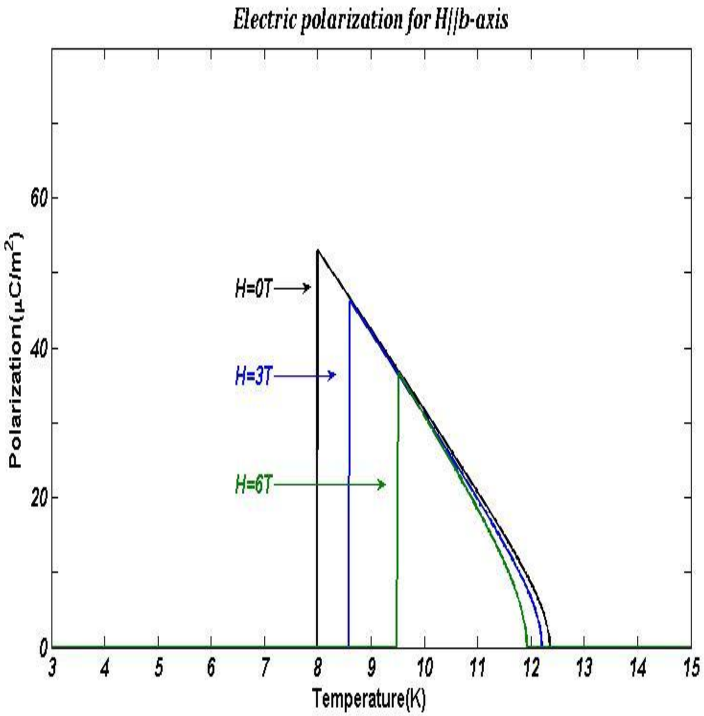


Arkenbout *et al.*, PRB **74**, 184431 (2006)

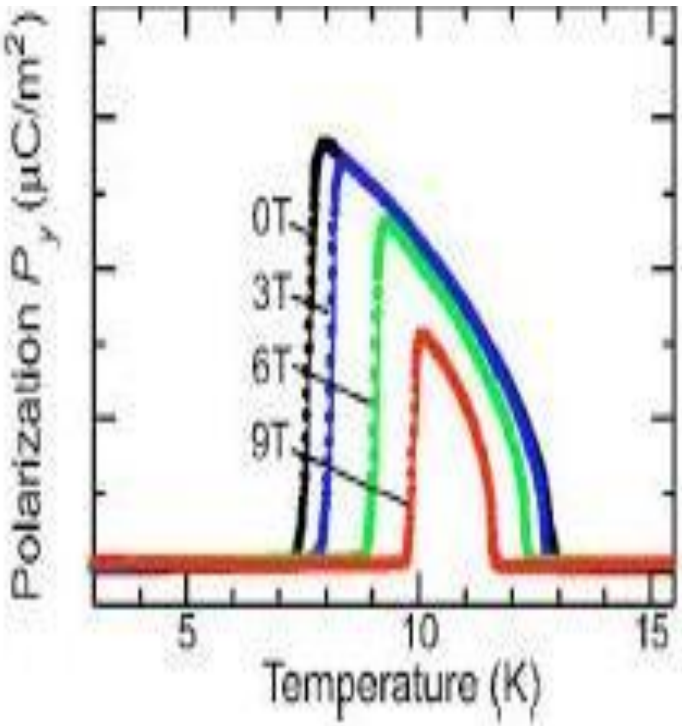
$$f_{int} = r\,|\sigma_x(\overrightarrow{q}_{IC})|\,|\sigma_b(\overrightarrow{q}_{IC})|\sin(\varphi_x - \varphi_b)P_b$$

Results - Electric polarization of $MnWO_4$

Theory



Experiment



Arkenbout *et al.*, PRB **74**, 184431 (2006)

Conclusions

- Input: Experimental exchange couplings plus very few additional parameters: spin anisotropy *D*, quartic coefficient *b* and dilution coefficients c_i.
- Output: several H-T phase diagrams of pure and dilute $MnWO_4$.
- Output: the induced ferroelectric polarization.
- **Landau theory works excellently well** for phase diagrams!
- Can **exclude other sets** of proposed exchange couplings!