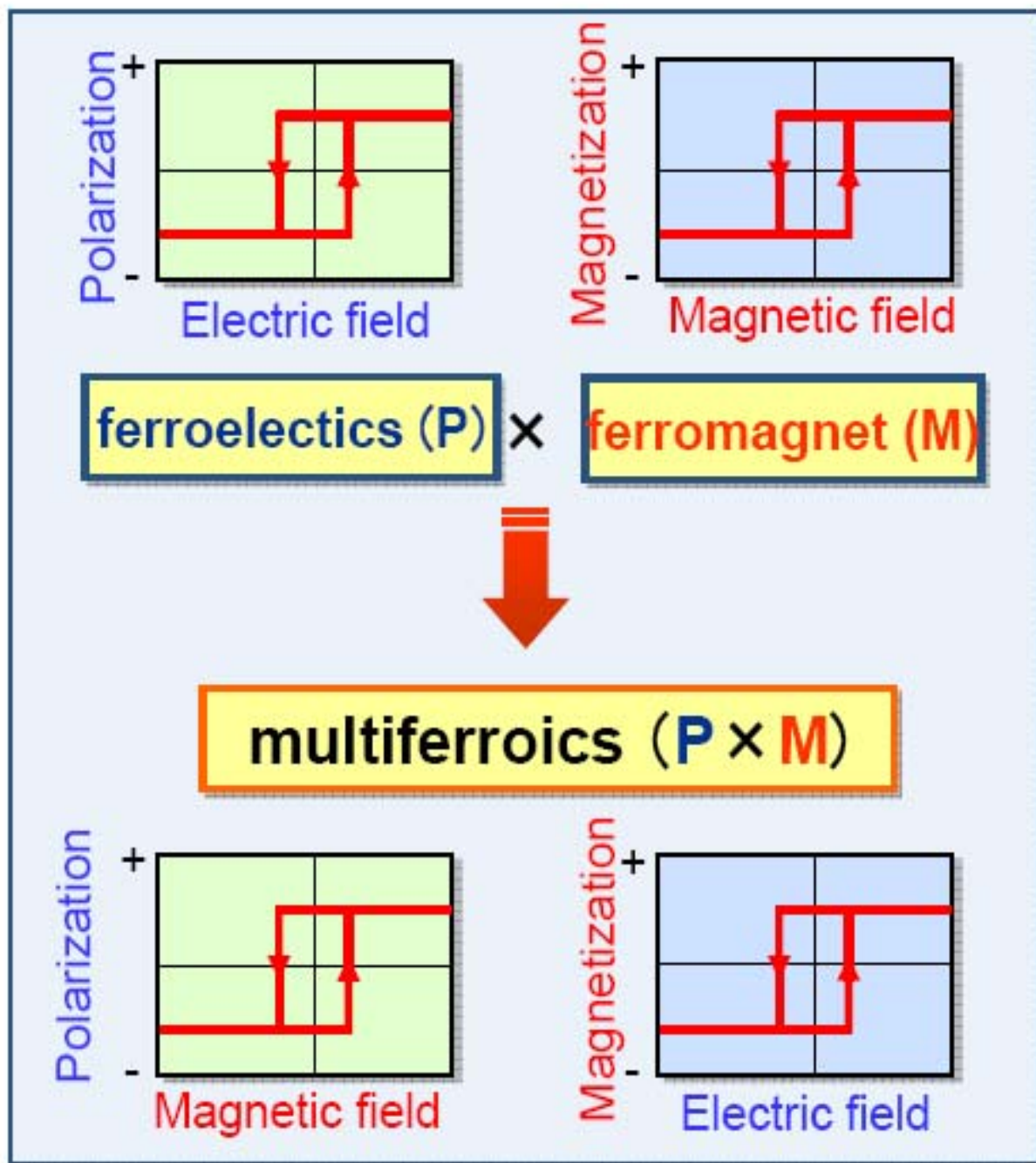
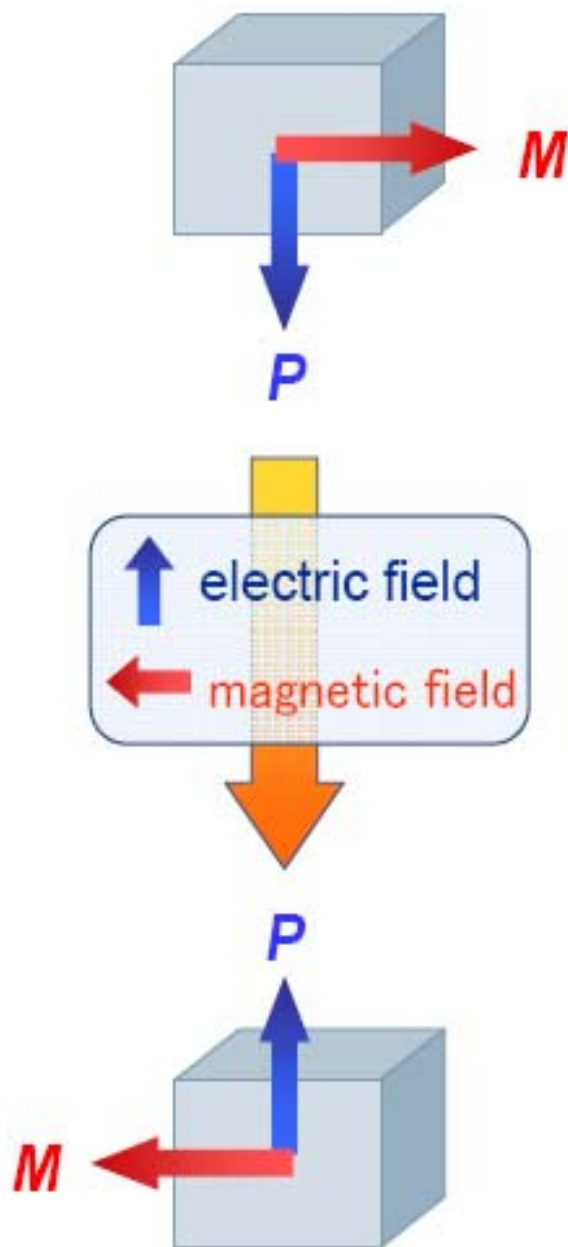








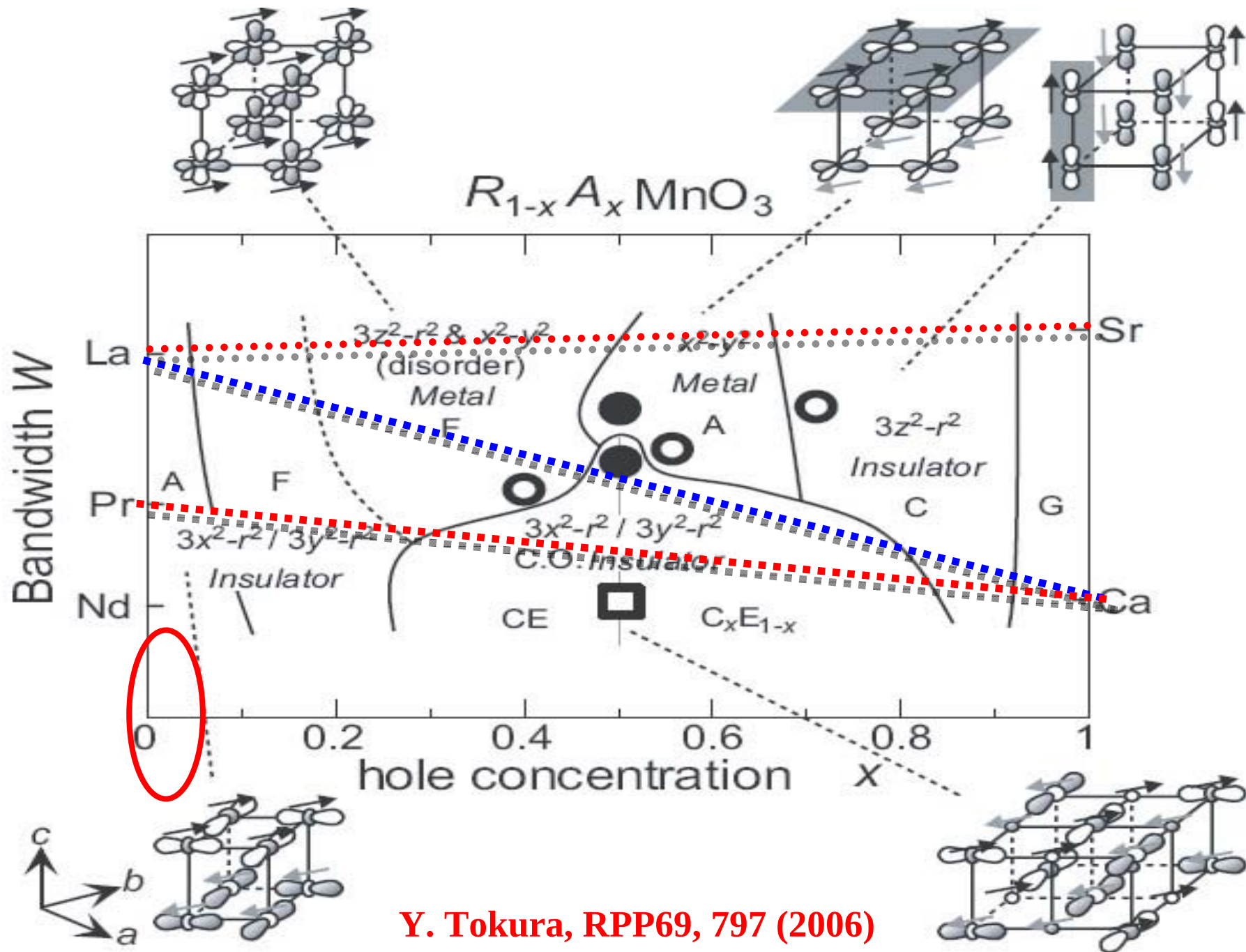
Multiferroicity: Our experiences beyond manganites

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Nanjing University

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Group page <http://pld.nju.edu.cn/>



Y. Tokura, RPP69, 797 (2006)



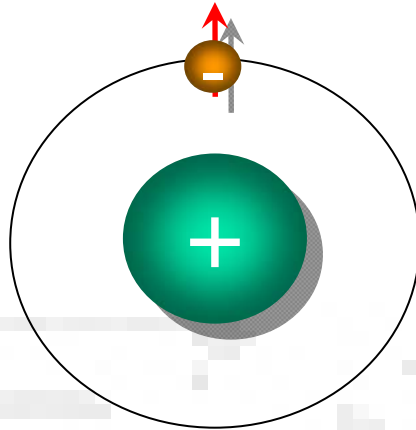
Content

- **Background & motivations**
- **Origin of spiral spin order in manganites**
- **Predictions of novel multiferroics**
- **Phase competition and beyond**
- **Exchange bias in multiferroic heterostructure**
- **Summary & perspectives**

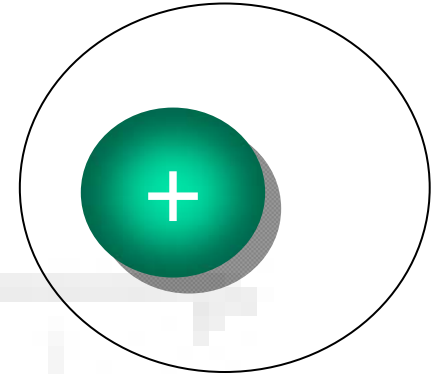


Background: symmetry argument

Magnetism



Ferroelectricity



Partially filled d shells
break **Time** reversal
symmetry $t \rightarrow -t, M \rightarrow -M$

Empty d shells break
Space reversal symmetry
 $x \rightarrow -x, P \rightarrow -P$

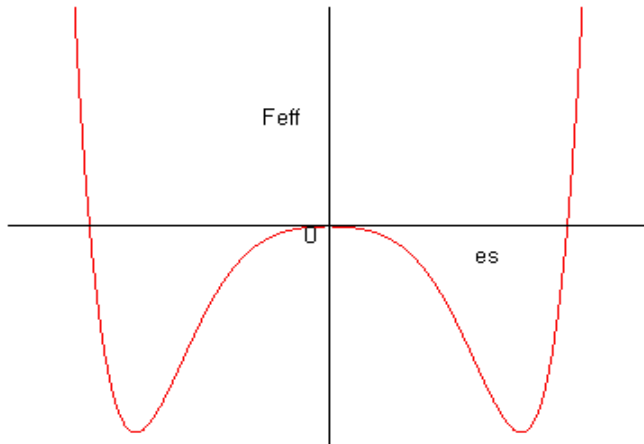
$$H=f(M, P)=f(-M, -P) = f(-M, P)=f(M, -P)$$



Background: symmetry argument

Mostovoy, PRL 96, 067601 (06)

If spin order is spatially inhomogeneous, symmetry allows for the 3rd-order coupling $P\partial M$ and then P may appear.



$$\Phi_{em}(\mathbf{P}, \mathbf{M}) =$$

$$\gamma \mathbf{P} \cdot [\mathbf{M}(\nabla \cdot \mathbf{M}) - (\mathbf{M} \cdot \nabla) \mathbf{M} + \dots].$$

$$\Phi = \Phi_{em} + \mathbf{P}^2 / 2\pi\epsilon$$

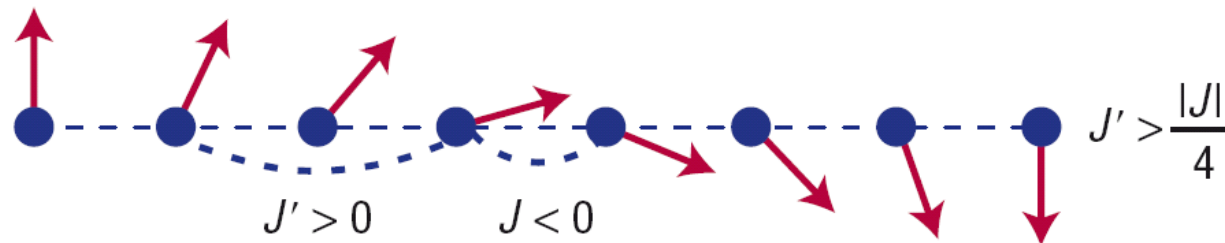


$$\mathbf{P} \propto [(\mathbf{M} \cdot \partial) \mathbf{M} - \mathbf{M}(\partial \cdot \mathbf{M})].$$

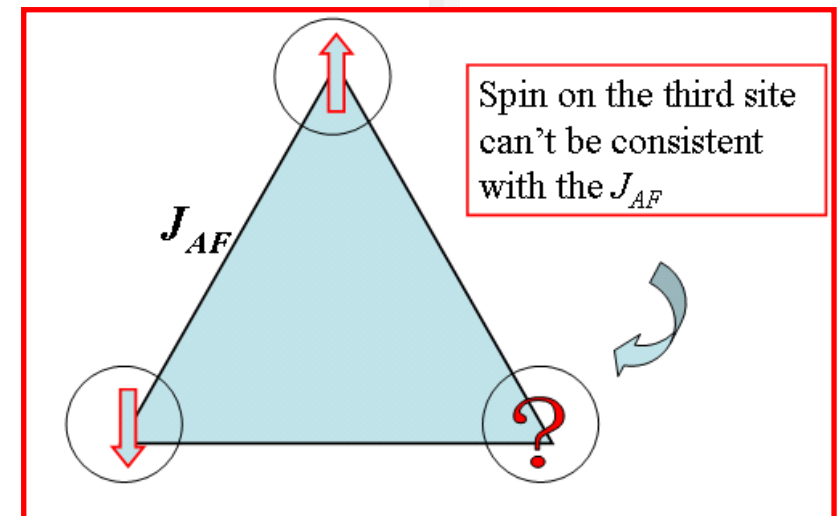


Background: spin configuration argument

- 1D chain magnet with the competition between NN FM coupling (J) and NNN AFM coupling (J') favors FSO if $|J'/J| > 1/4$. (JPCM 7, 8605 (1995))



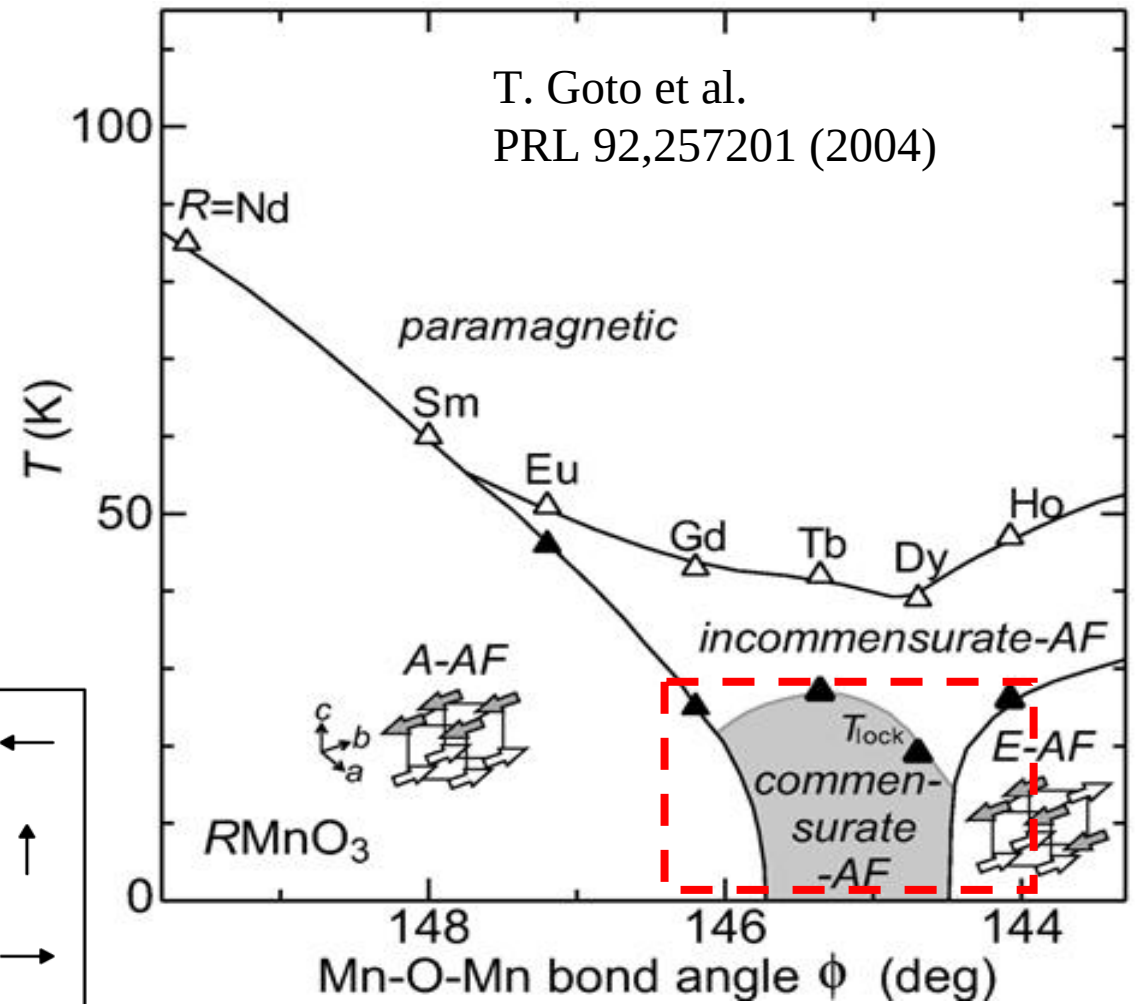
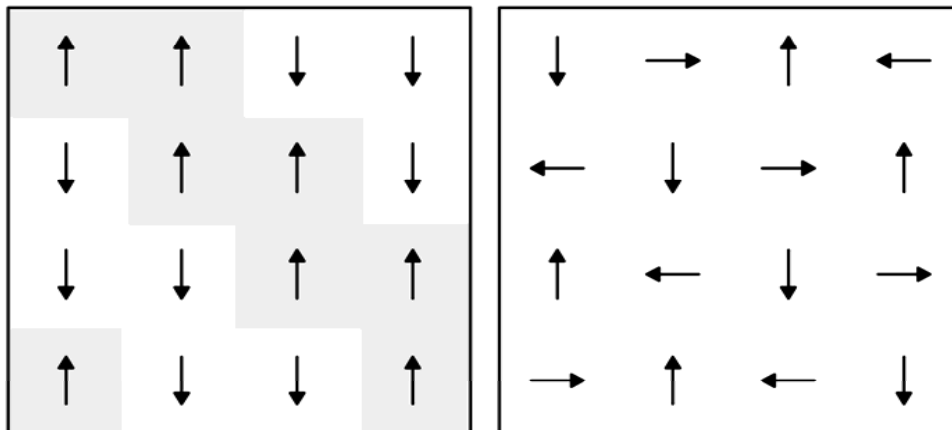
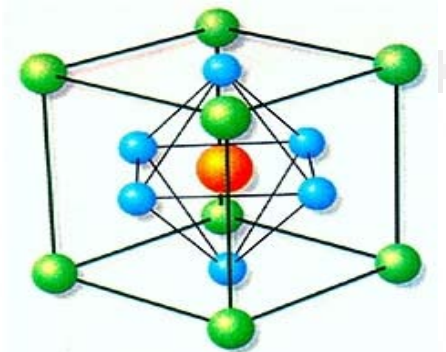
- AFM triangular-lattice favors FSO.





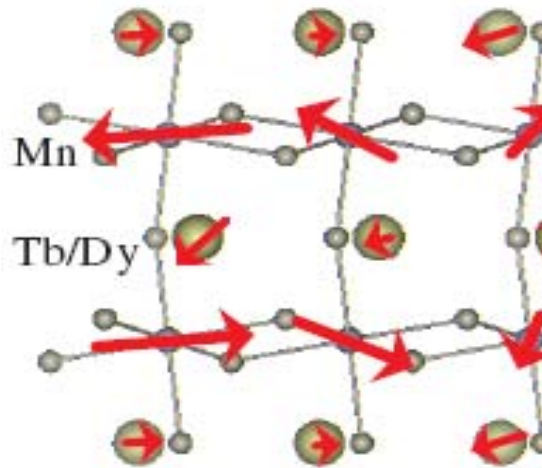
Background: structures and facts

RMnO_3 phases

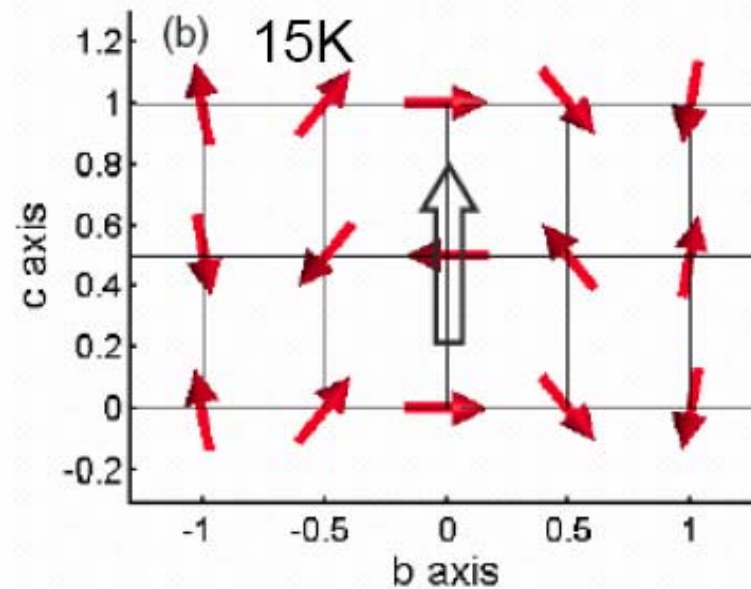
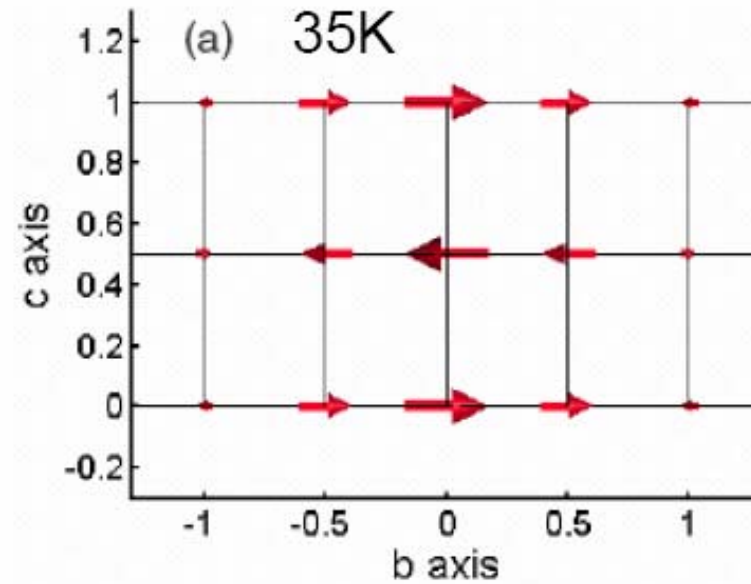




Background: structures and facts



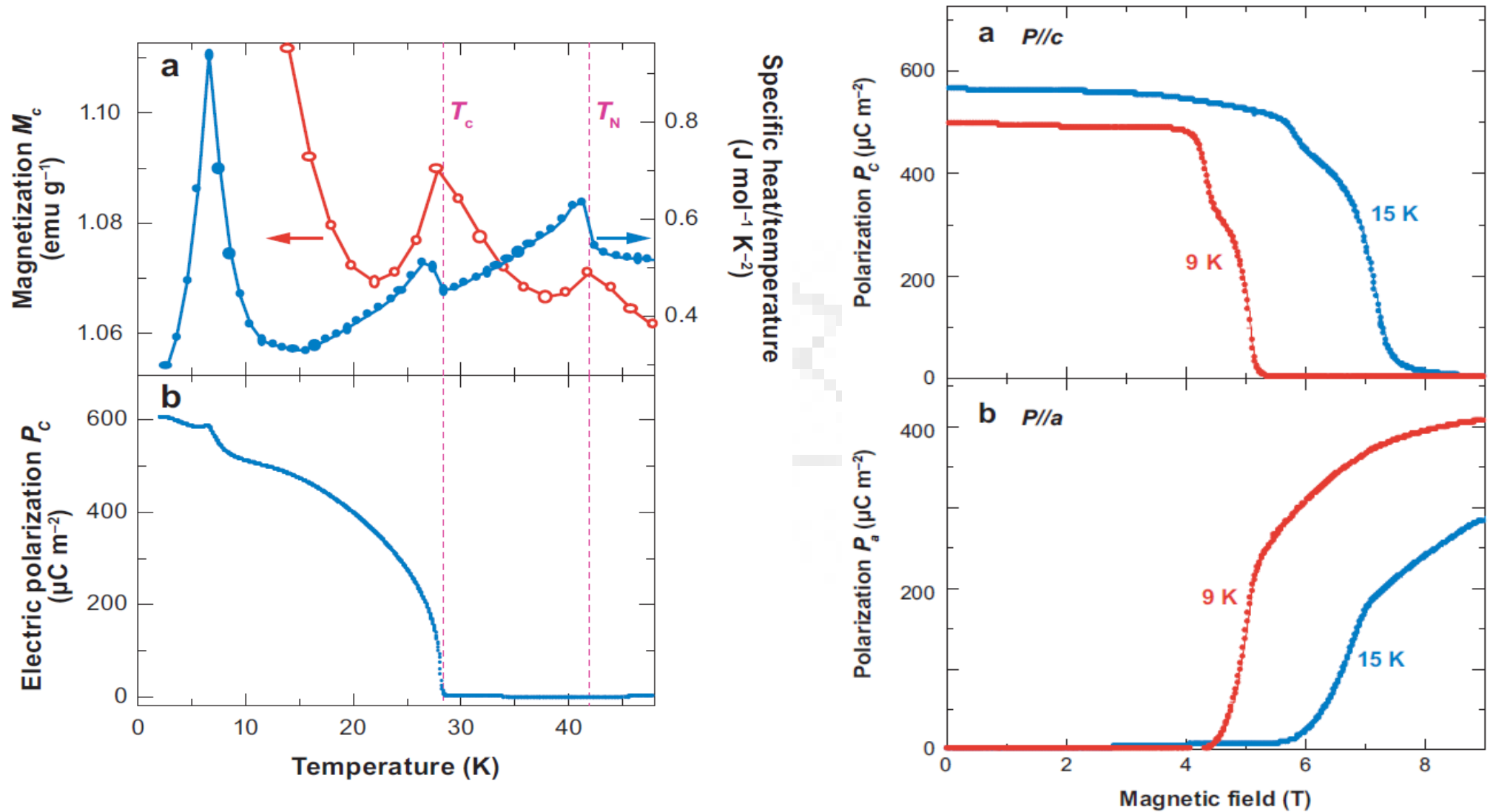
TbMnO_3



T. Arima et al.
PRL 96, 097202(2006)



Background: structures and facts

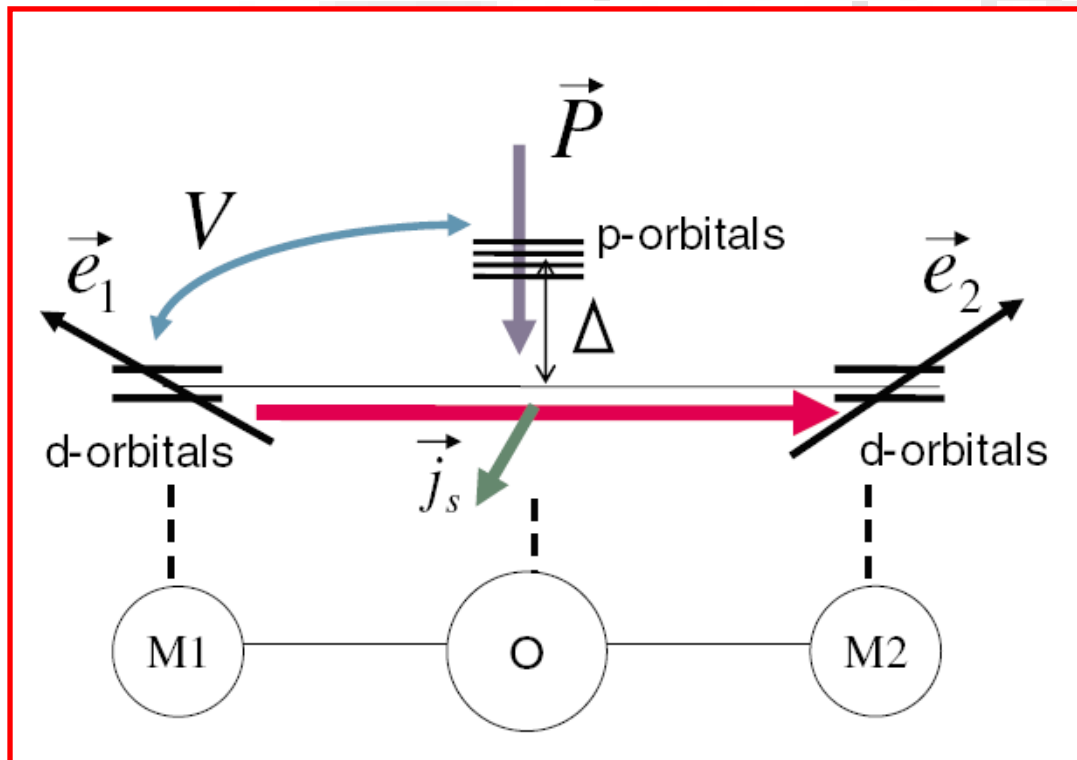


Kimura, Annu. Rev. Mater. Res.37, 387, 2007



Background: microscopic mechanism

- Frustrated spin-orbital coupling, **Dzyaloshinskii-Moriya** effect between two *d*-orbital ions with canted spins produces a dipole.
- KNB theory on spin-orbital coupling giving similar prediction.



Katsura et al, PRL 95, 057205 (05)
Sergienko et al, PRB 73, 094434 (06)

$$P = \eta e_{ij} \times (S_i \times S_j)$$

$$\eta \approx ea(t_{dp} / \Delta_{dp}) / \cos(\theta_{ij} / 2)$$

double-exchange

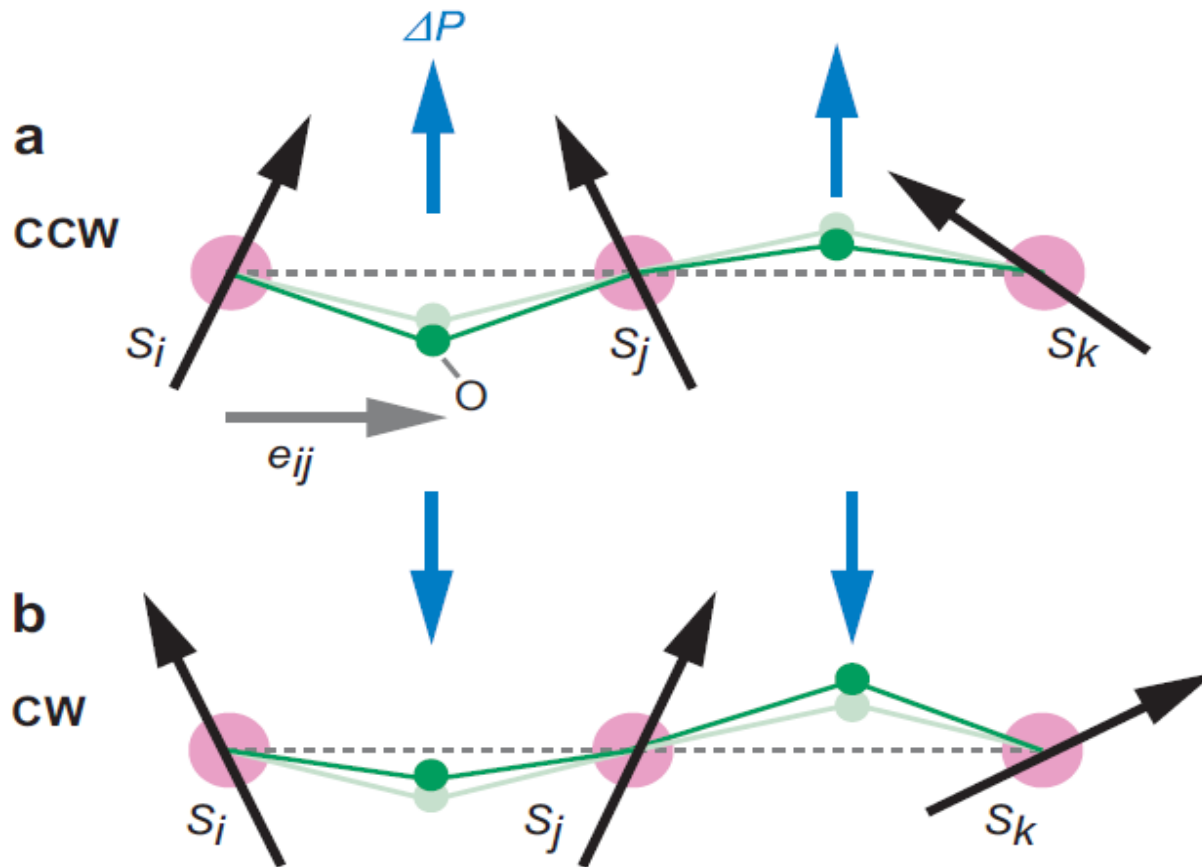
$$\eta \approx ea(t_{dp} / \Delta_{dp})^3$$

super-exchange



Background: mechanism

Cooperative GdFeO₃ distortion



$$\vec{P} \propto -\vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)$$

Katsura, Nagaosa, Balatsky
PRL95,057205, 2005

Mostovoy
PRL96, 067601, 2006

Sergienko, Dagotto
PRB73,094434, 2006

Xiang et al.
PRL101,037209, 2008

Malashevich, Vanderbilt
PRL101,037210, 2008

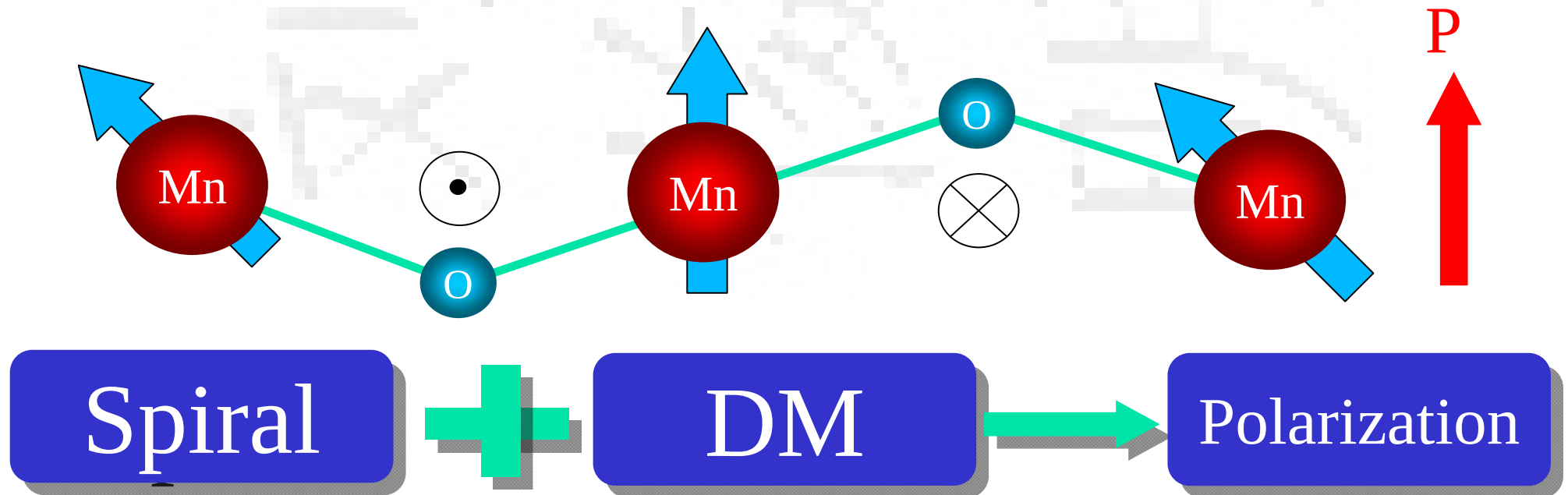
Kimura, Annu. Rev. Mater. Res.37, 387, 2007



Origin of spiral-spin order: picture

$$\mathbf{D}^a(\mathbf{r}_n) \cdot [\mathbf{S}_n \times \mathbf{S}_{n+1}] \quad E = -\lambda x + kx^2: \lambda \sim \lambda_0 (\mathbf{S} \times \mathbf{S})$$

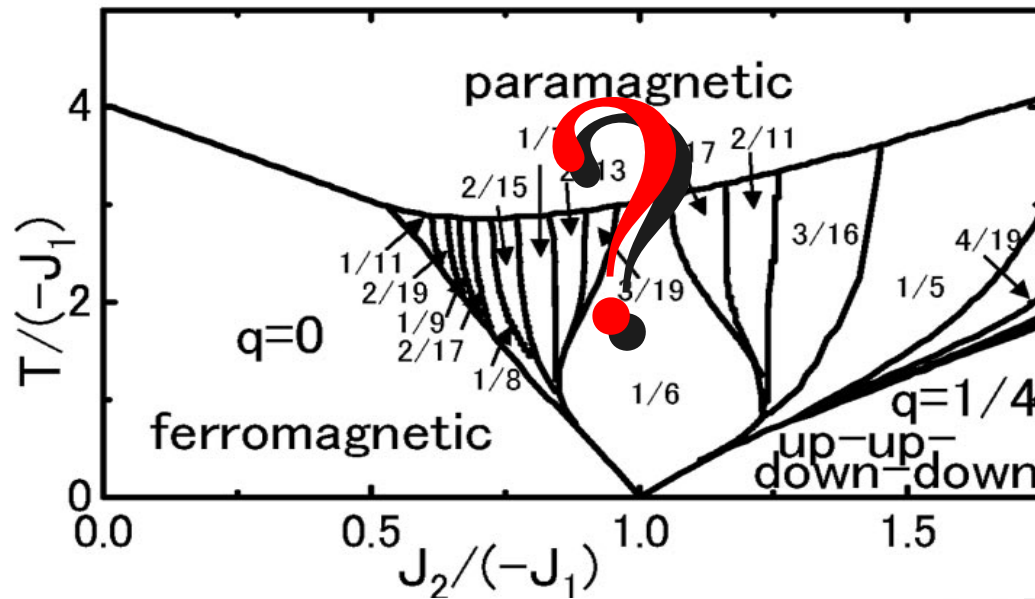
Cooperative GdFeO_3 distortion



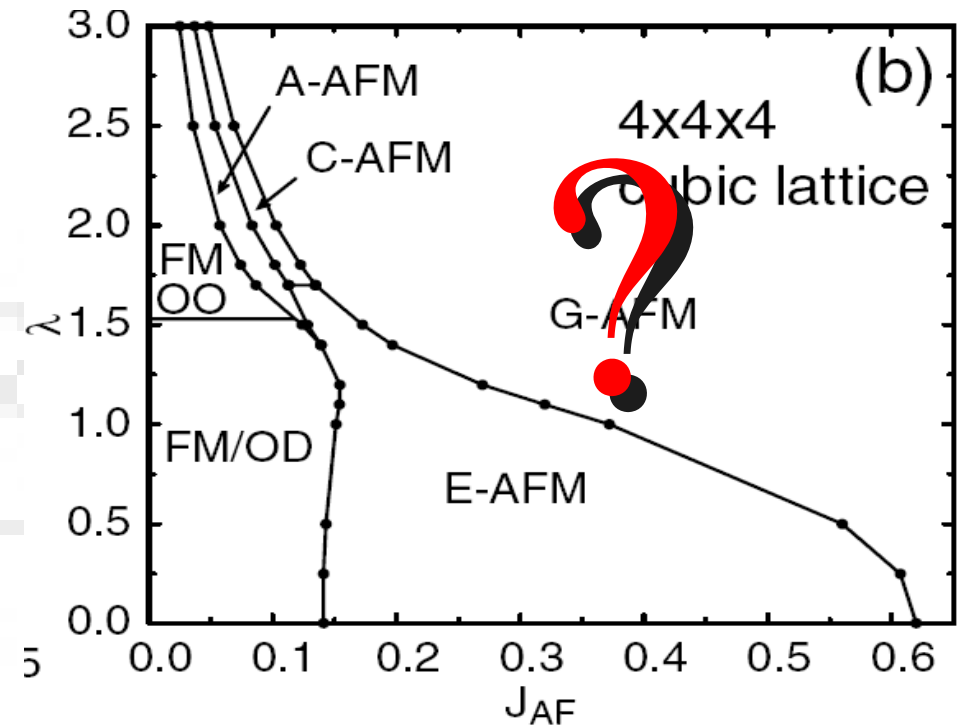
Dzyaloshinsky, J. Phys. Chem. Solids 4, 241 (1958); Moriya, Phys. Rev. 120, 91 (1960)



Origin of spiral-spin order: picture



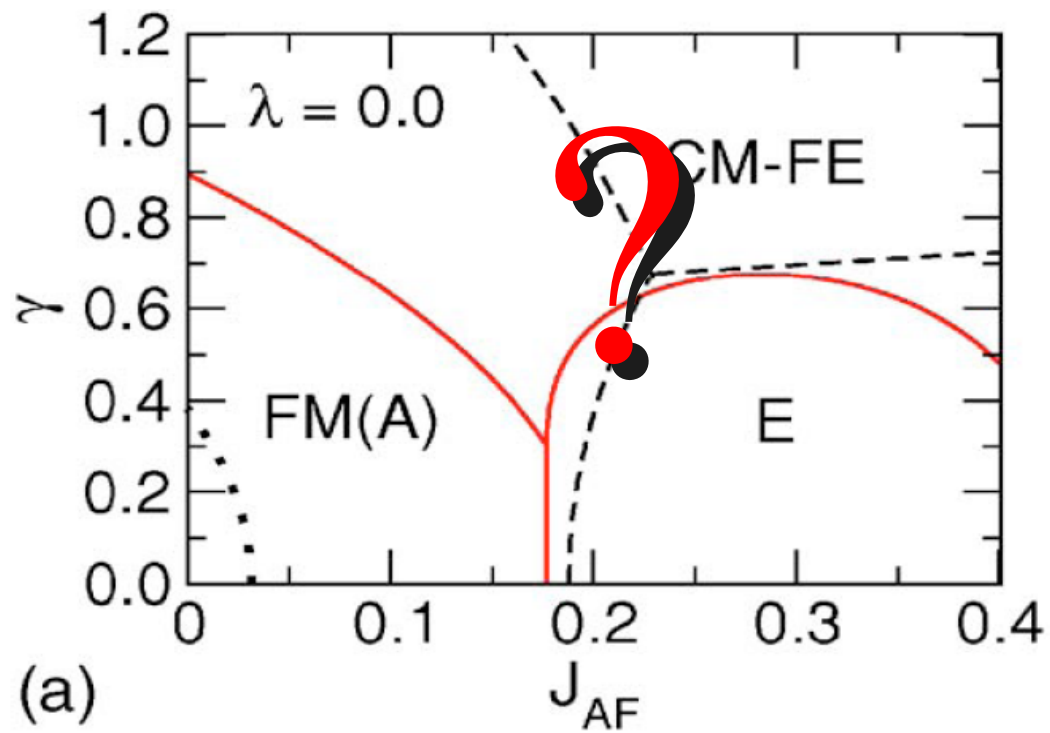
Kimura, Ishihara et al.
PRB68, 060403(R) (2003)



Hotta et al.
PRL 90, 247203 (2003)



Origin of spiral-spin order: picture

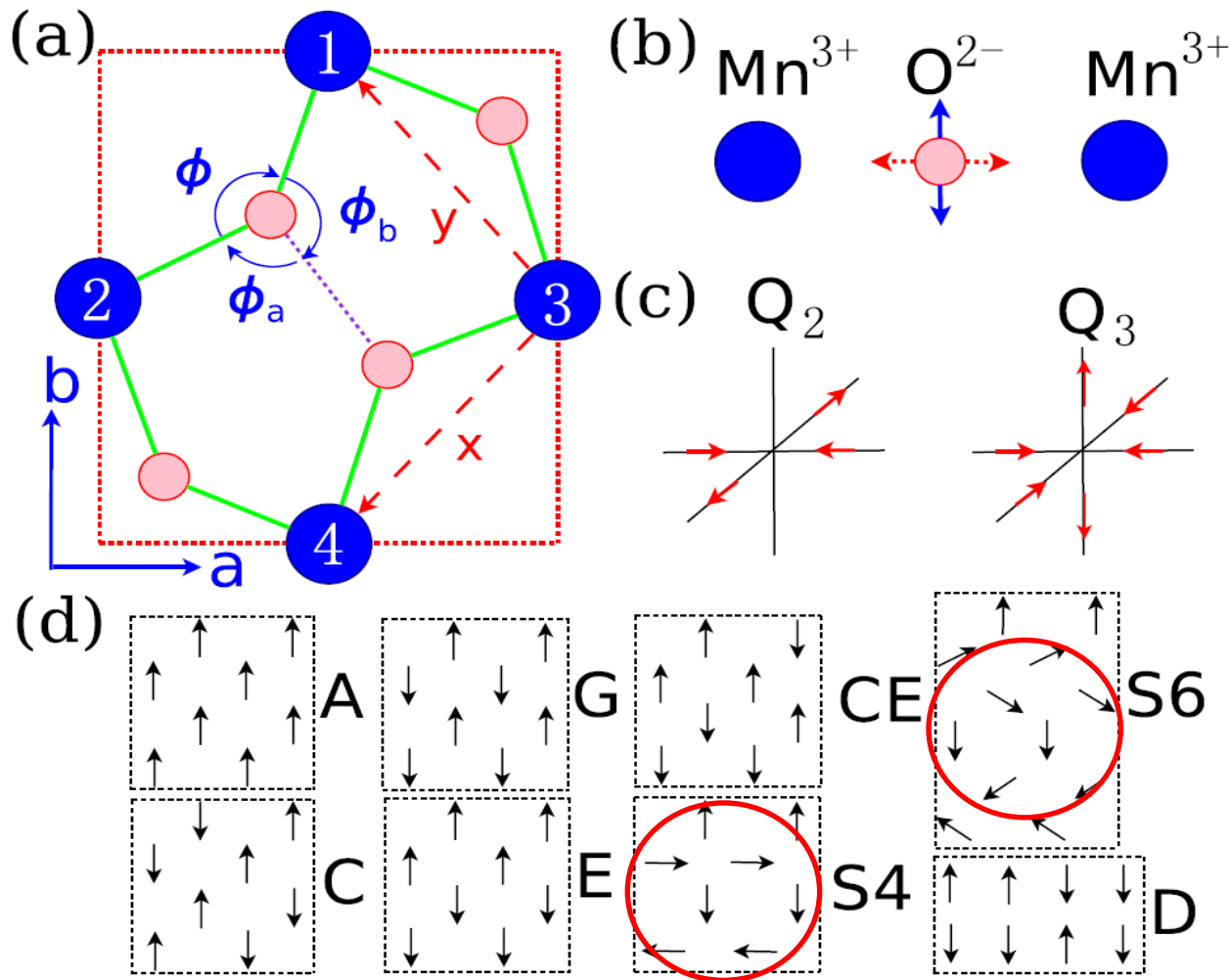


Sergienko and Dagotto
PRB73, 094434 (2006)



Origin of spiral-spin order: picture

- NNN anisotropic AFM interactions: $J_{2b} > J_{2a}$.

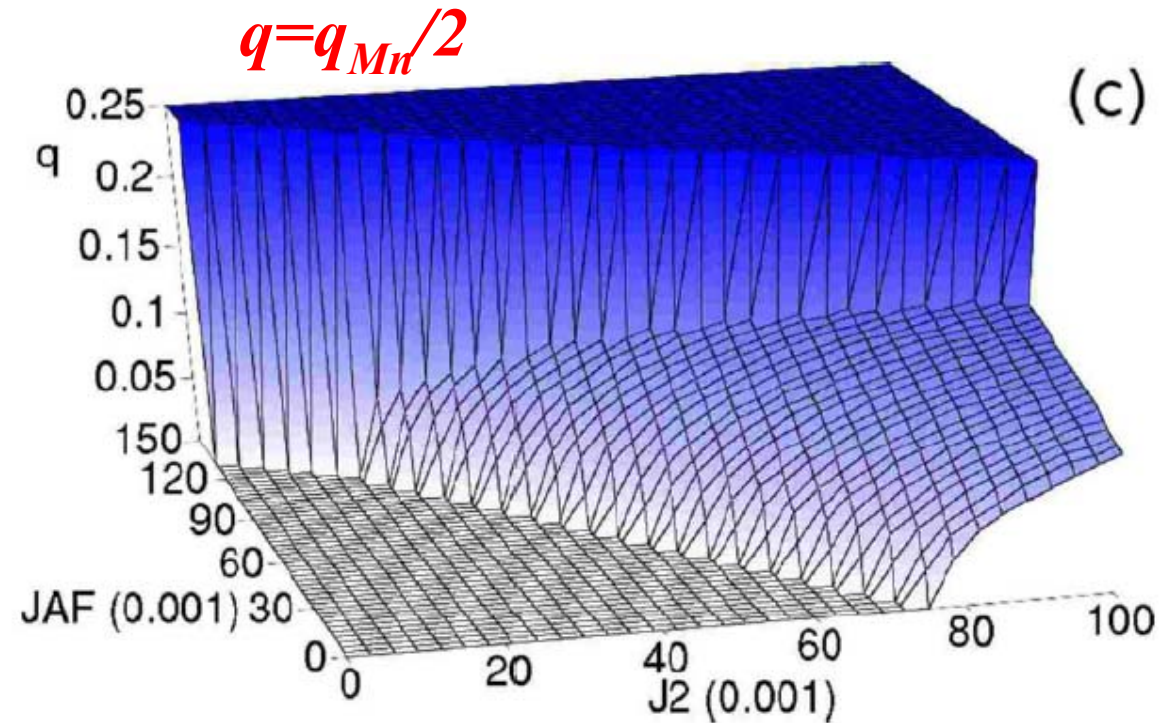
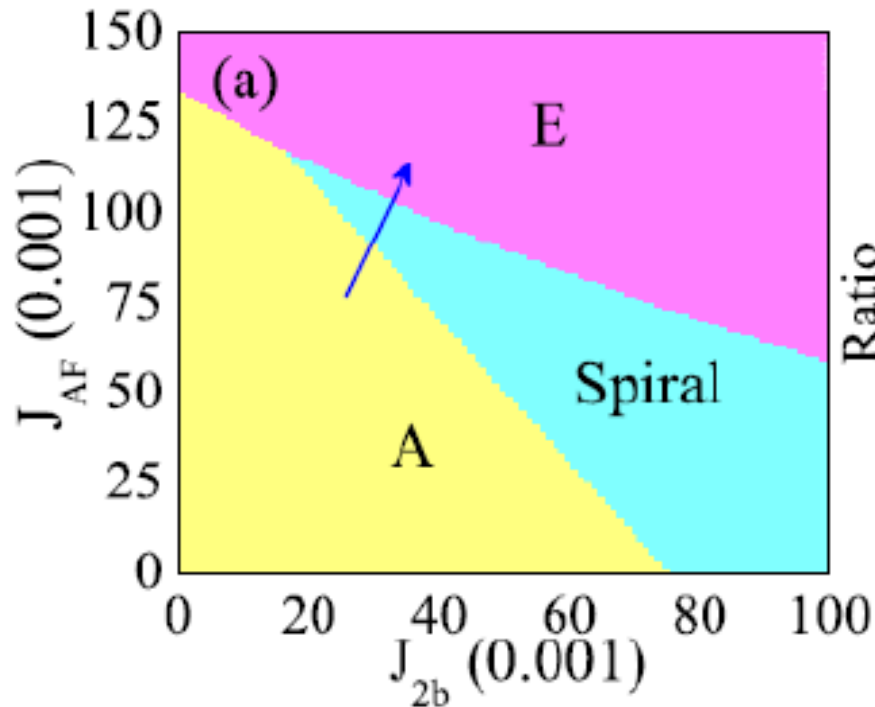


An approach without counting the DM interaction.



Origin of spiral-spin order: back to origin

- DE+SE+NNN anisotropic AFM interactions: $J_{2b} > J_{2a}$.



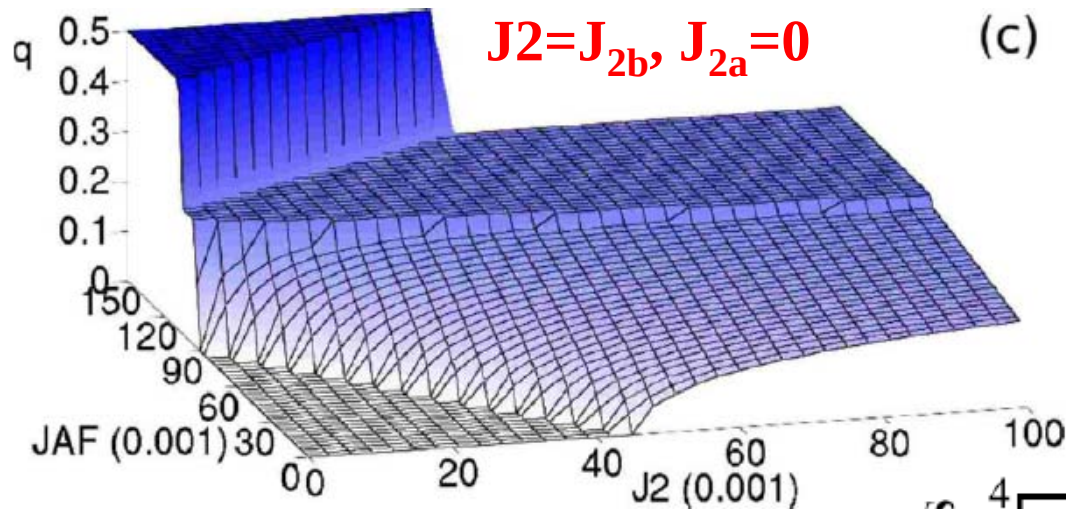
SSO is coming out!

(1) small wave-number, (2) phase transitions, (3) no energy gap

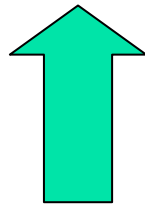


Origin of spiral-spin order: back to origin

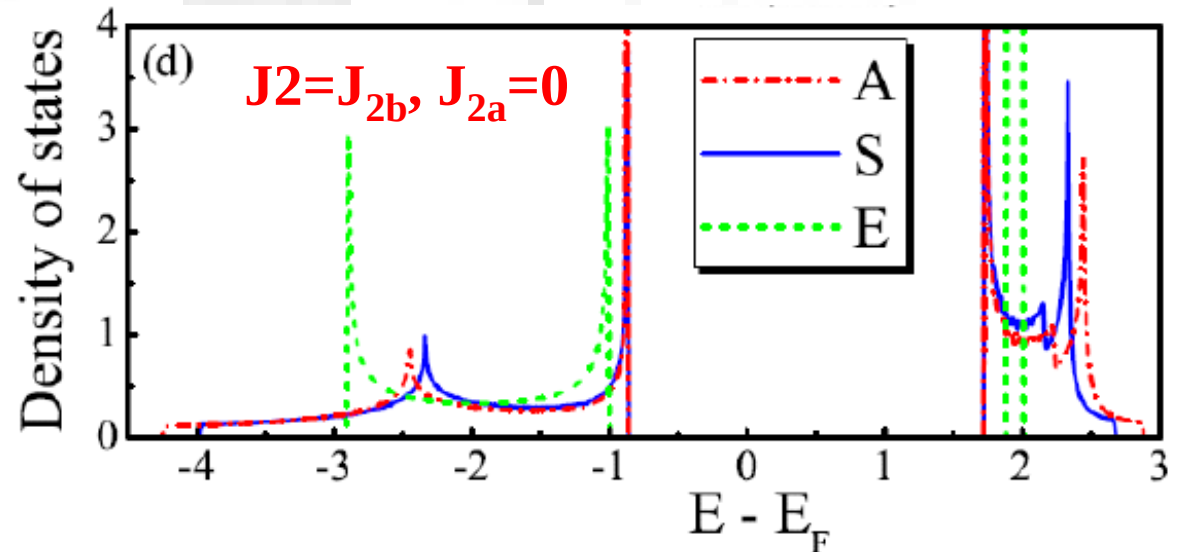
■ DE+SE+NNN AFM+JT term



(1) proper wave-number



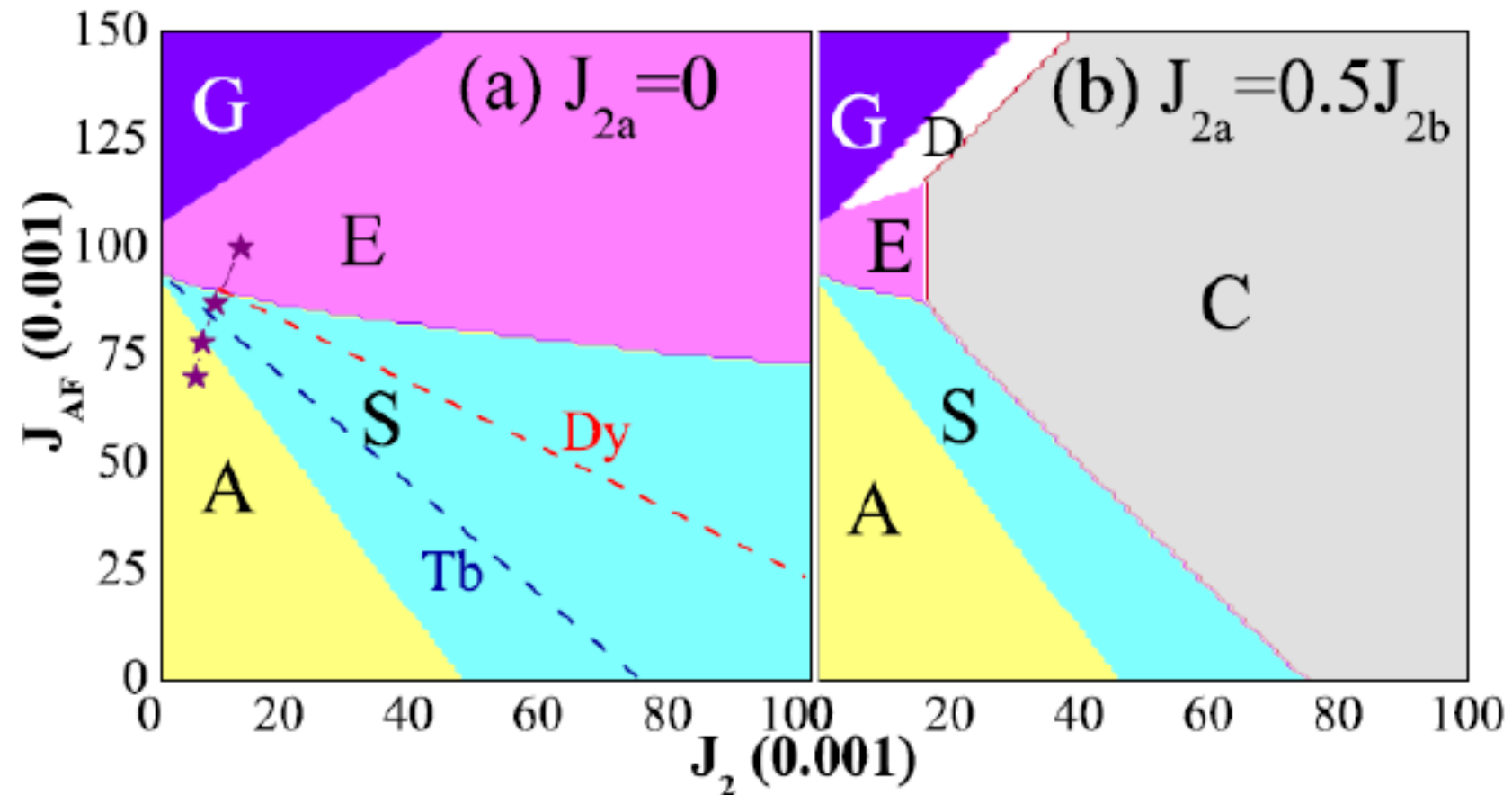
(3) energy gap





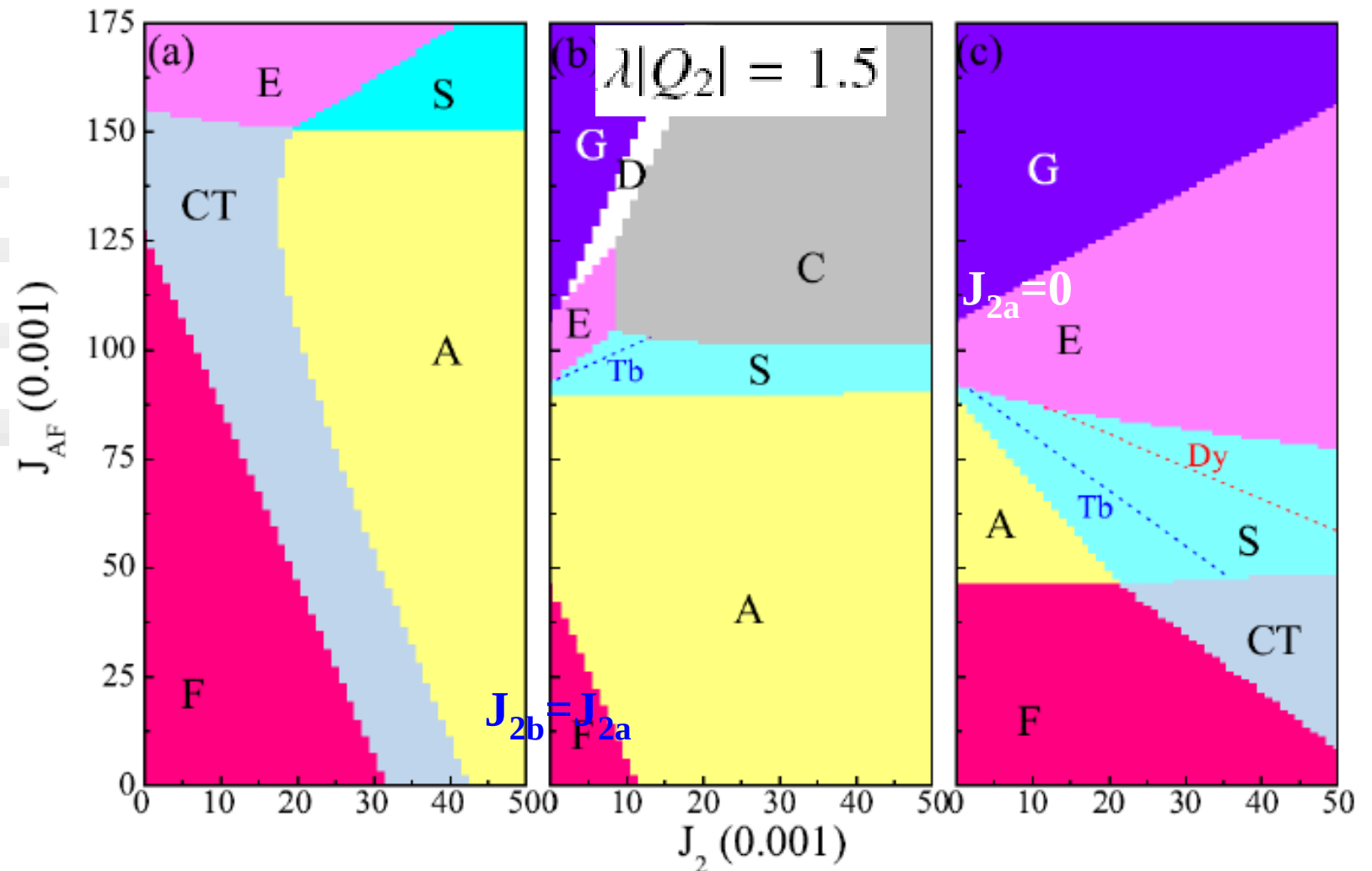
Origin of spiral-spin order: back to origin

- Role of NNN anisotropic SE interaction



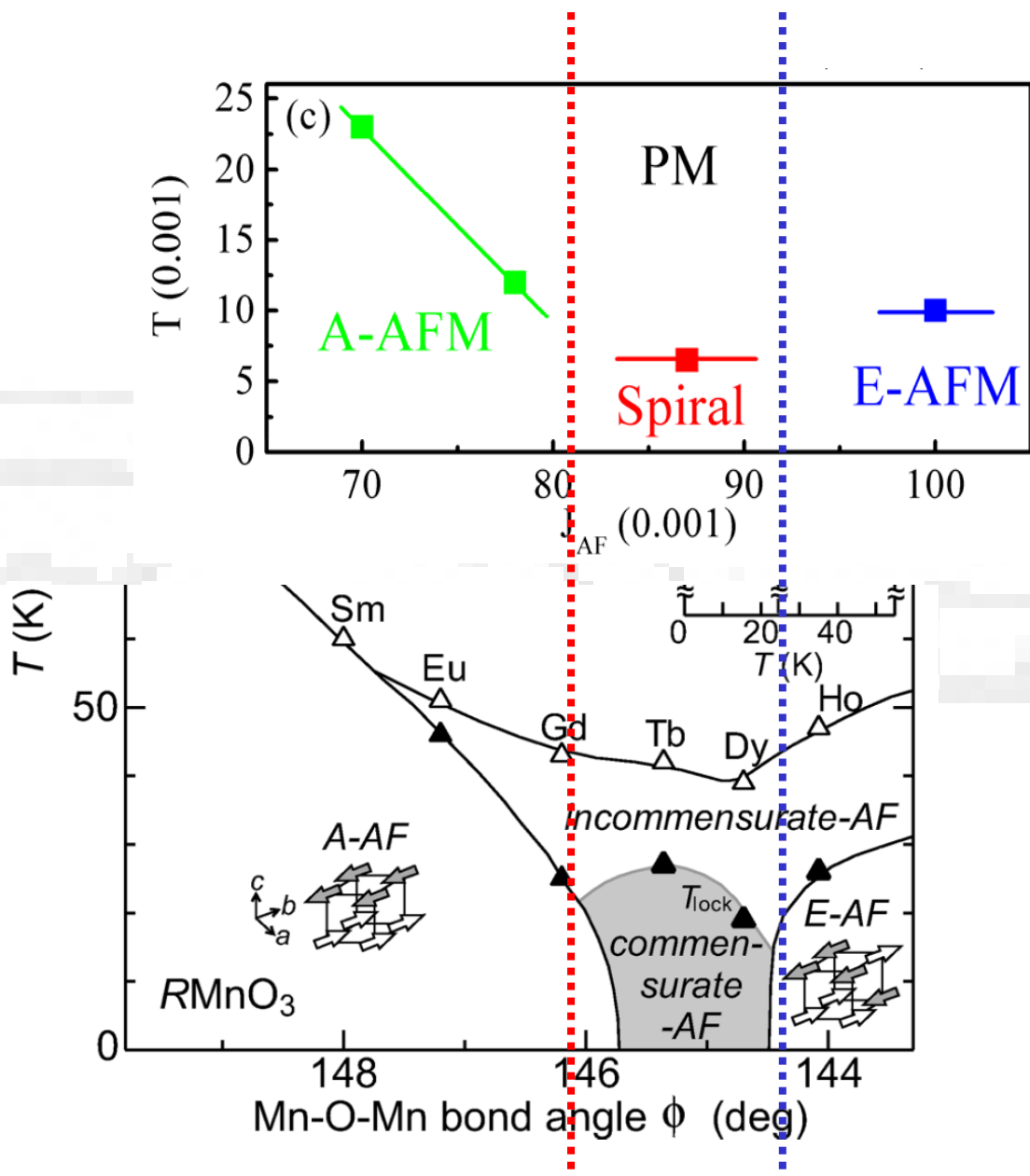


- No JT**
 $J_{2b} = J_{2a}$





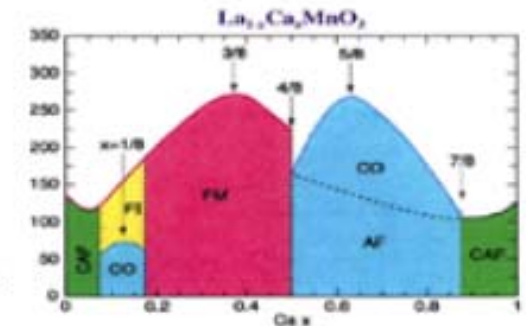
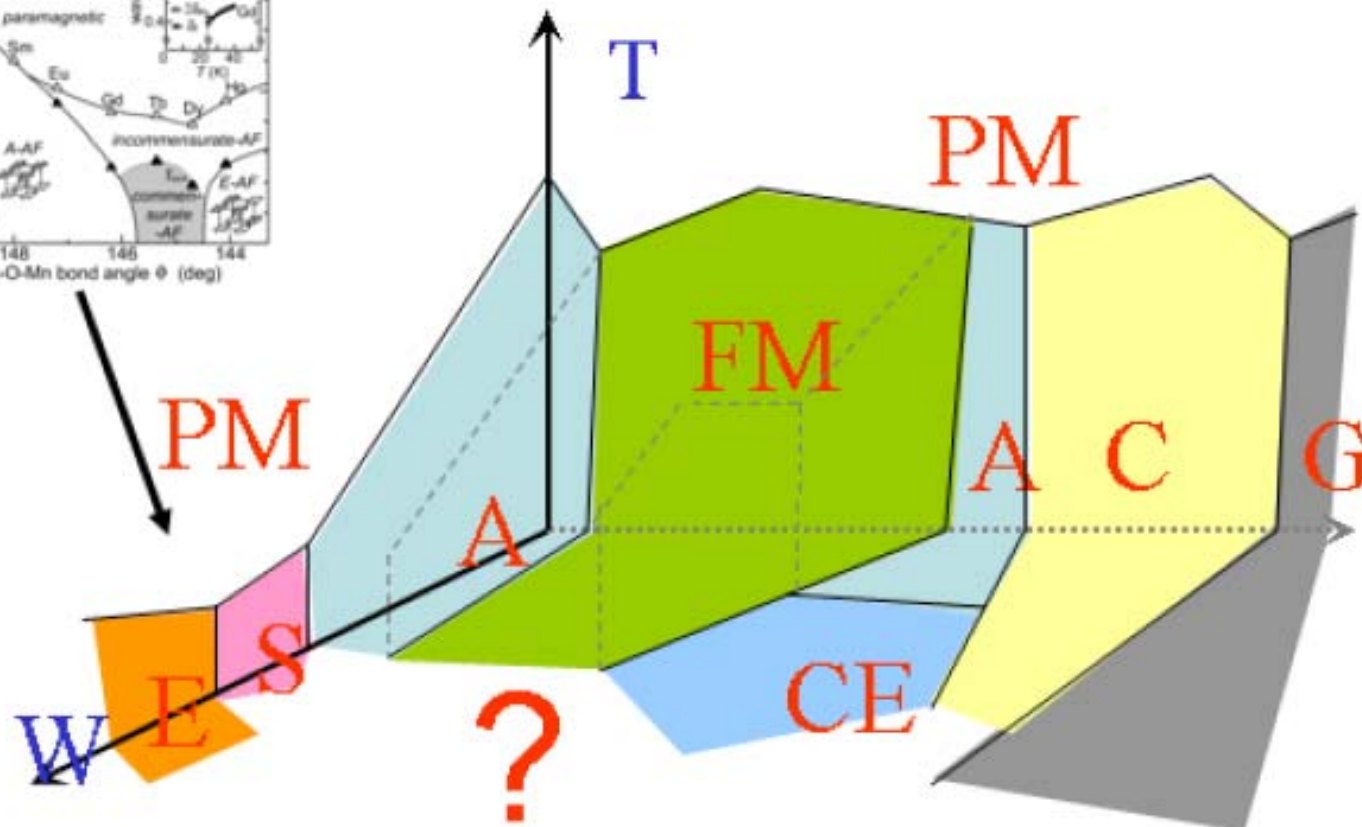
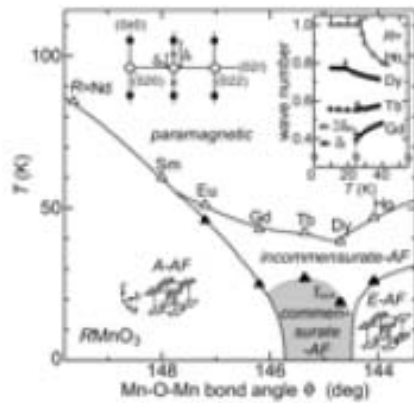
Origin of spiral-spin order: ugly phase diagram





Novel multiferroics: prediction

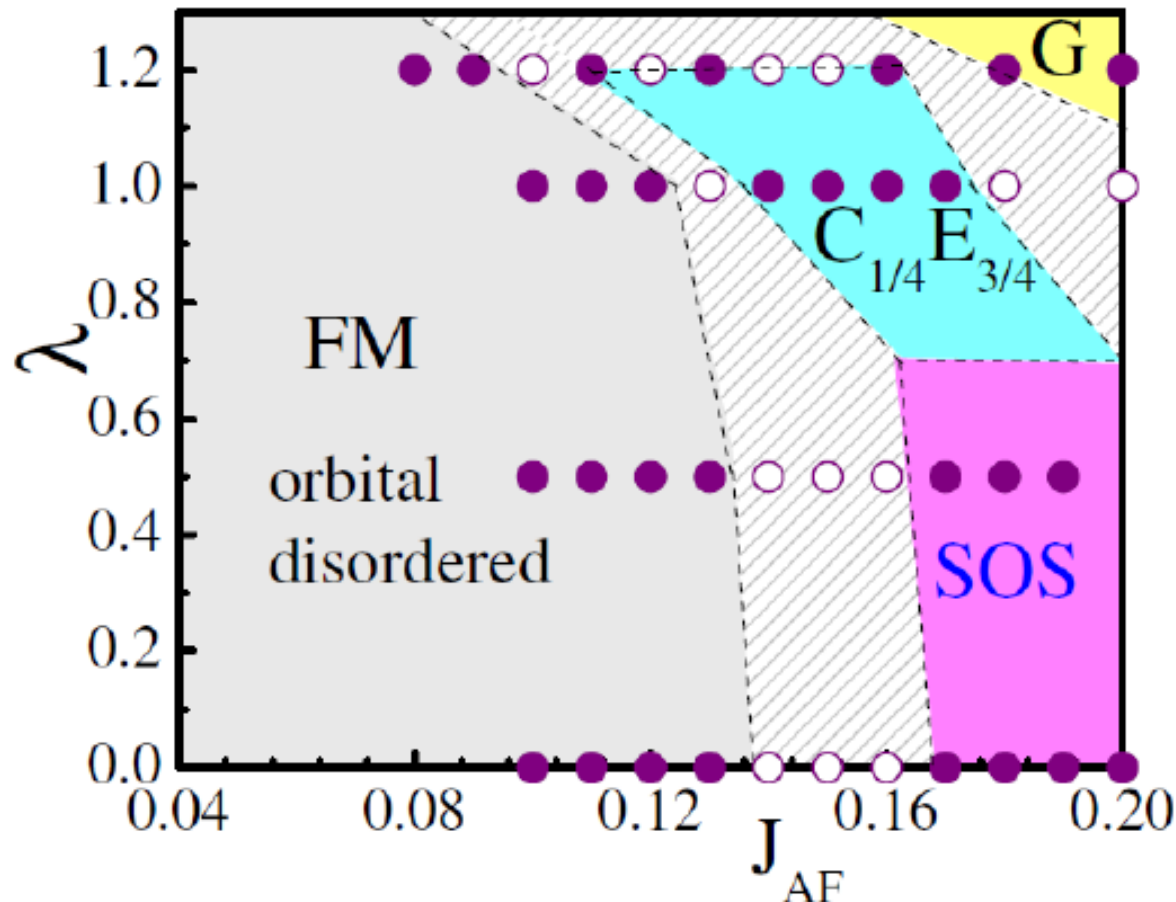
- Unknown region in X-W-T phase diagram





Novel multiferroics: prediction

- For doped manganites: $R_{1-x}A_x\text{MnO}_3$, $x=1/4$.
- DE+NN-SE+JT, without DMI and NNN-SE



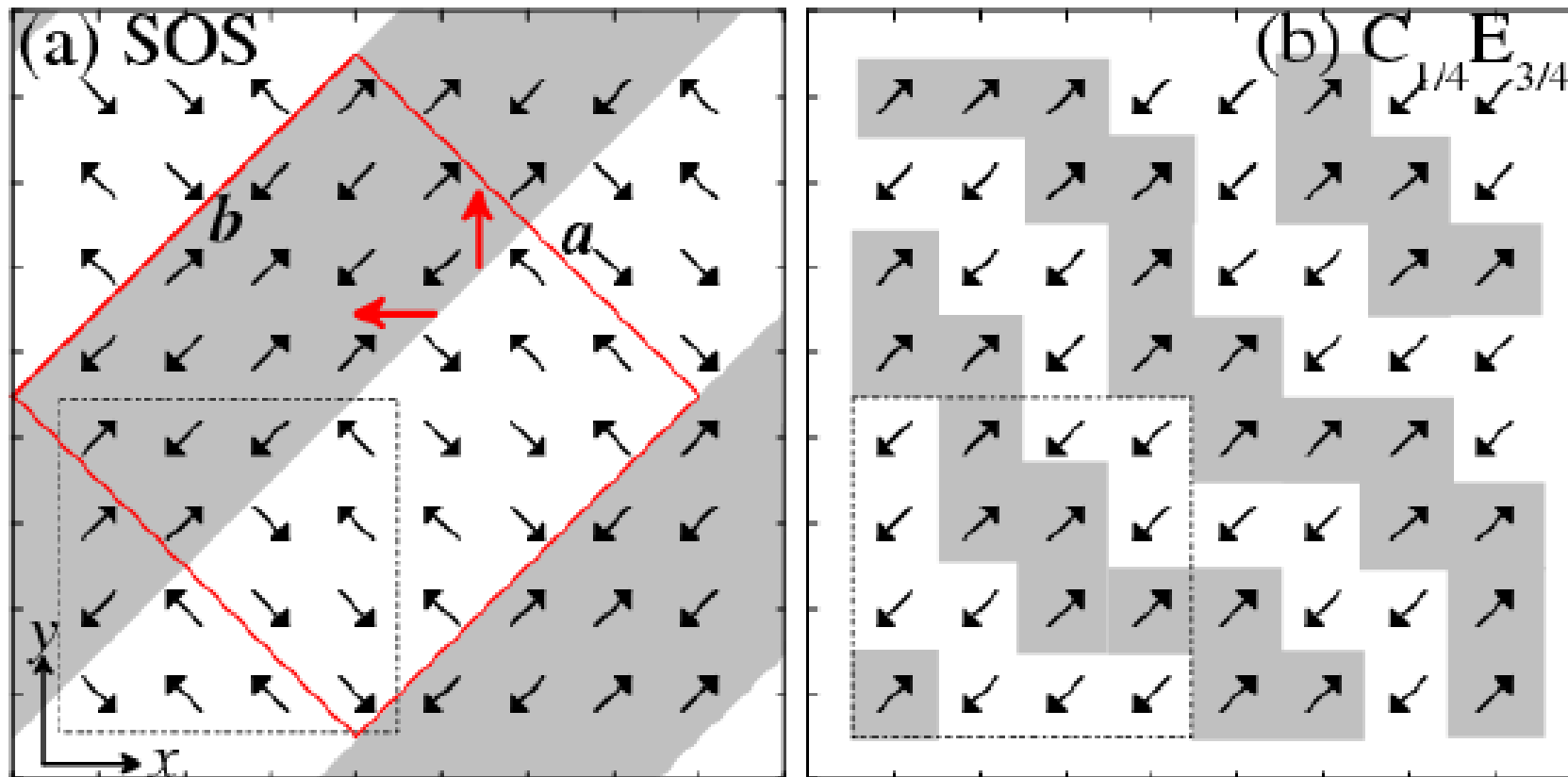
- ✓ New phase: spin-orthogonal stripe (SOS) phase.
- ✓ Large J_{AF} & small JT (λ).
- ✓ C_xE_{1-x} phase: x C-AFM+(1-x)E-AFM.

Dong et al. PRL



Novel multiferroics: prediction

- SOS phase: polarization at the stripe-boundaries

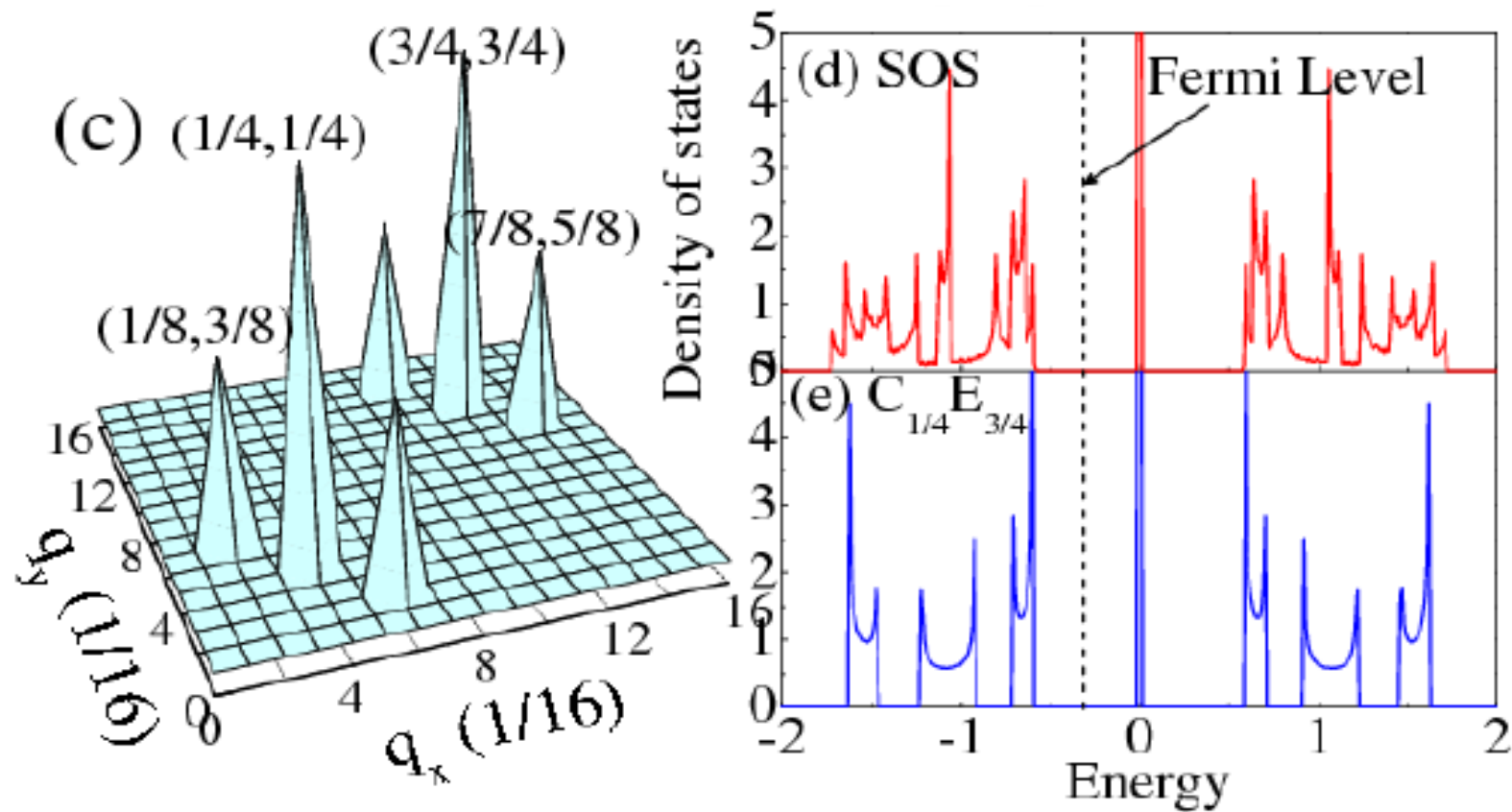


Dong et al. PRL



Novel multiferroics: prediction

- SOS phase & $C_{1/4}E_{3/4}$ phase: $S(q_x, q_y)$ & DOS

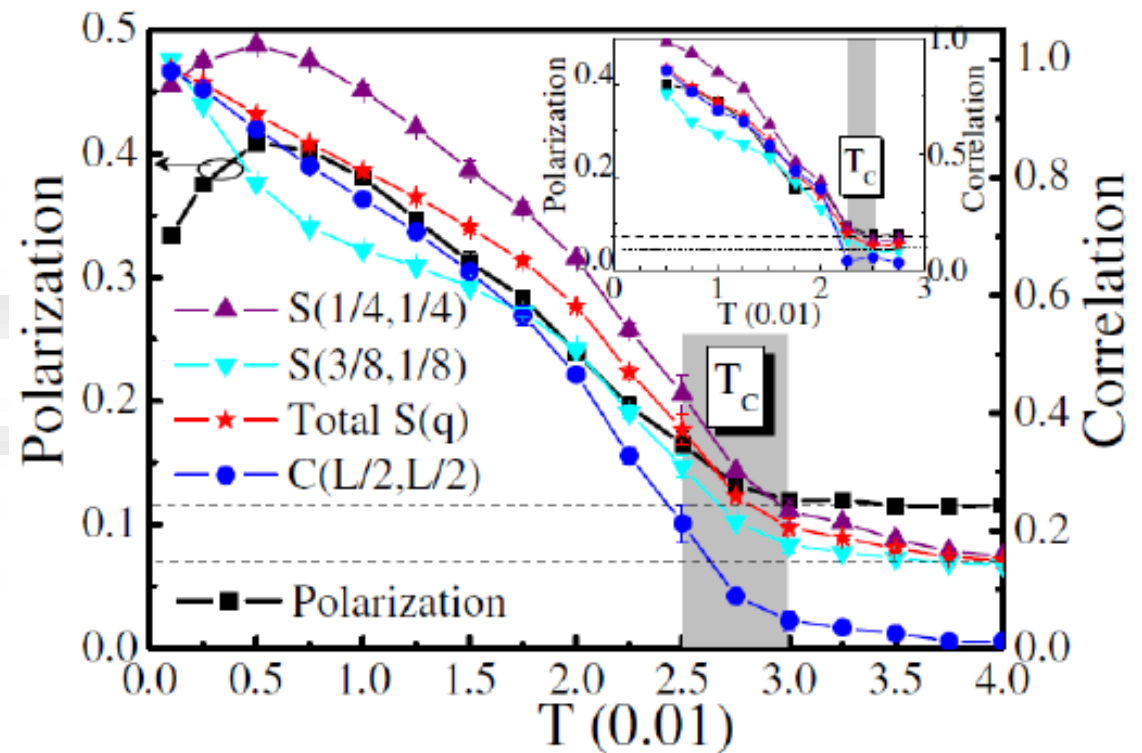
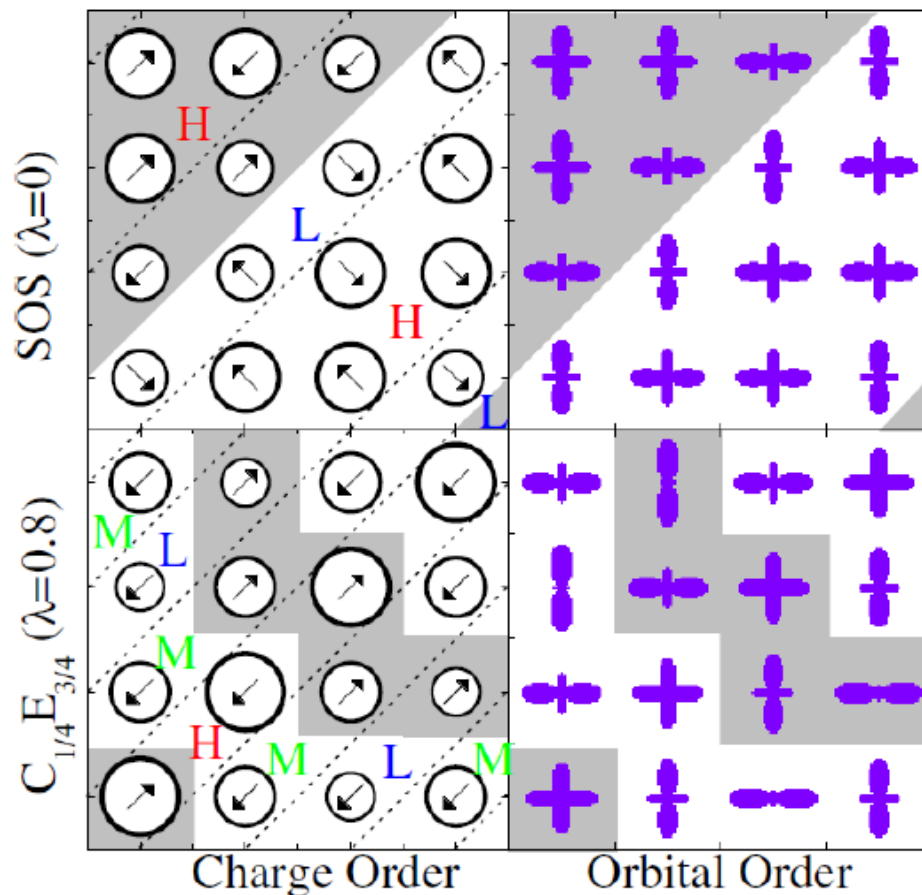


Dong et al. PRL



Novel multiferroics: prediction

- Charge-ordered phase associated with SOS & $C_{1/4}E_{3/4}$



Higher T_c & larger polarization

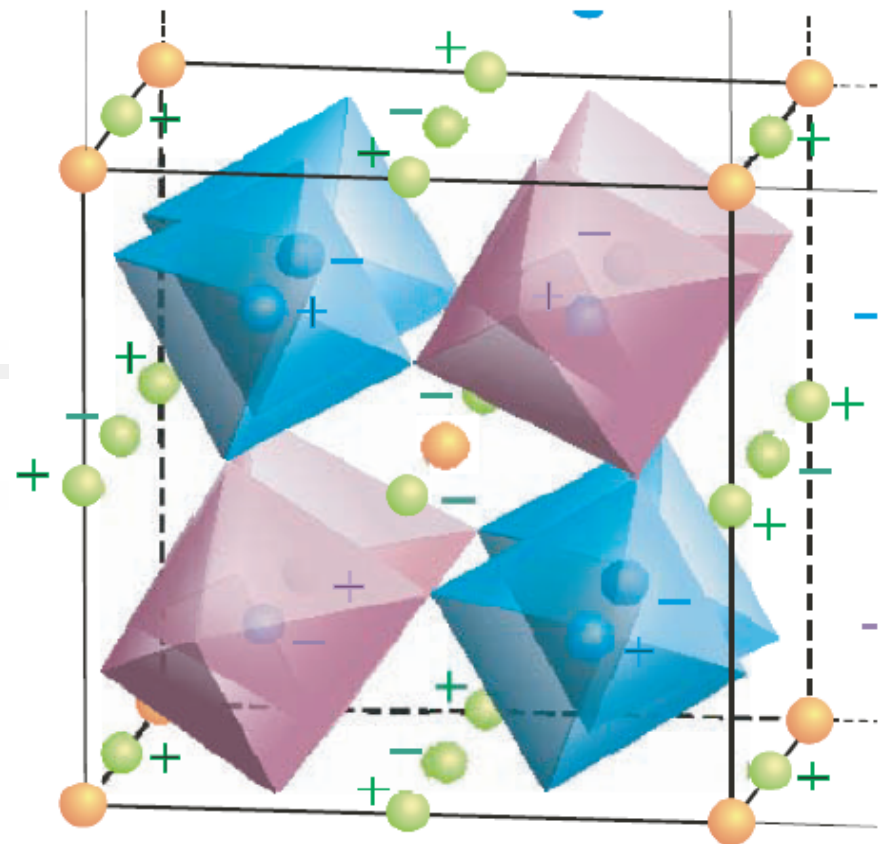
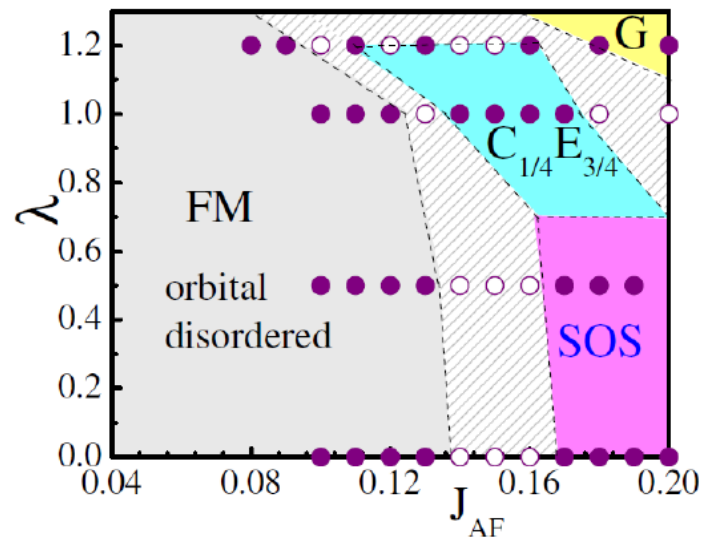
Dong et al. PRL



Novel multiferroics: candidate

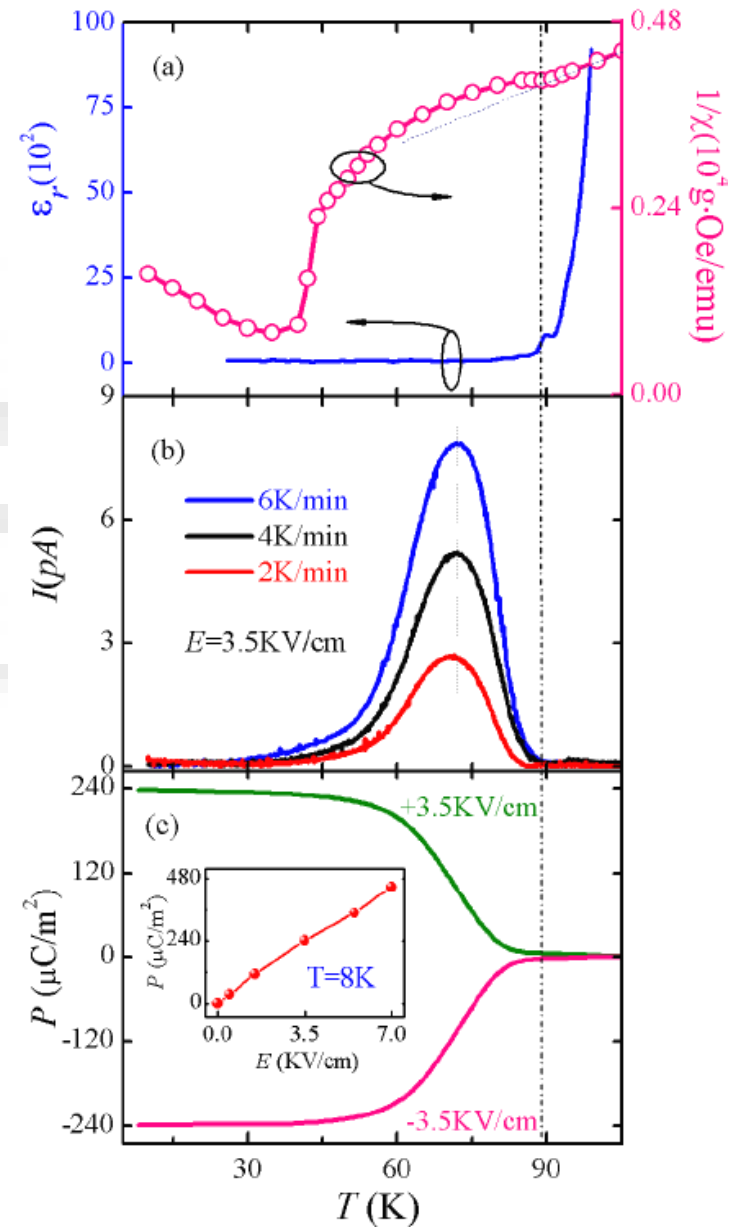
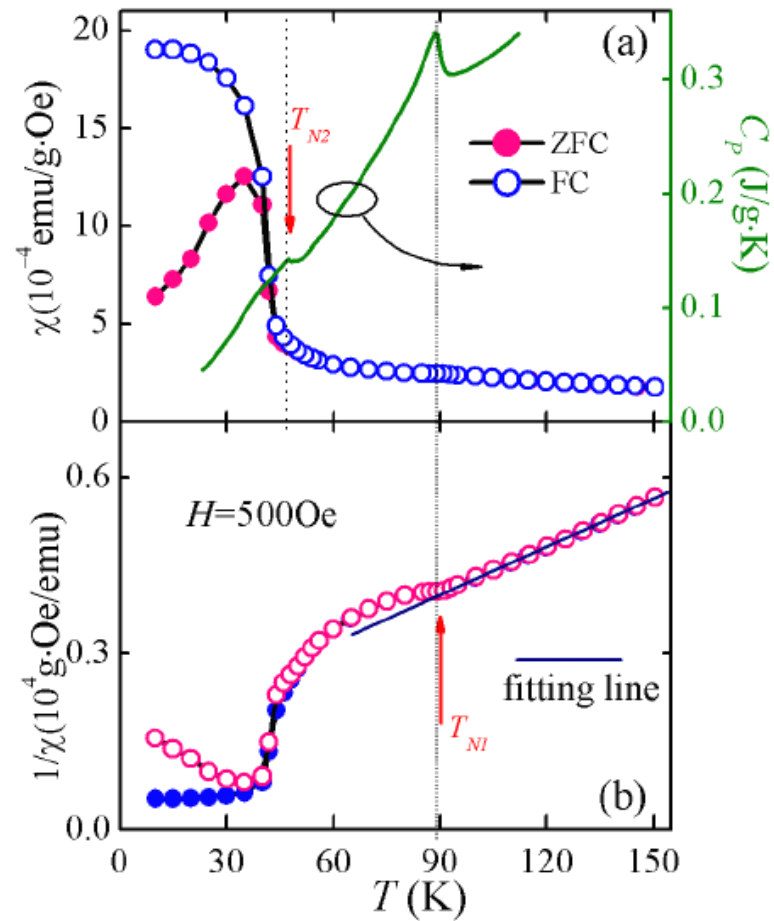
- Large J_{AF} (narrow bandwidth) and small JT distortion
- quadruple $(AA'_3)B_4O_{12}$ family, e.g. $(A^{2+}B_3^{3+})(B_3^{3+}B_4^{4+})O_{12}$.
- B-O-B angle less than 140° and the JT Q_2 mode can be weak.

Zhang et al. unpublished





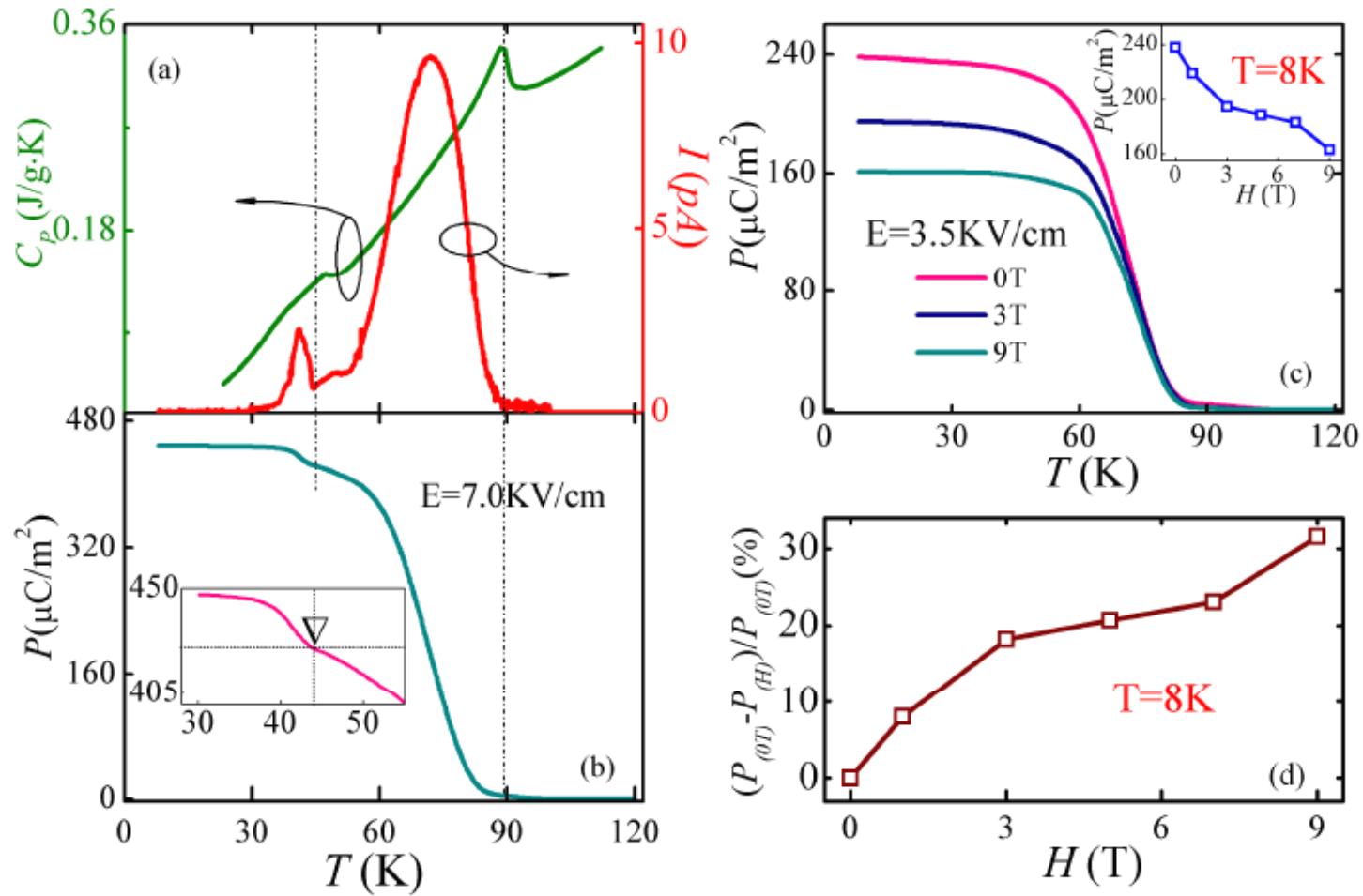
Novel multiferroics: candidate



Zhang et al. unpublished



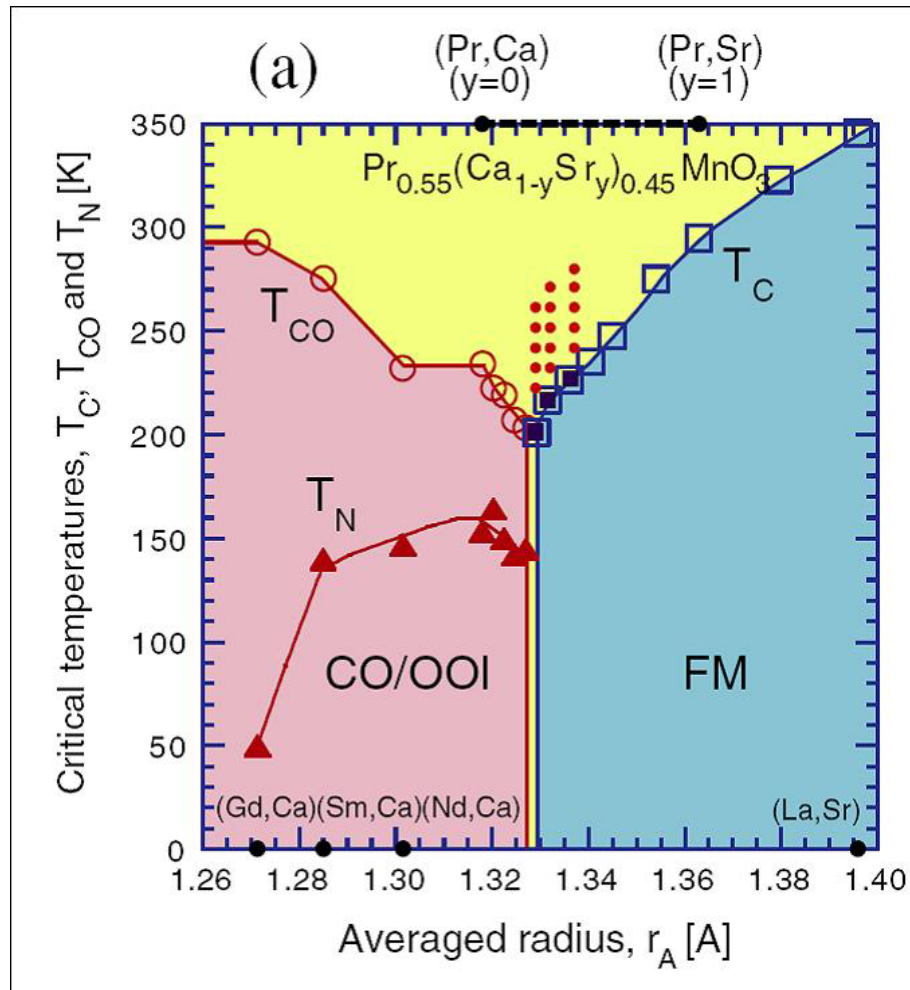
Novel multiferroics: candidate



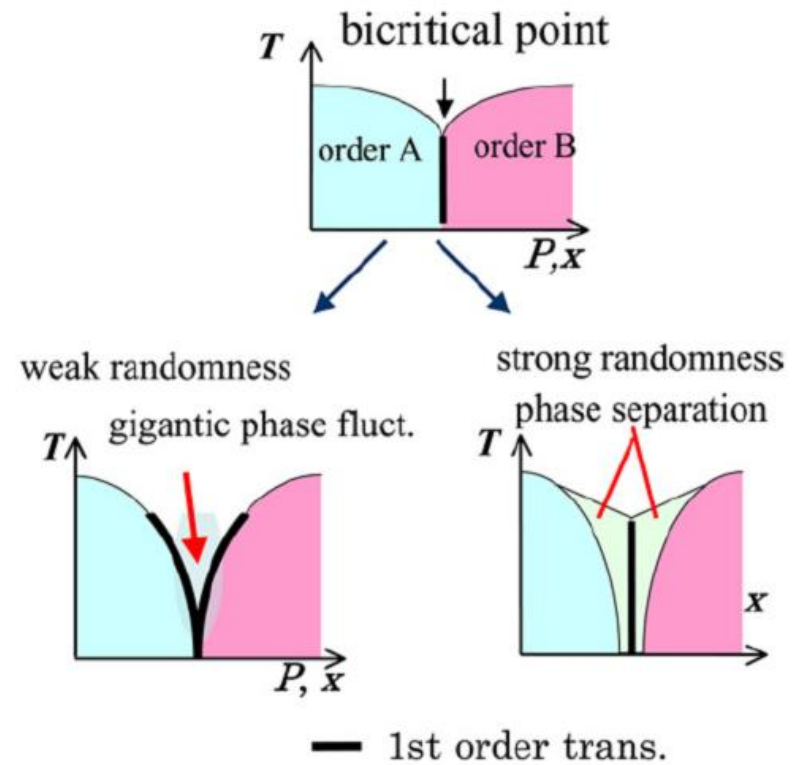
Zhang et al. unpublished



Phase competition & beyond: picture



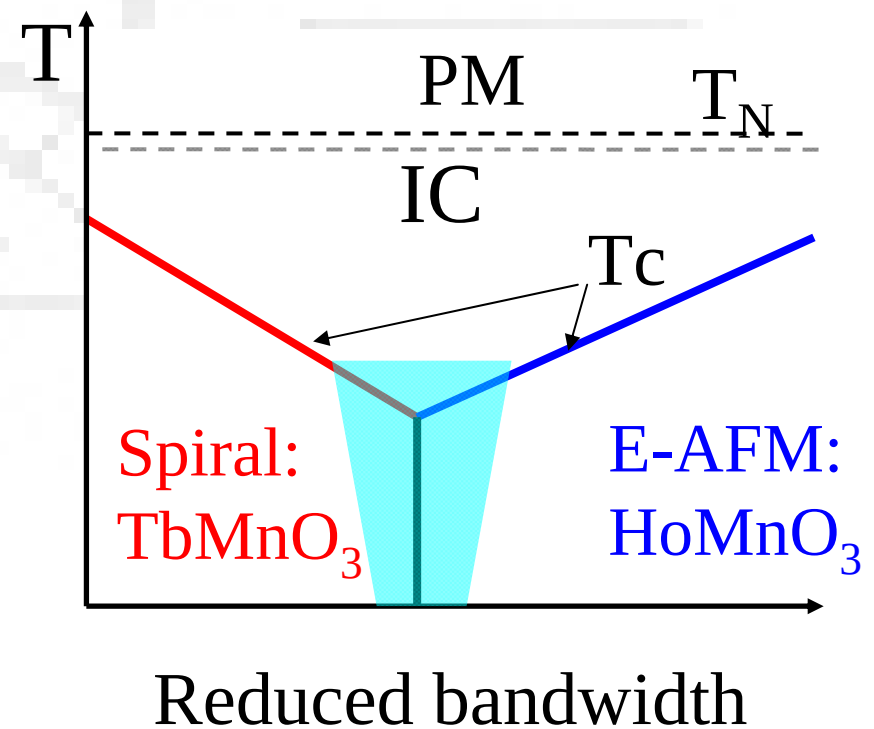
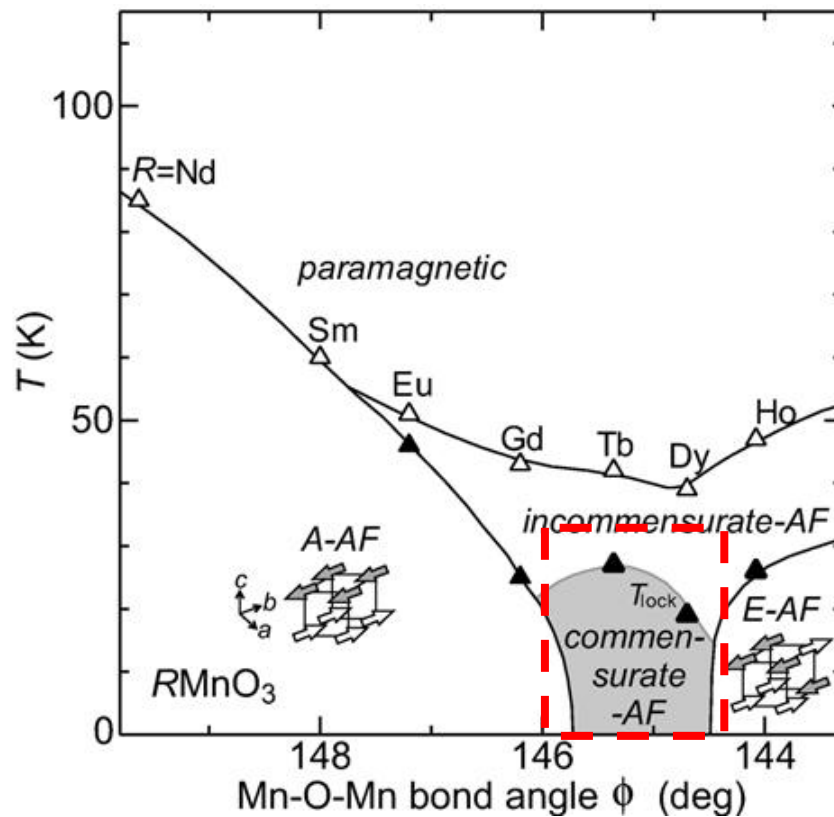
CMR manganites: bicritical point





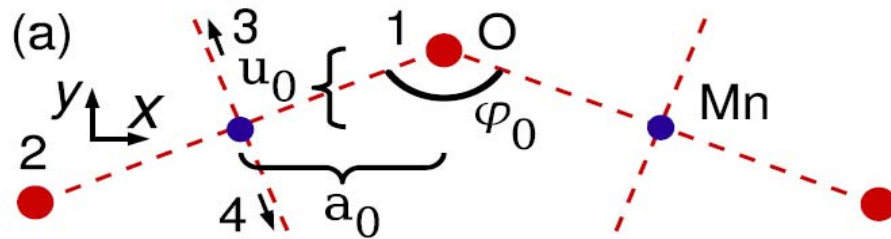
Phase competition & beyond: picture

Bicritical point of
dual multiferroic phases?
Phase separation by disorder?

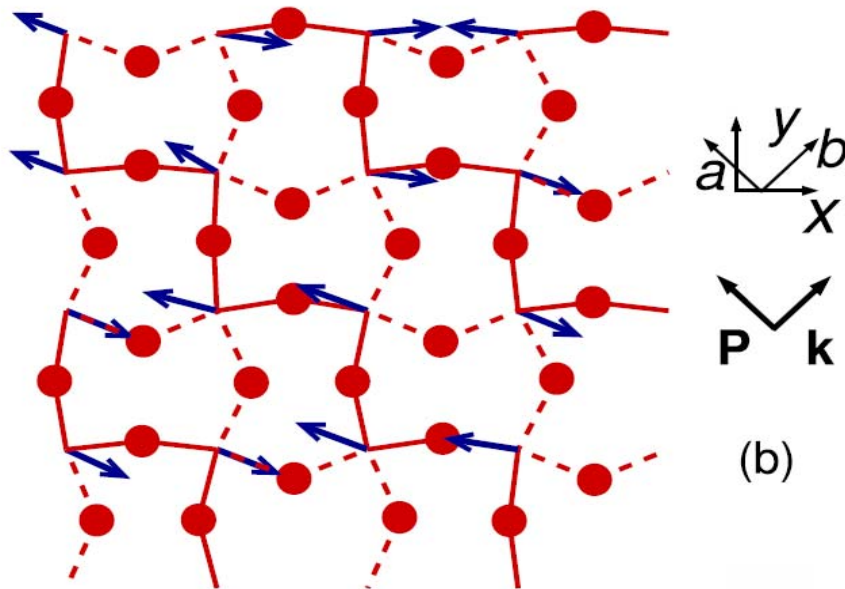




Phase competition & beyond: picture



Driven force: Double-exchange
 $-tx + kx^2 \quad t \sim t_0(1 + S \cdot S)^{1/2}$



Large $P \sim 2 \mu\text{C}/\text{cm}^2$, waiting for experimental confirmation!

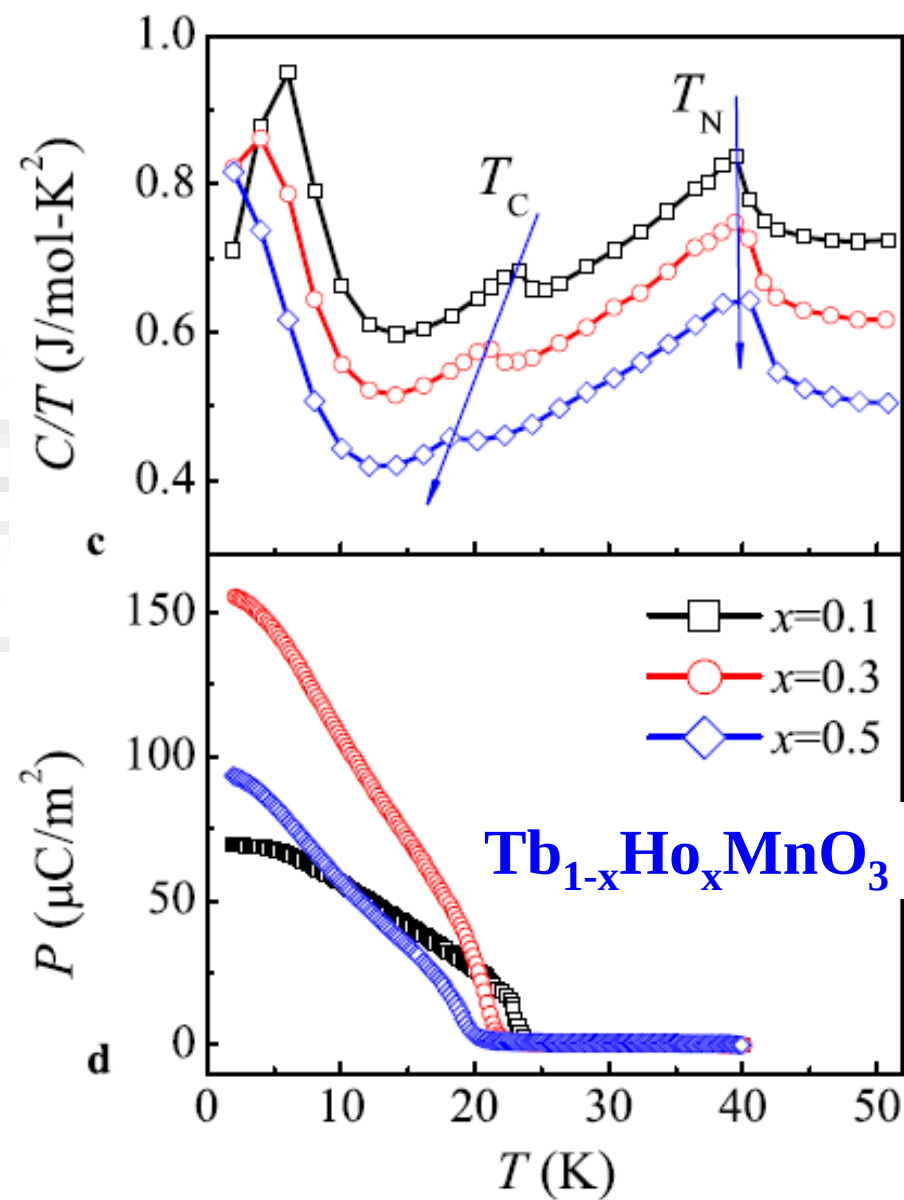
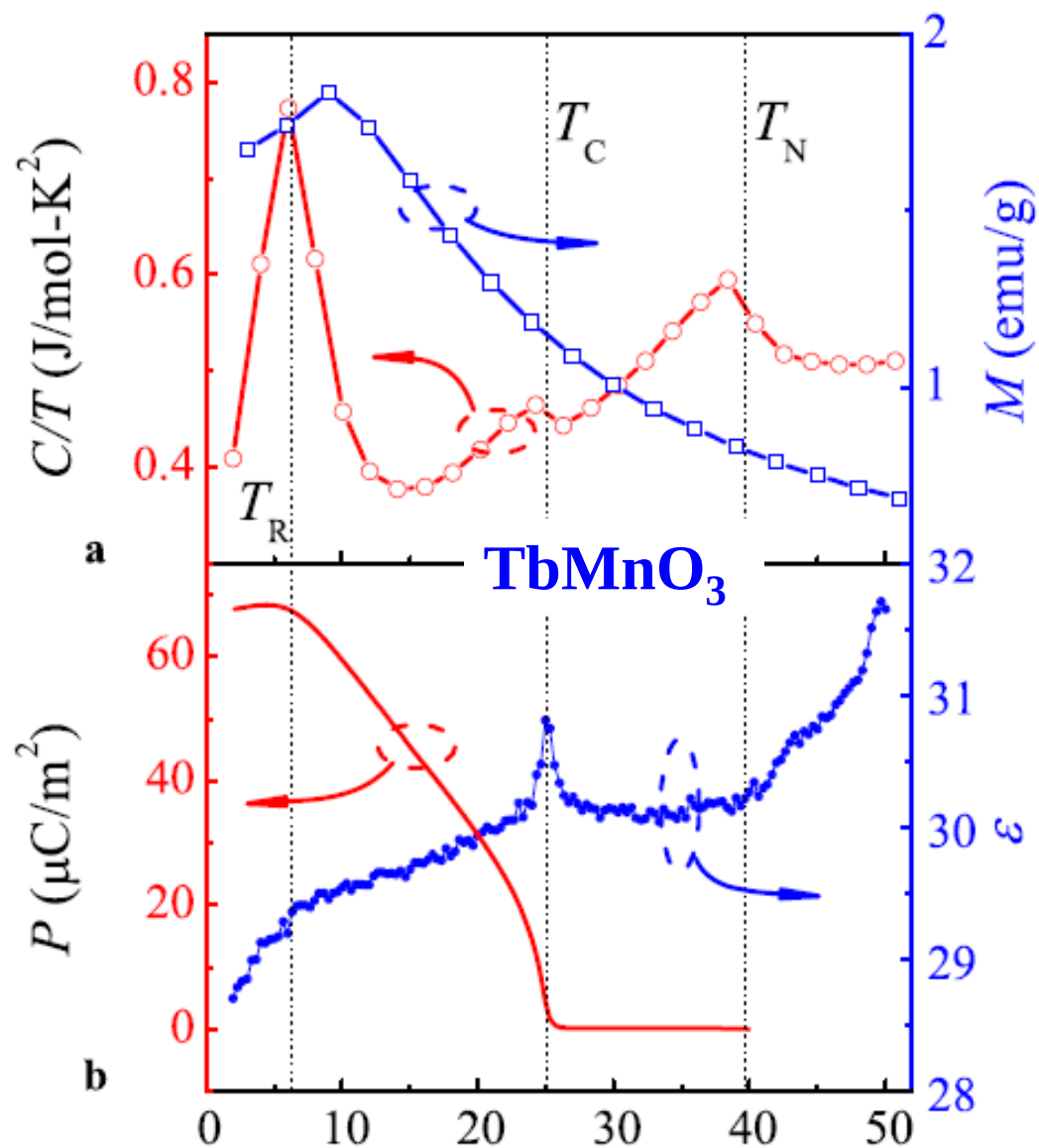
Polycrystal: $100 \mu\text{C}/\text{m}^2$

Lorenz et al. PRB76, 104405 (07)

Prediction of FE in the E-AFM phase (HoMnO_3), I. Sergienko et al., PRL 97, 227204 (2006)

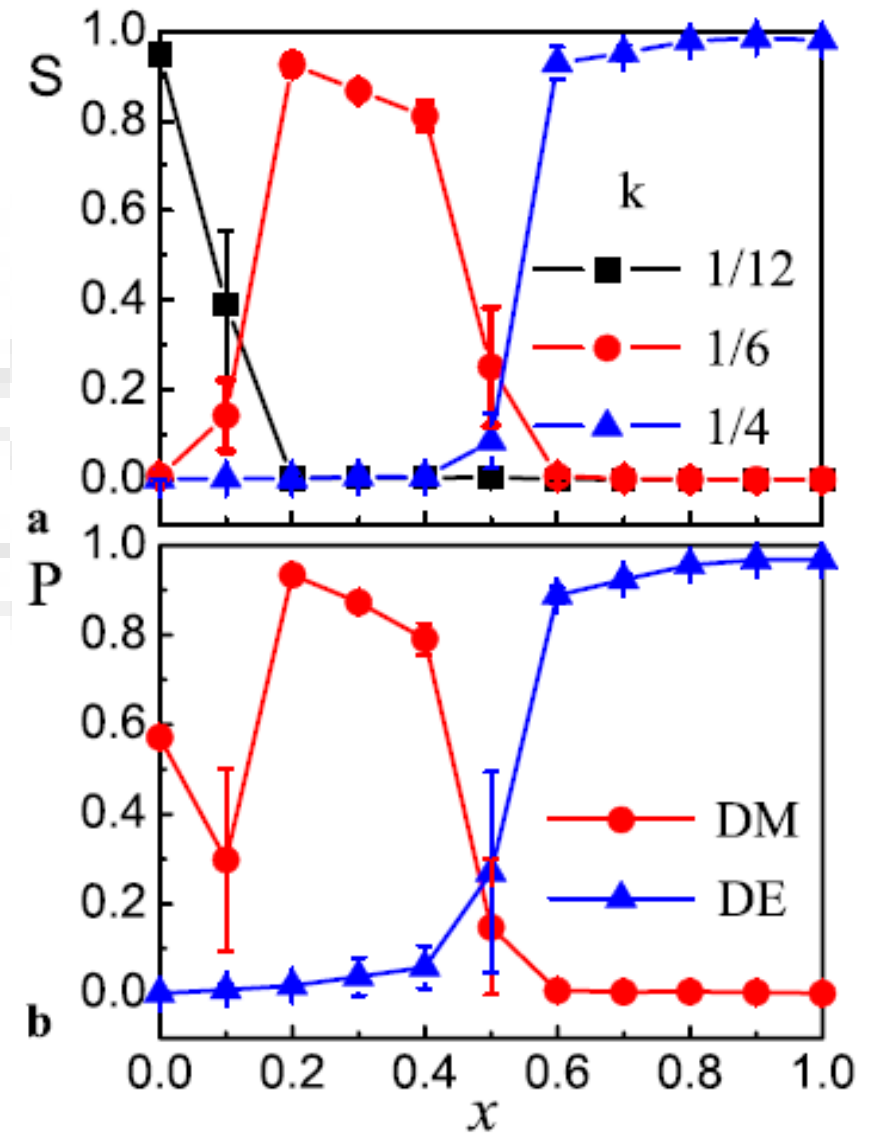
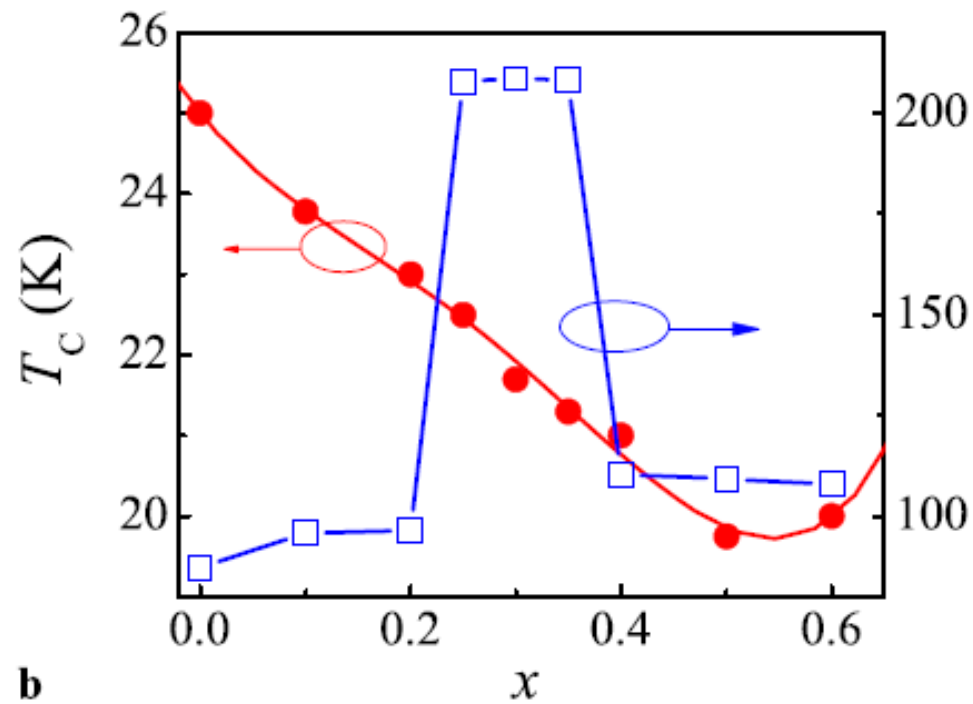


Phase competition & beyond: let's try



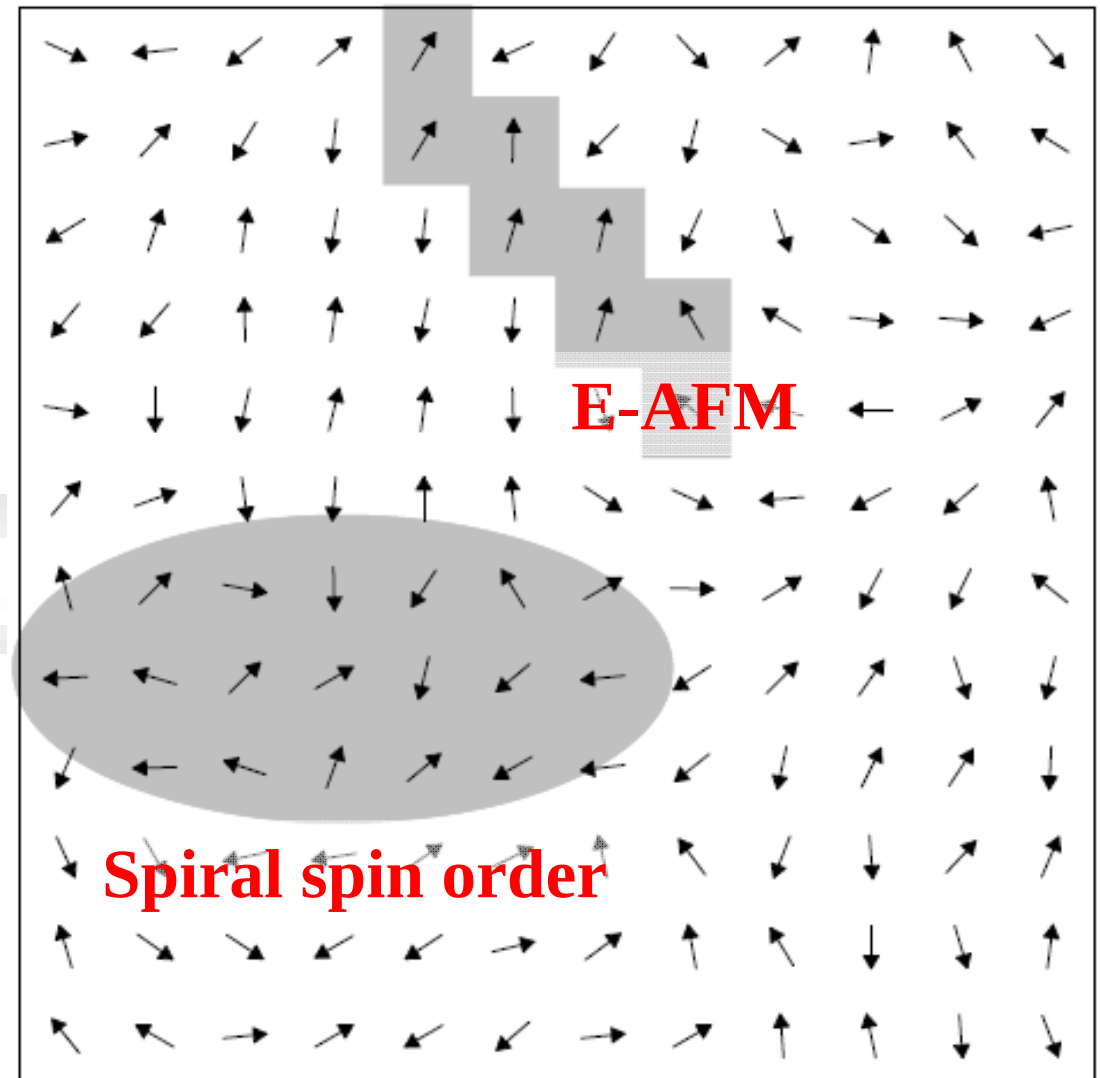
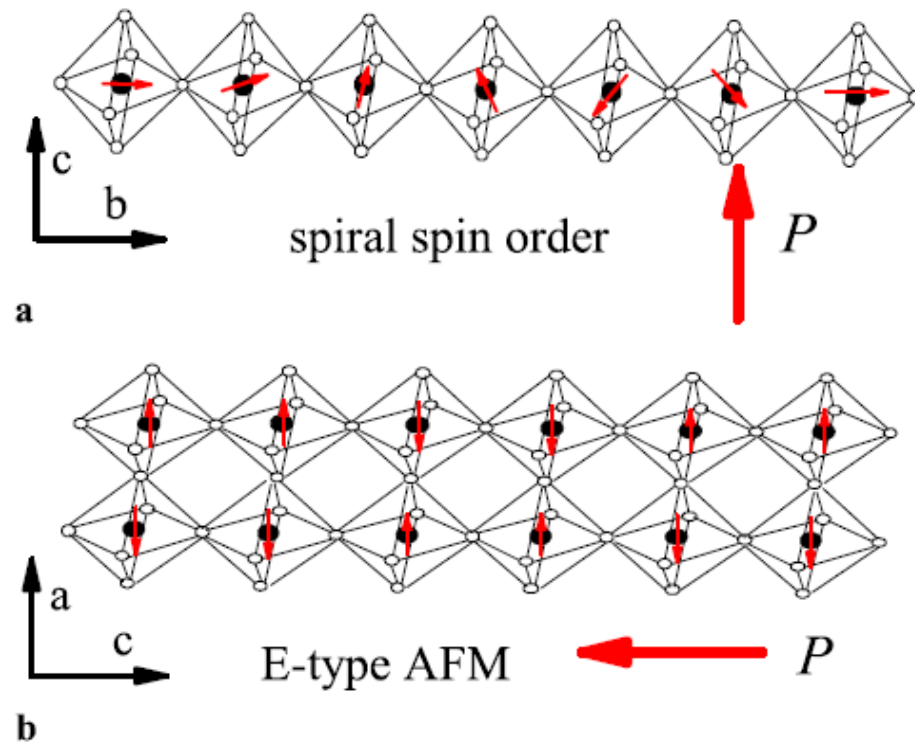


Phase competition & beyond: let's try



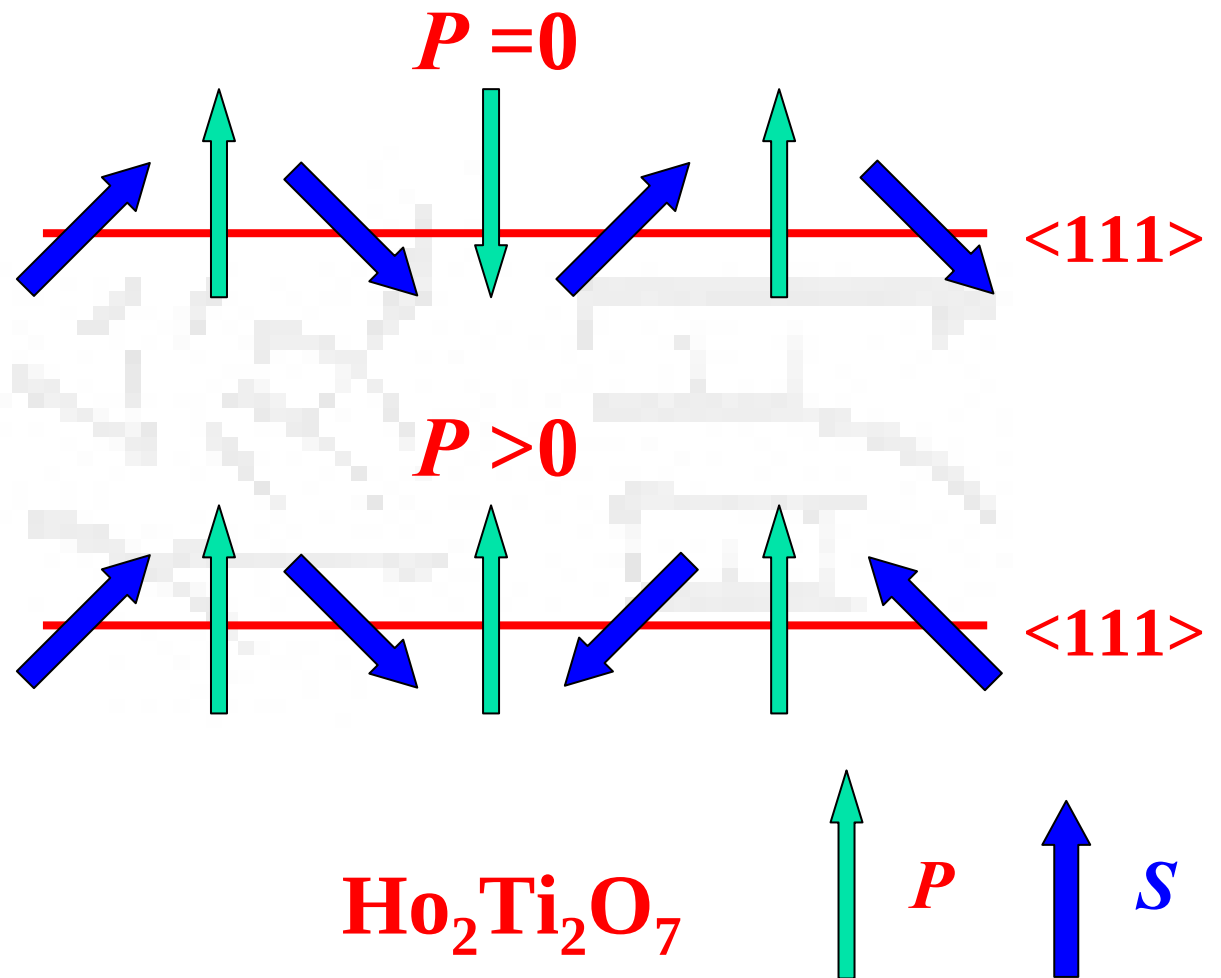
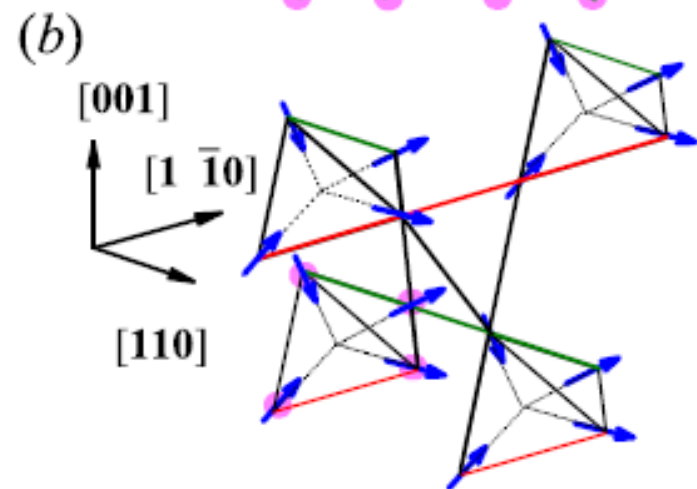
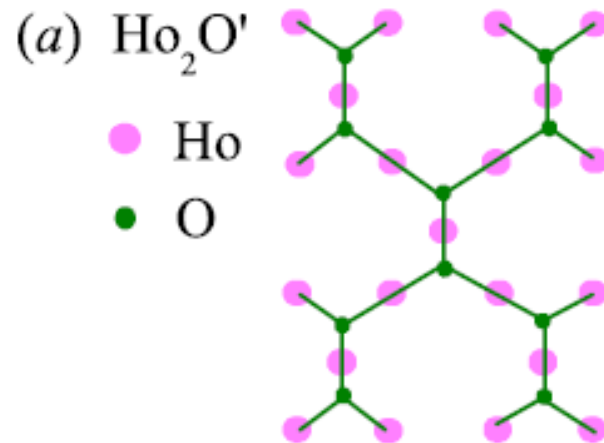


Phase competition & beyond: let's try



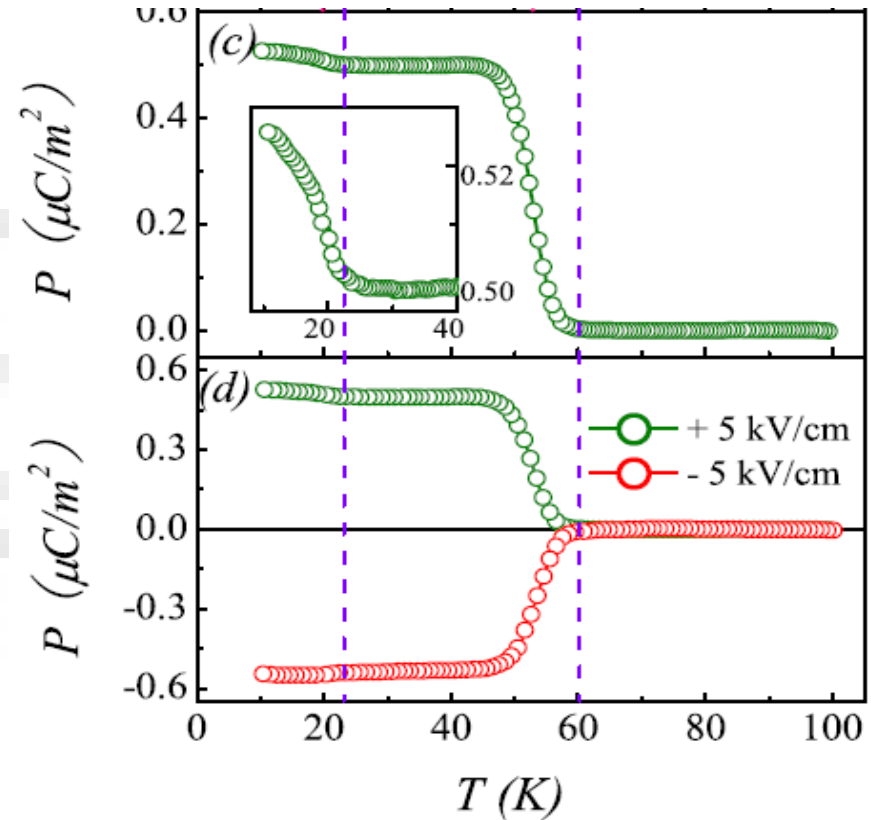
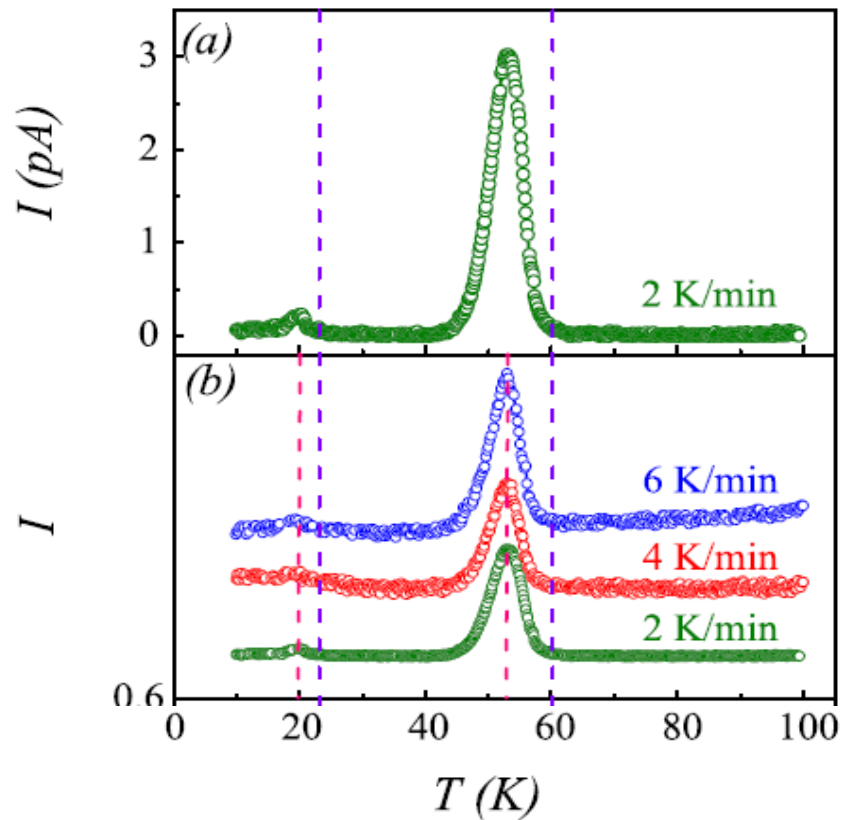


Phase competition & beyond: spin ice



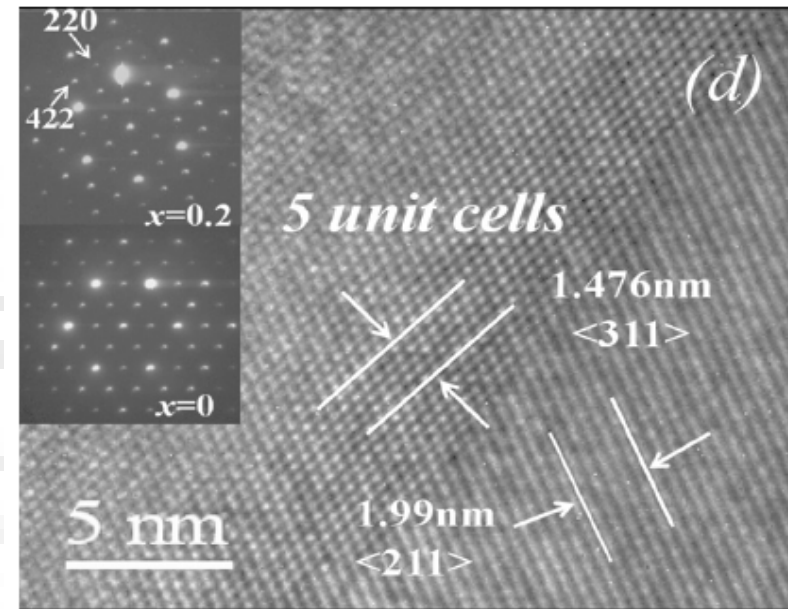
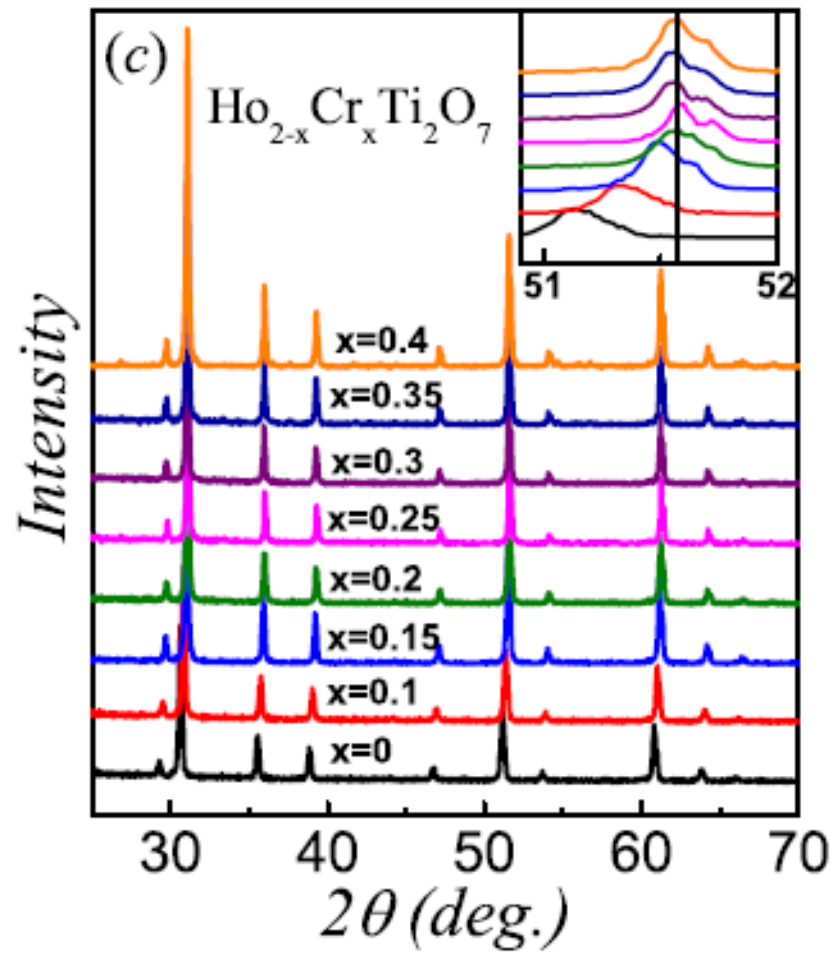


Phase competition & beyond: spin ice



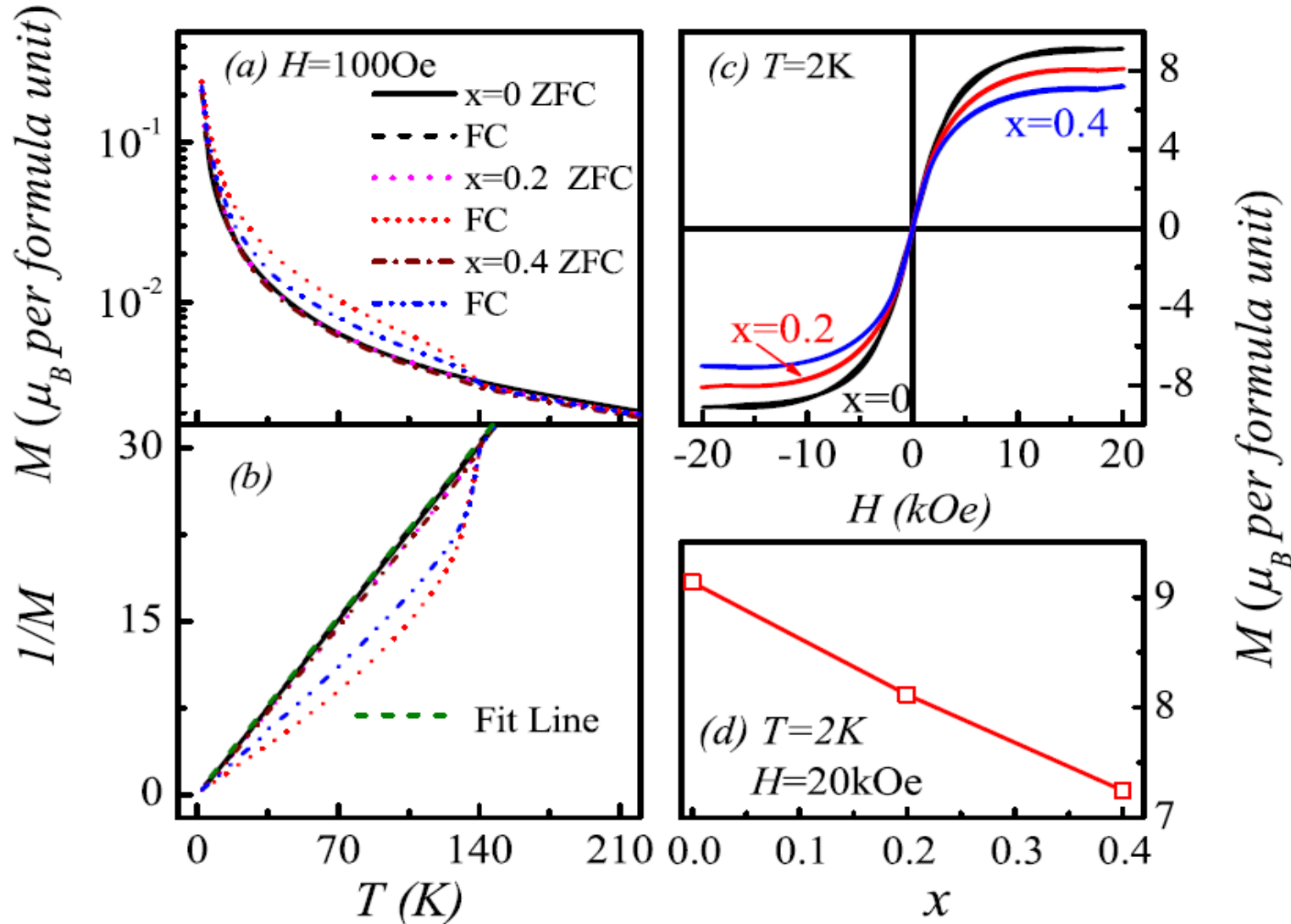


Phase competition & beyond: spin ice



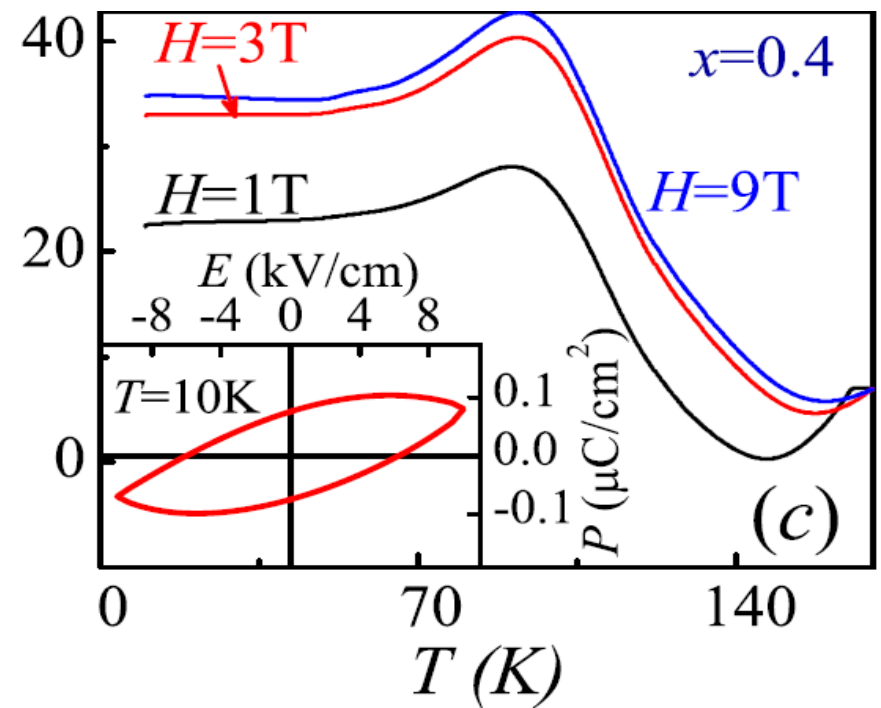
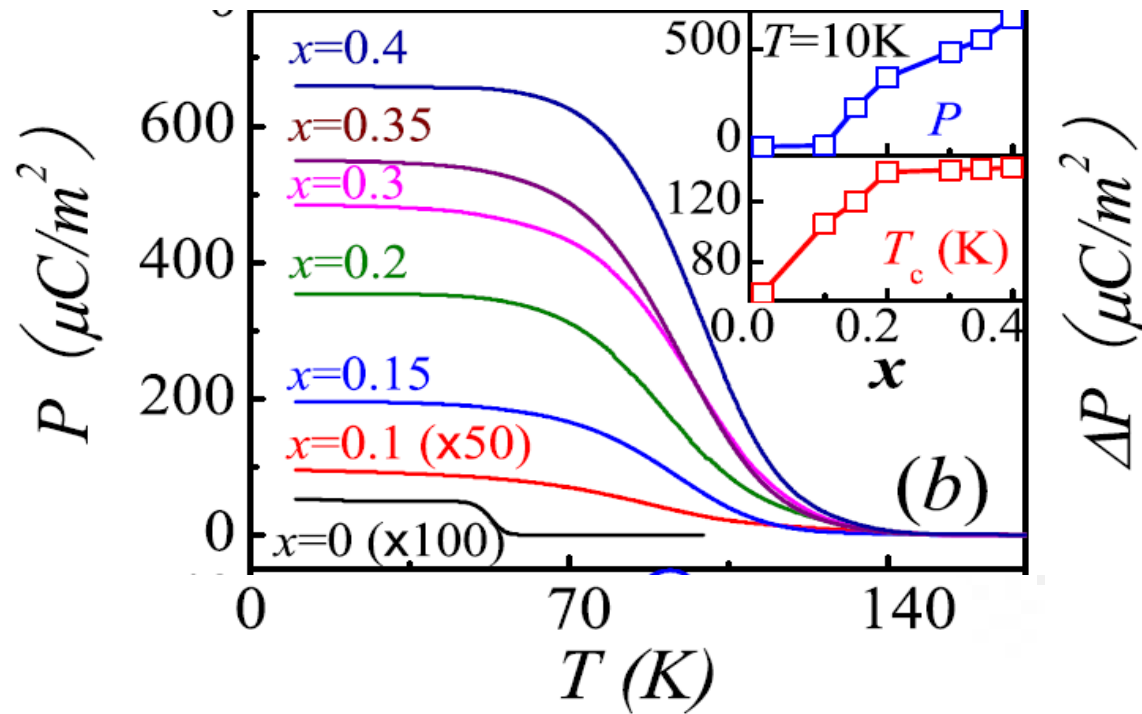


Phase competition & beyond: spin ice





Phase competition & beyond: spin ice

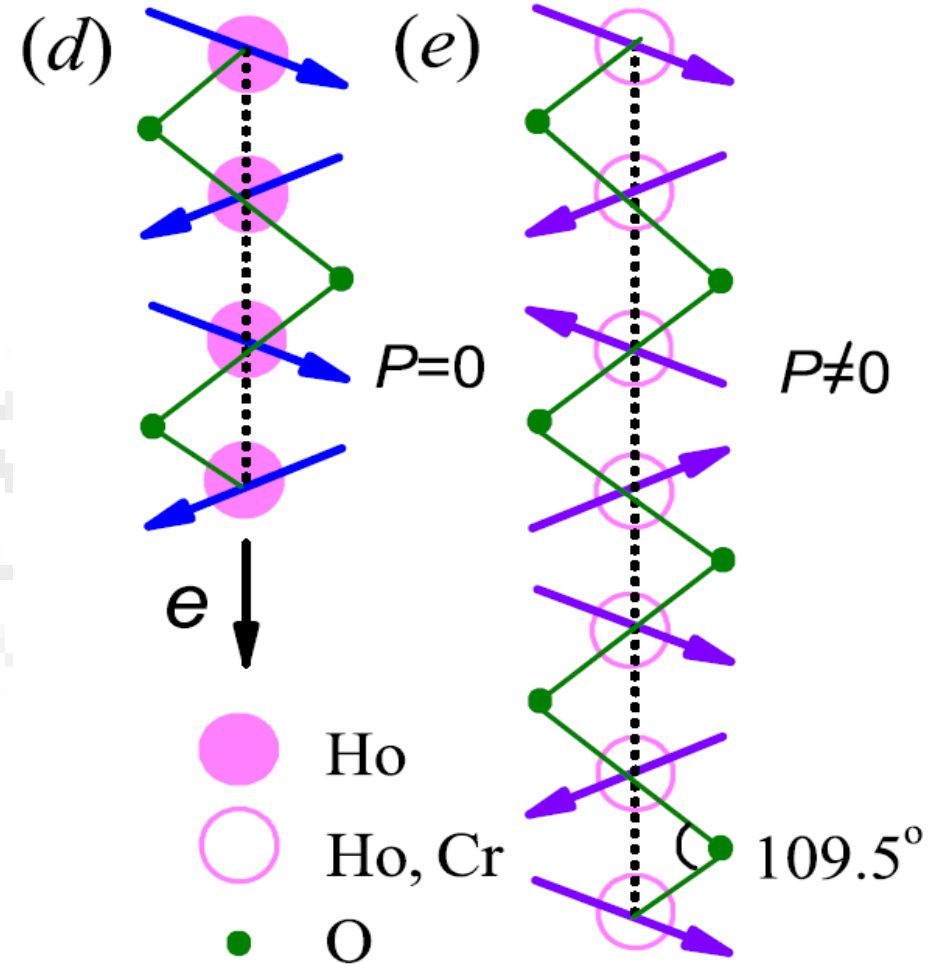




Phase competition & beyond: spin ice

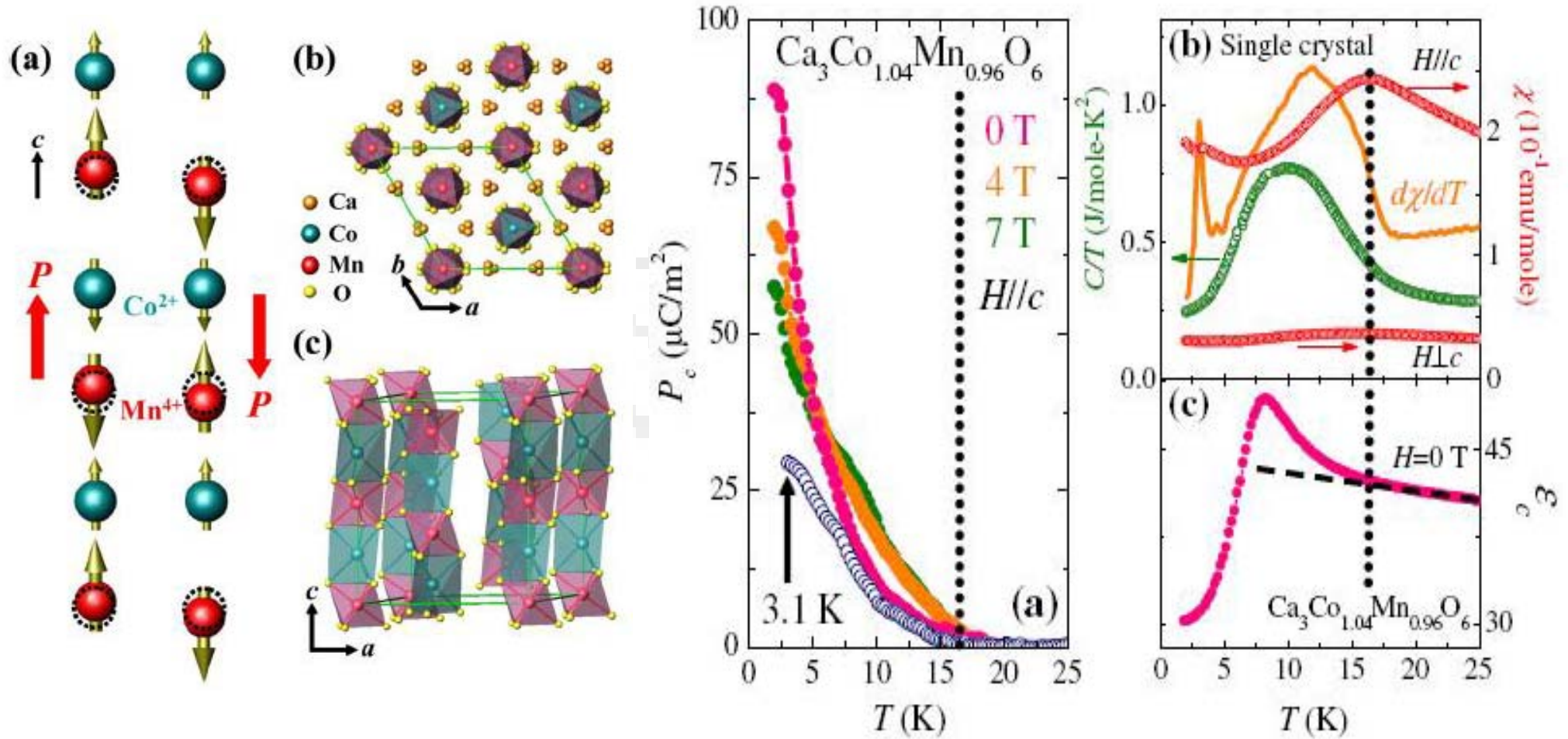
 S_{Ho}
 $S_{\text{Ho}}, S_{\text{Cr}}$

$$P = \eta e_{ij} \times (S_i \times S_j)$$





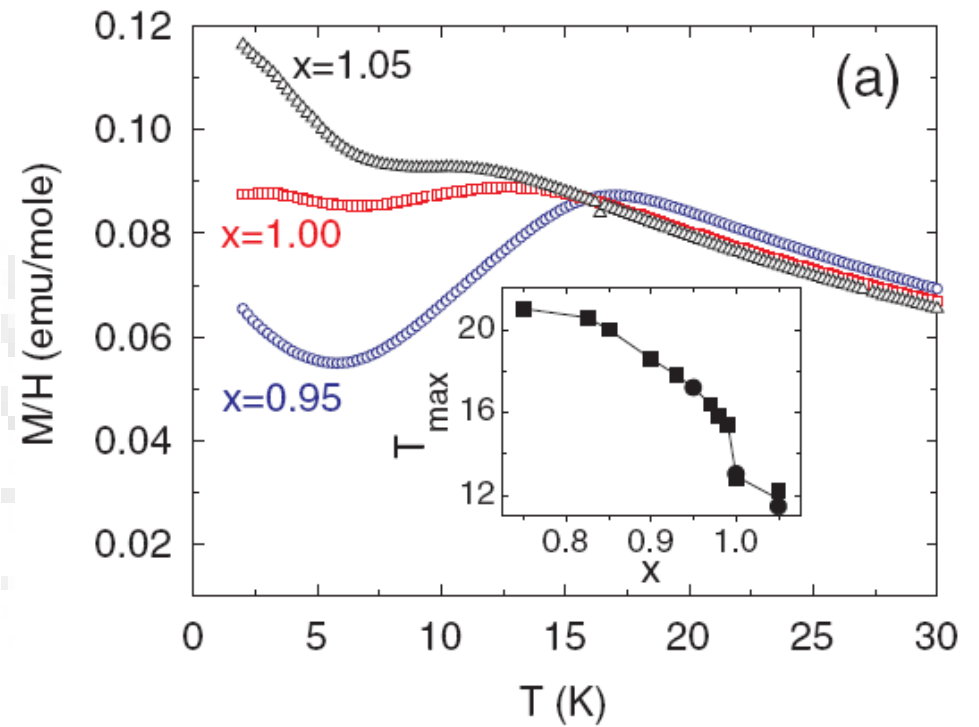
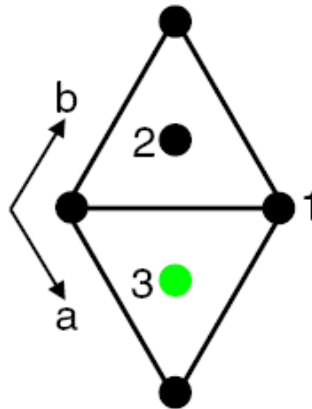
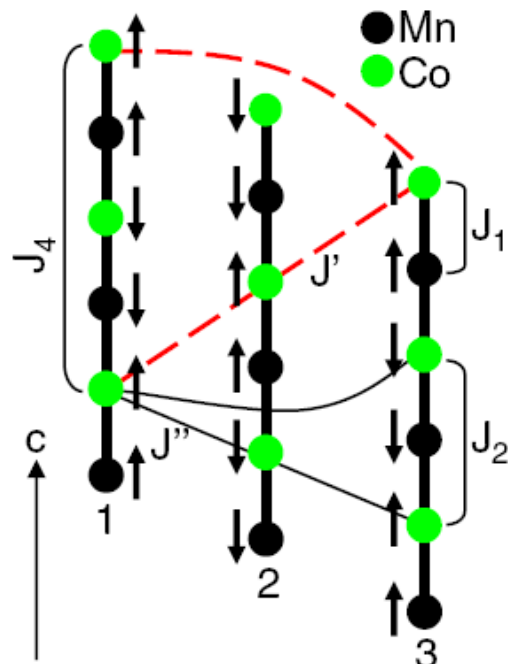
Phase competition & beyond: $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$



PRL 100, 047601 (2008).



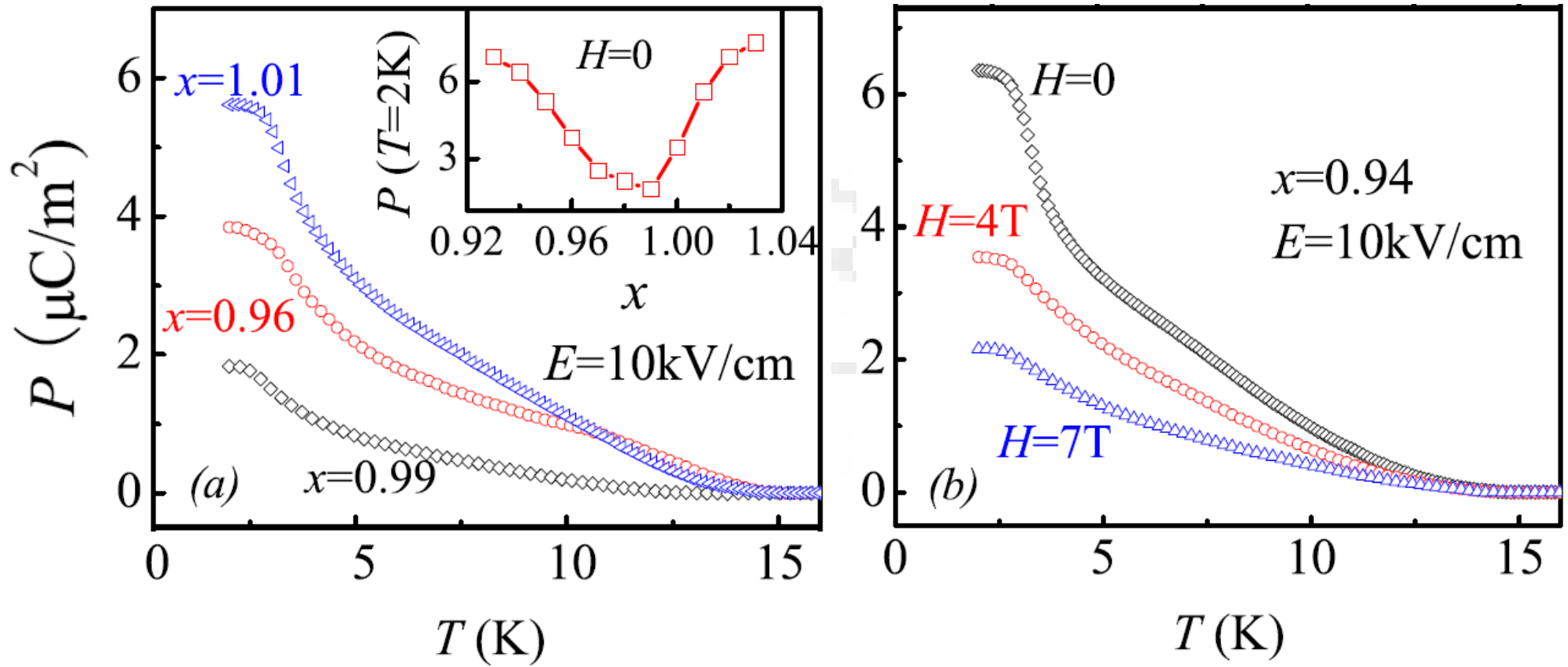
Phase competition & beyond: $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$



PRL 102, 187202 (2009).

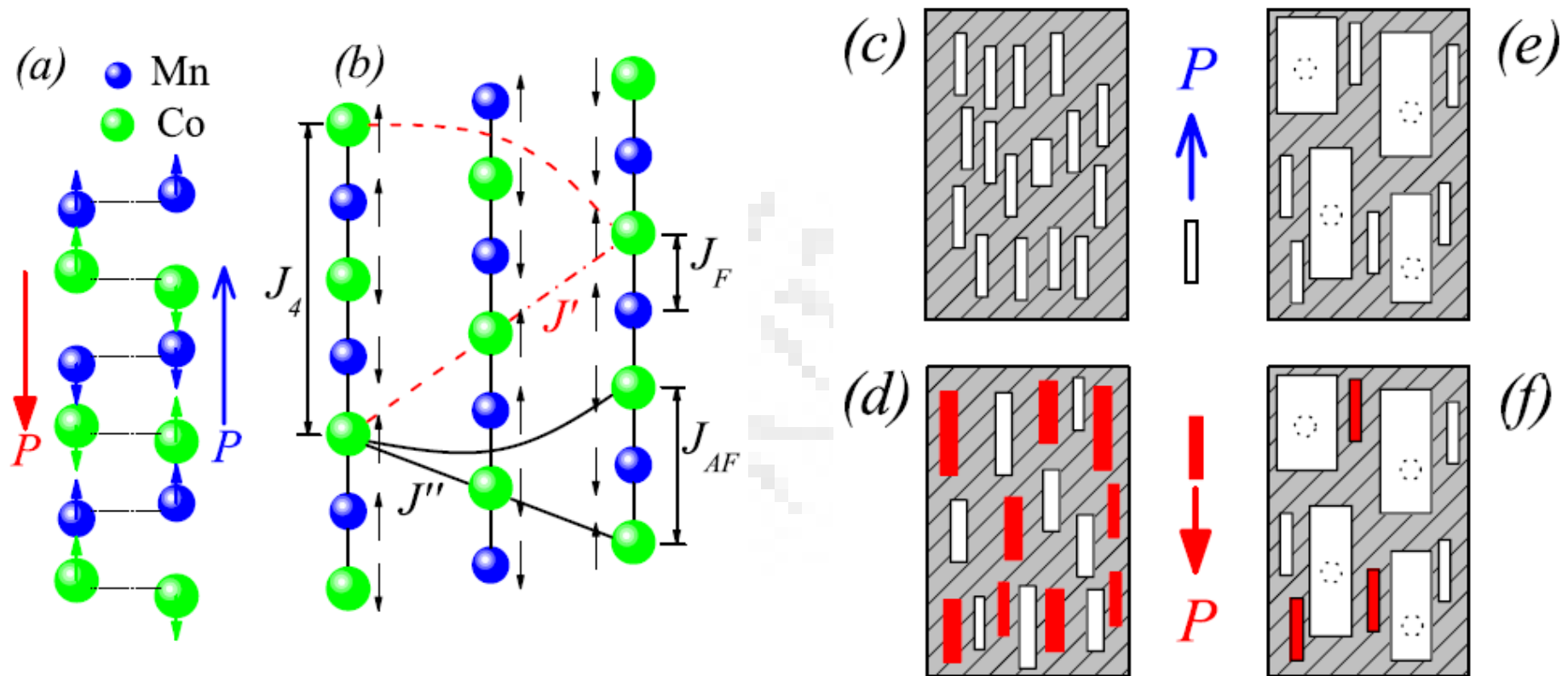


Phase competition & beyond: $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$



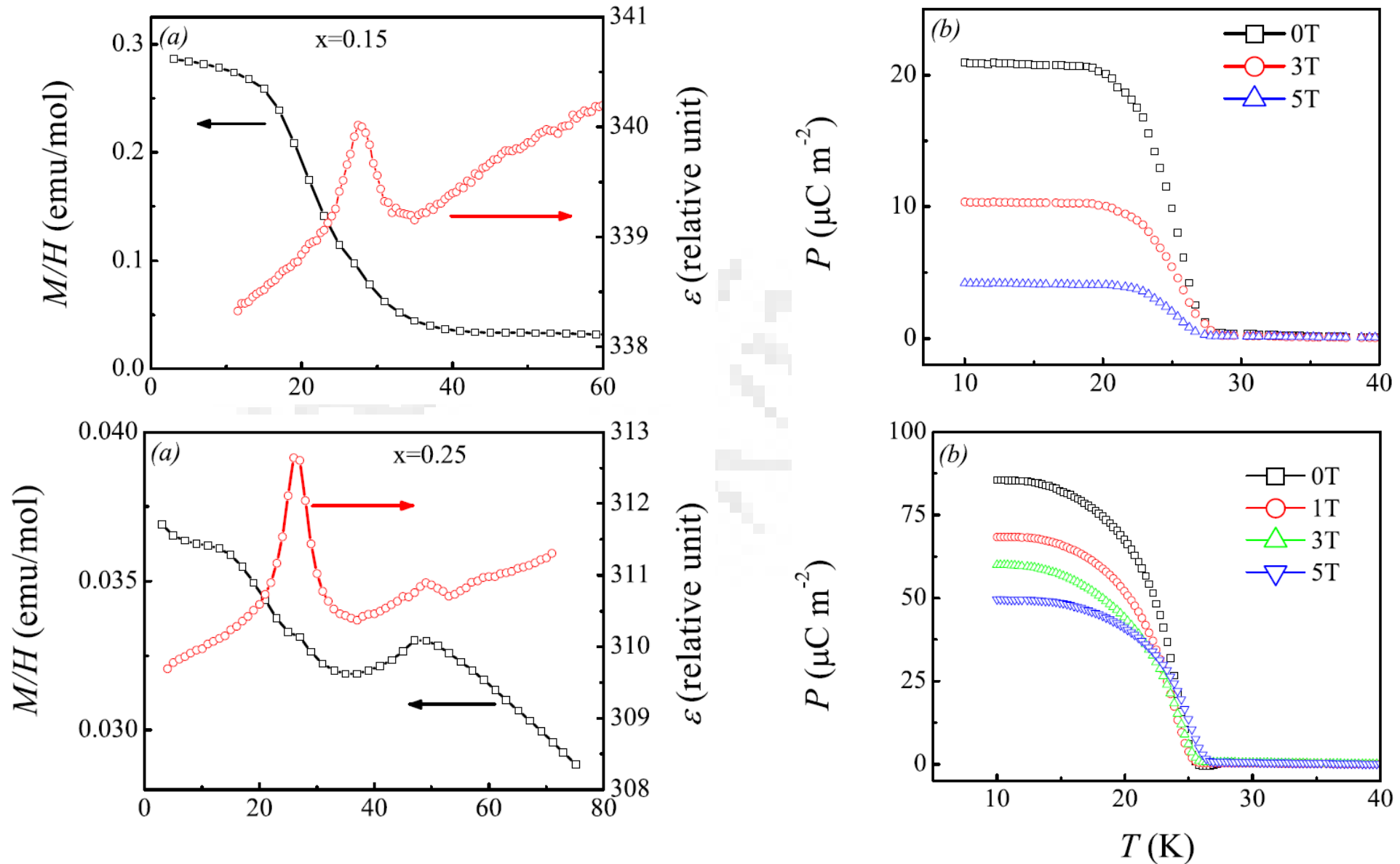


Phase competition & beyond: $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$



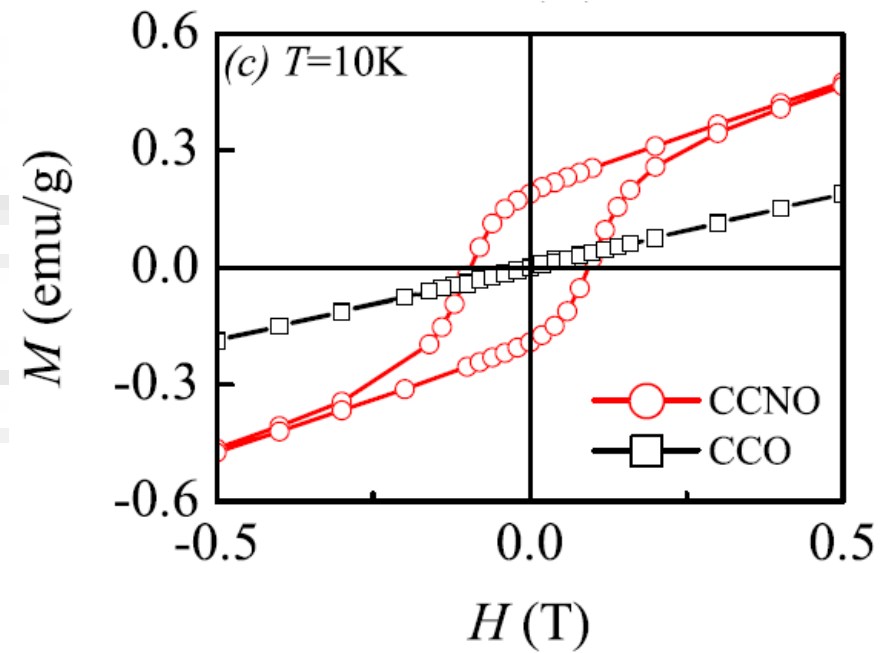
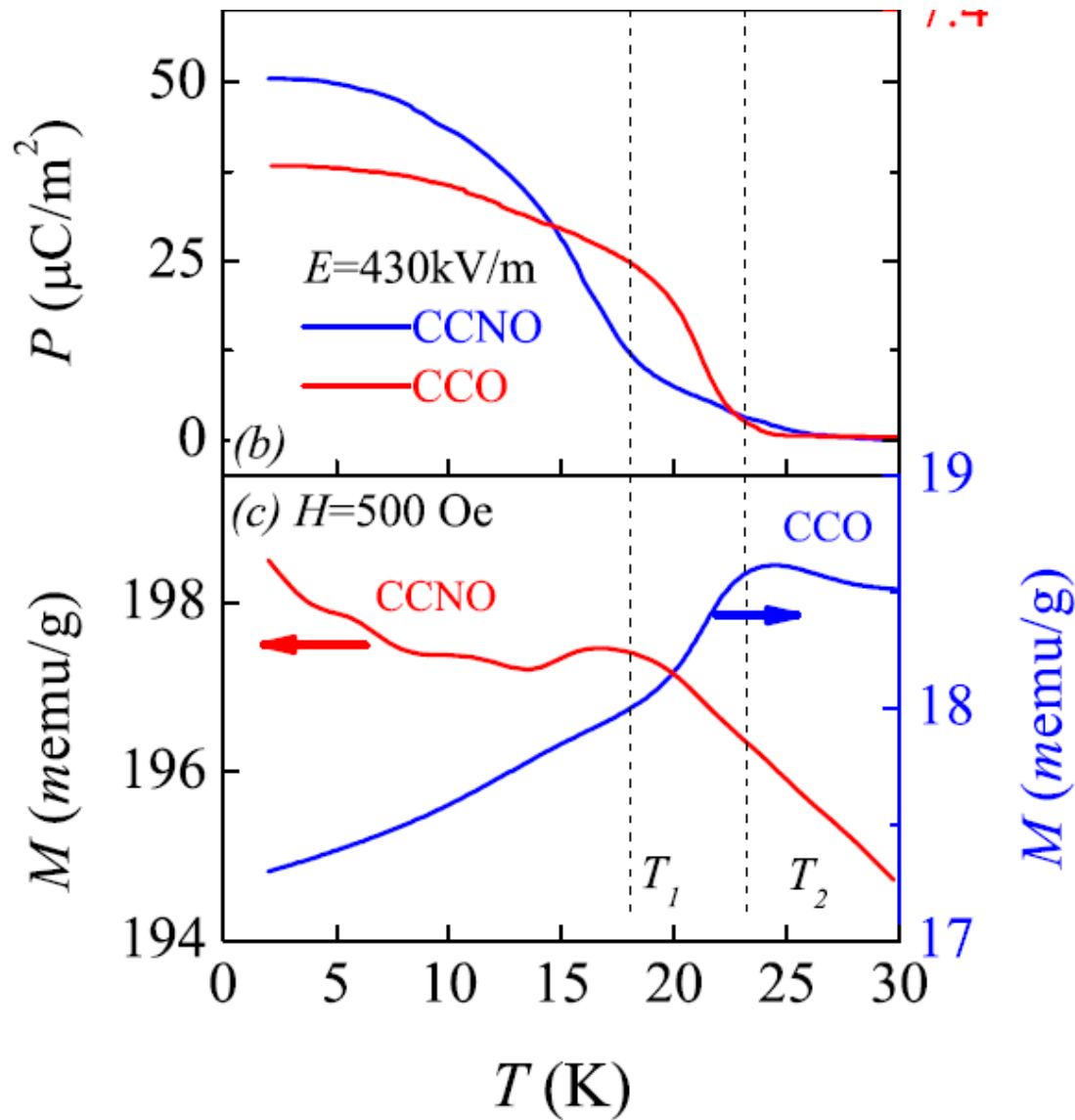


Phase competition & beyond: $\text{Eu}_{1-x}\text{Y}_x\text{MnO}_3$



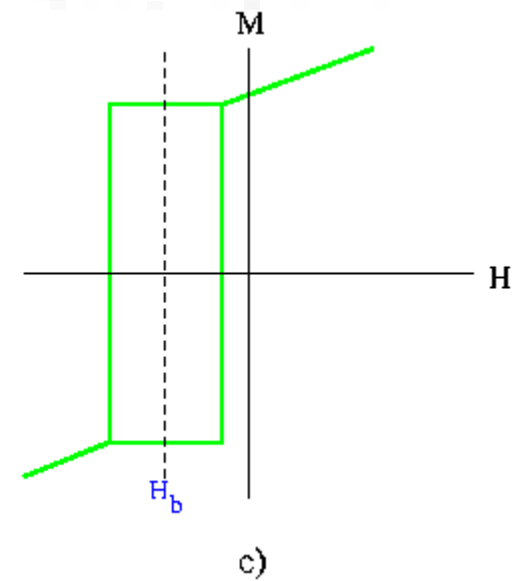
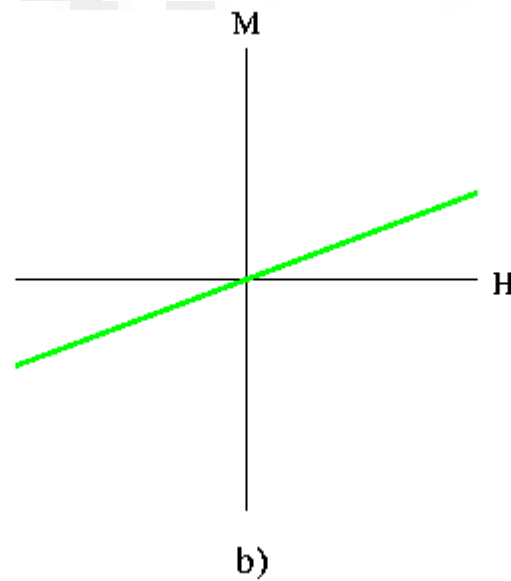
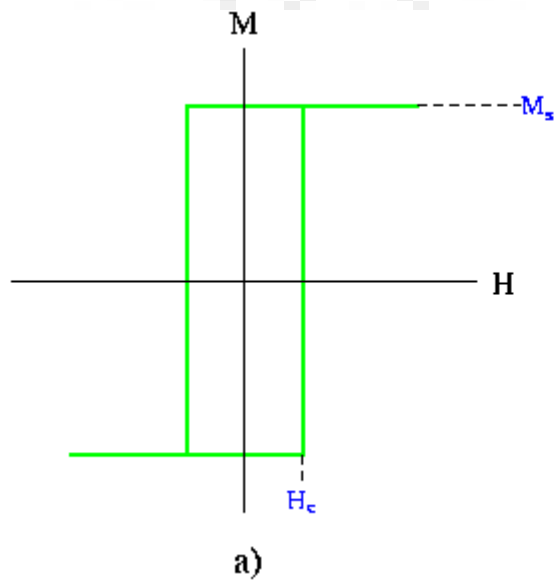
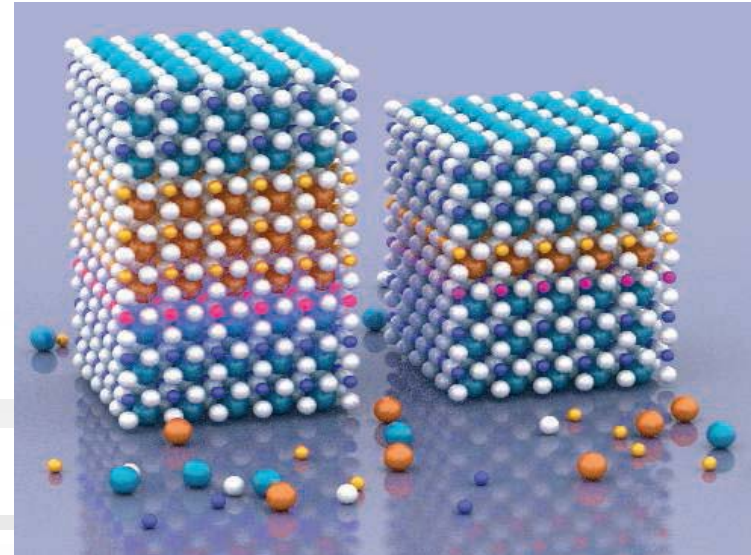
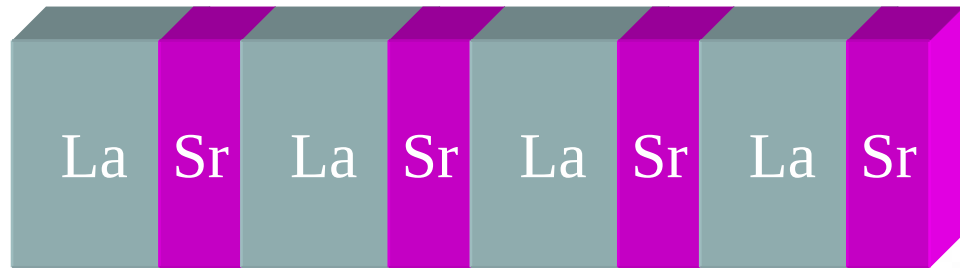


Phase competition & beyond: $\text{CuCr}_{1-x}\text{Ni}_x\text{O}_2$





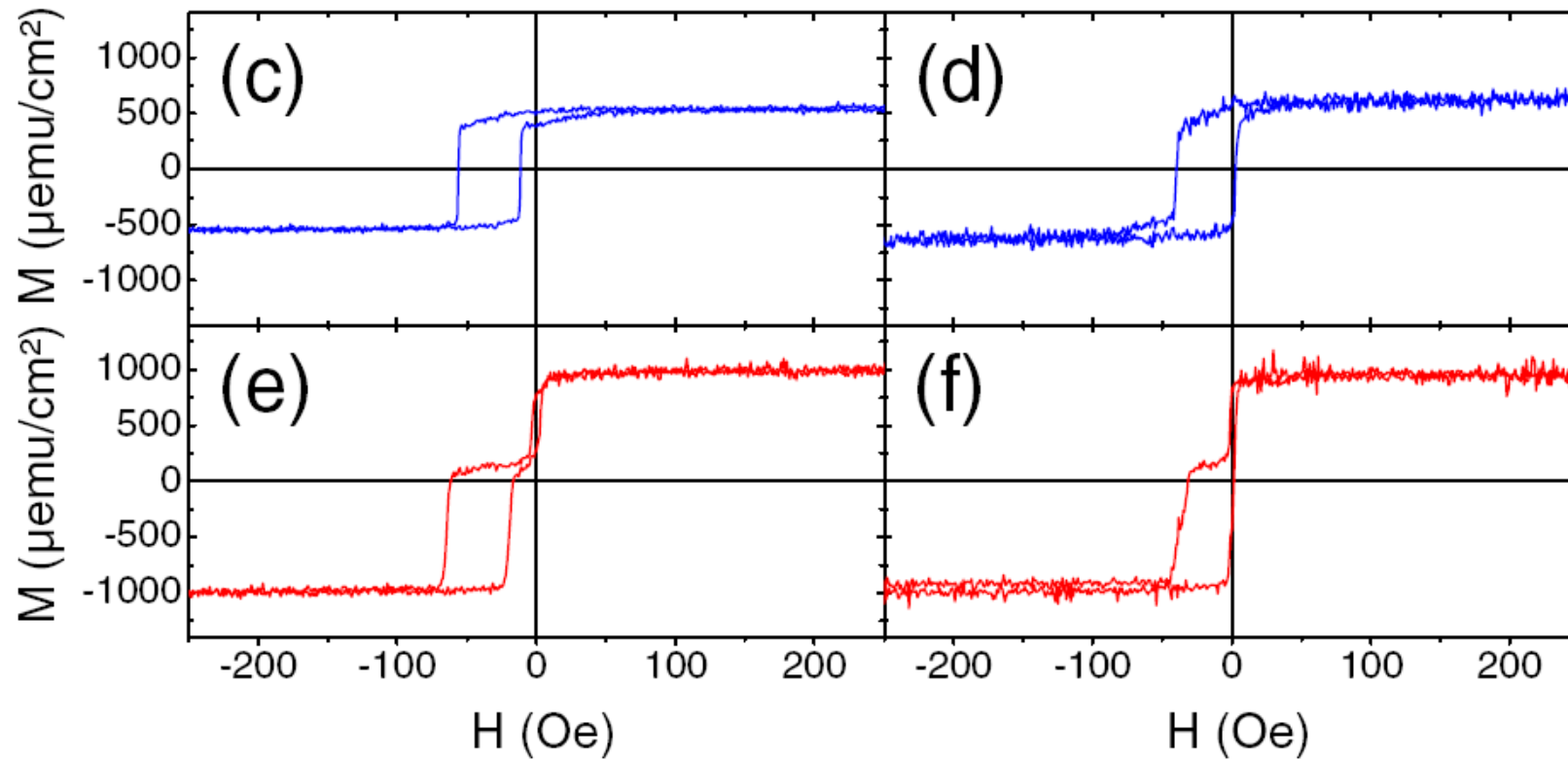
Exchange bias in heterostructures: story





Exchange bias in heterostructures: story

Bea et al, PRL 100, 017204 (08)



$\text{CoFeB}/\text{BiFeO}_3$ (c,d) & $\text{CoFeB}/\text{BiFeO}_3/\text{LSMO}$ (e,f) on STO substrates



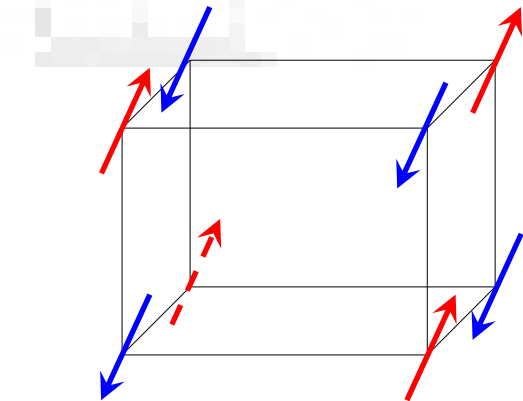
Exchange bias in heterostructures: story

- $\text{LaMnO}_3\text{-SrMnO}_3$: No Bhattacharya
- $\text{SrRuO}_3\text{-SrMnO}_3$: Yes Chmaissem
- $\text{Co}_{0.9}\text{Fe}_{0.1}\text{-BiFeO}_3$: Yes Ramesh, Barthelemy, Blamire
- $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{-BiFeO}_3$: Yes Ramesh

**G-type AFM
(001) interface**



Electric-controllable

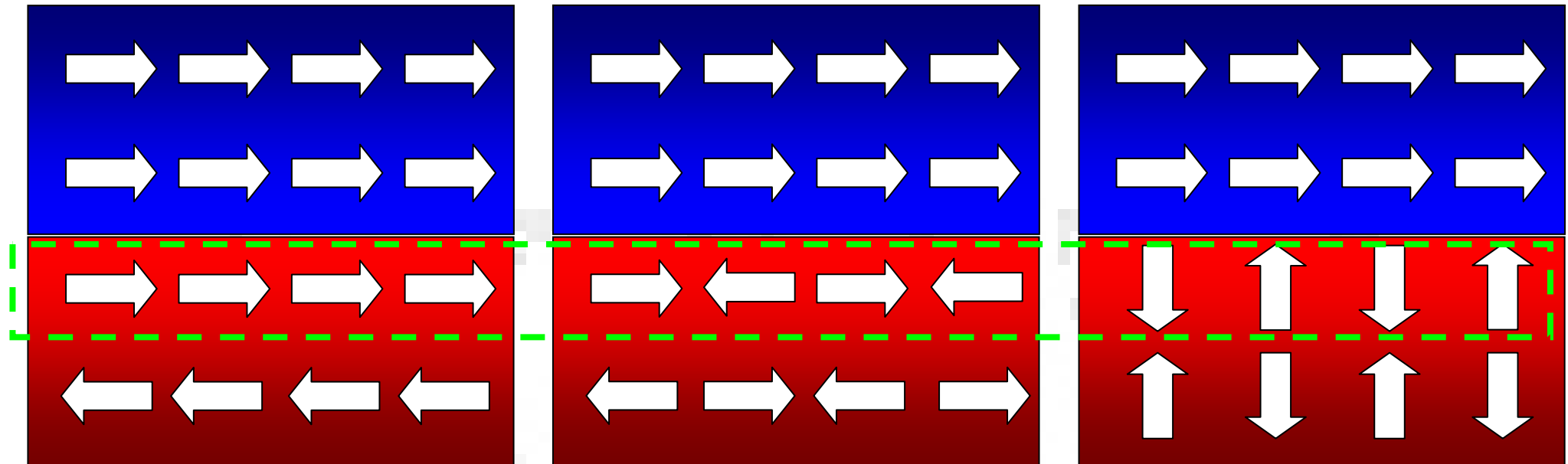




Exchange bias in heterostructures: story

EB in case of uncompensated interface

M. Kiwi, JMMM, 234, 584 (2001)



uncompensated



Broken symmetry:
exchange bias

compensated

long term debate!

Roughness? Dipole interaction?
Domain? Spin canting?

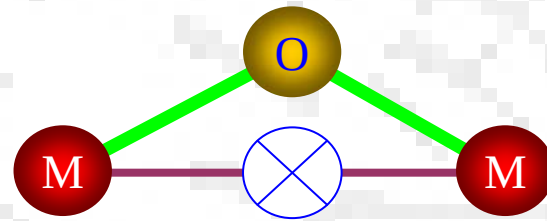
compensated
Non-collinear



Exchange bias in heterostructures: novel idea

Dzyaloshinskii-Moriya interaction in perovskites

$$\mathbf{D}^a(\mathbf{r}_n) \cdot [\mathbf{S}_n \times \mathbf{S}_{n+1}]$$



$$\vec{D} \perp \vec{d}$$

$$\vec{D} \perp \vec{r}$$

$$\vec{D} \propto \vec{d}$$



Exchange bias in heterostructures: approach

Dzyaloshinskii-Moriya interaction in perovskites

$$H = \sum_{\langle ij \rangle} [J_{i,j} \vec{S}_i \cdot \vec{S}_j + \vec{D}_{i,j} \cdot (\vec{S}_i \times \vec{S}_j)]$$

$$\vec{J} = \begin{pmatrix} J_x & D_z & -D_y \\ -D_z & J_y & D_x \\ D_y & -D_x & J_z \end{pmatrix}$$

DM interaction comes from
spin-orbital coupling

$$D/J \sim 10^{-3}$$

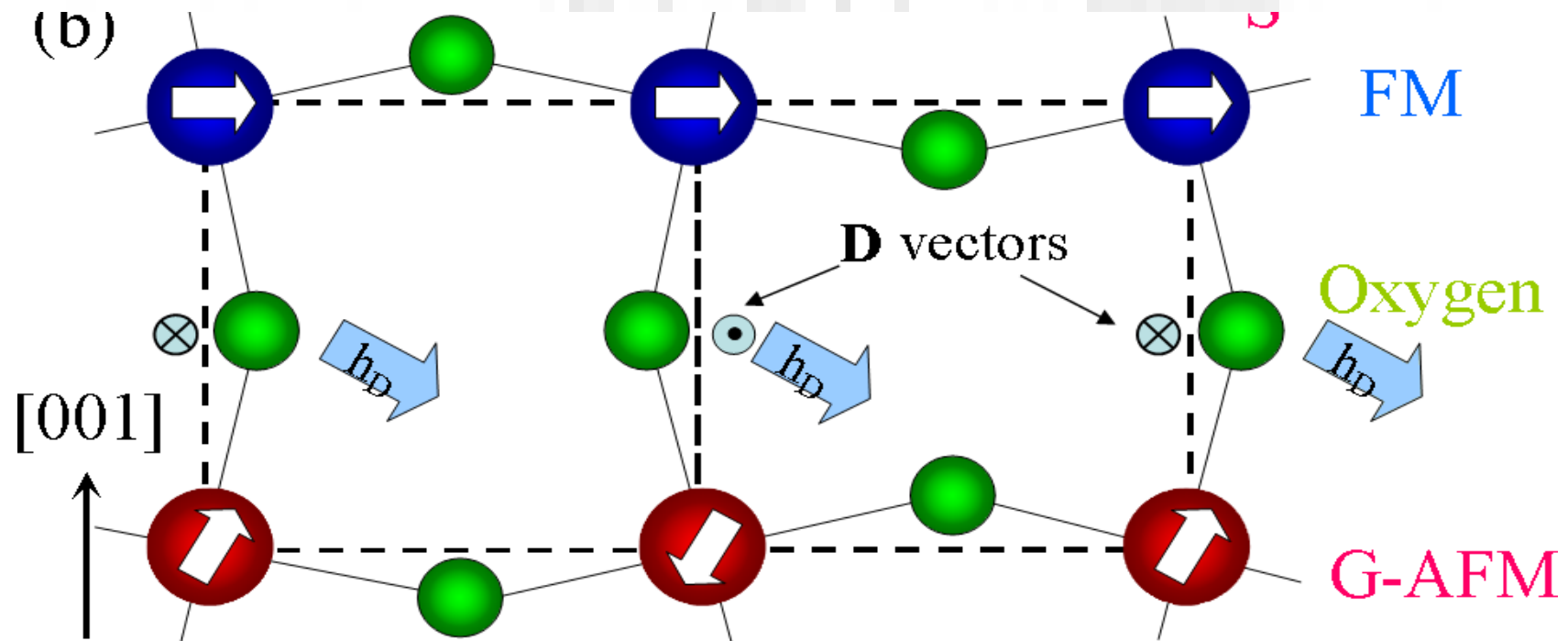


Exchange bias in heterostructures: approach

$$H_{\text{DM}}^{\text{interface}} = \sum_{\langle ij \rangle} \vec{D}_{ij} \cdot (\vec{S}_i^{\text{FM}} \times \vec{S}_j^{\text{AFM}}) = -\vec{h}_{\text{D}} \cdot \sum_i \vec{S}_i^{\text{FM}}$$

DMI @ FM/G-AFM interface

$$\vec{D} \times \vec{S}^{\text{A}}$$





Exchange bias in heterostructures: approach

Estimation of the EB $h_{EB} \approx |\vec{h}_D| / d = H_{DM}^{\text{interface}} / (dm)$

H_{DM} : DM energy

d : Thickness of FM layer

m : FM magnetic moment h_{EB} : Loop shift

$$H_{DM}^{\text{interface}} \approx \gamma X_O \approx 0.0175 \text{ meV}$$

1.0 degree bending

$$a = 4.0 \text{ \AA}$$

$$\gamma = 1.0 \text{ meV/\AA}$$

$$J \sim 10 \text{ meV}$$

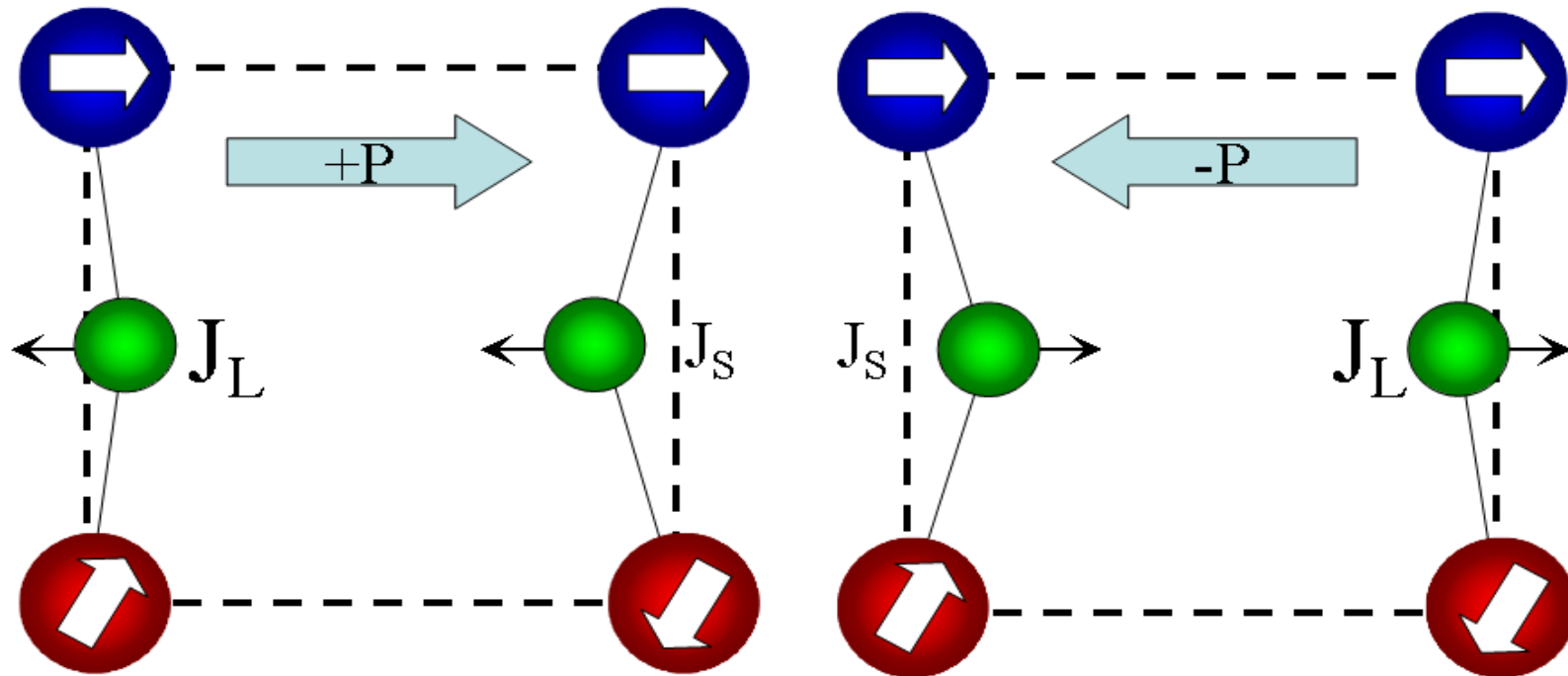


100 Oe if $d=10$, $m=3.0\mu_B$



Exchange bias in heterostructures: ferroelectricity

Ferroelectricity driven EB



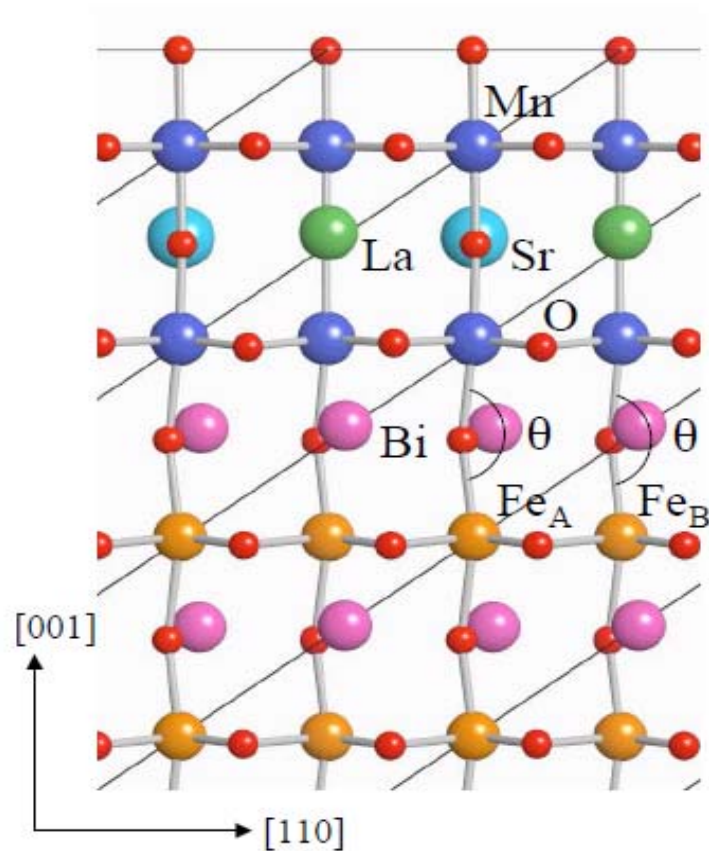
$$H_{SE}^{\text{interface}} = \sum_{\langle ij \rangle} J_{i,j} \vec{S}_i^{\text{FM}} \cdot \vec{S}_j^{\text{AFM}} = -\vec{h}_J \cdot \sum_i \vec{S}_i^{\text{FM}}$$

$$\text{Here, } \vec{h}_J = -\delta_J \vec{S}^A$$

$$\delta_J = (J_L - J_S)/2.$$



Exchange bias in heterostructures: ferroelectricity



Ferroelectricity driven EB

$\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3\text{-BiFeO}_3$

DFT calculation by

K. Yamauchi and S. Picozzi

$X_O \sim 0.01 \text{ A}$

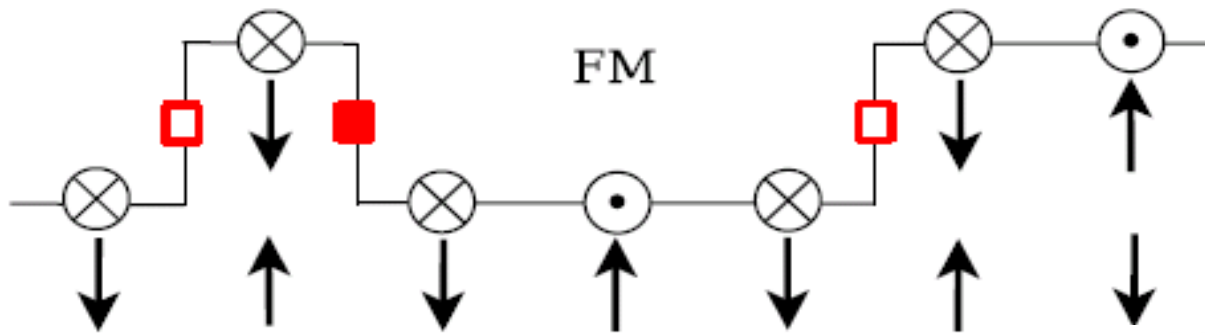
$X_{\text{FE}} \sim 0.1 \text{ A}$

	$\text{Mn}\downarrow\text{-Fe}_A\downarrow$	$\text{Mn}\uparrow\text{-Fe}_A\downarrow$	$\text{Mn}\uparrow\text{-Fe}_B\uparrow$	$\text{Mn}\downarrow\text{-Fe}_B\uparrow$
top	169.69	169.55	168.37	168.30
bottom	169.81	170.47	168.58	169.30



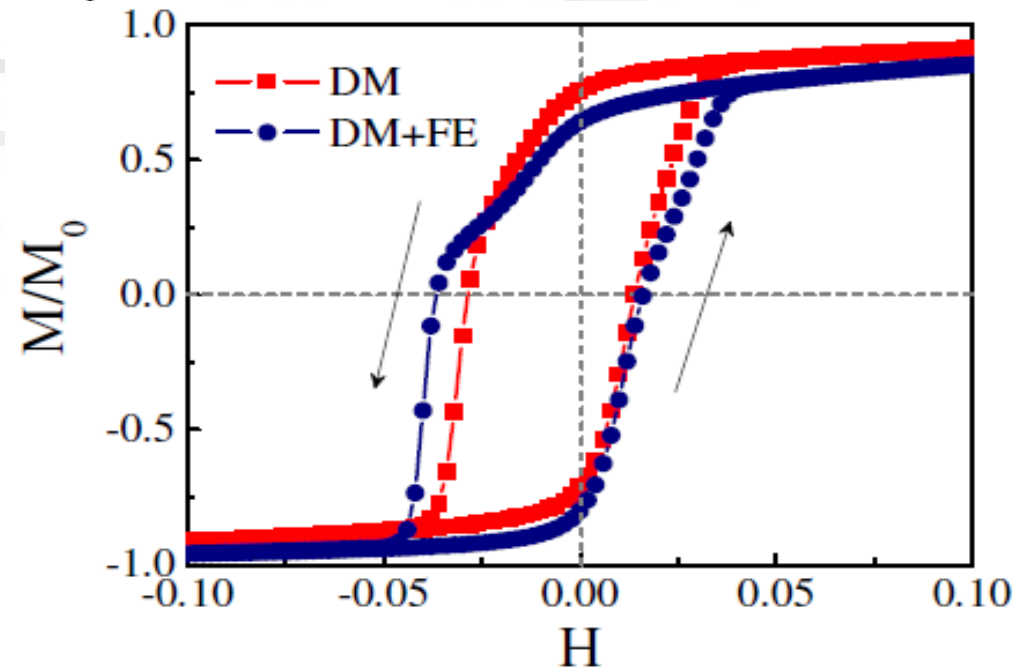
Exchange bias in heterostructures: Monte Carlo

Roughness-induced effect



h_{DM} and h_{FE} will not be canceled but may be decreased by roughness.

Spin canting effects (may originate from exchange coupling at the interface, or magnetic field reorientation etc.) are **NOT** found to affect our results **qualitatively**.





Perspectives: future of single-phase multiferroics?

- How to enhance P and the ordering temperature?
- How to make the spin-order ferromagnetic at high T ?
- Additional mechanism for spin-order induced ferroelectricity
- Quantitative theory of multiferroicity



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Thank you for your attentions

