Multiferroic and magnetoelectric materials

Maxim Mostovoy

University of Groningen
Zernike Institute
for Advanced Materials

ICMR Summer School
on Multiferroics

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Lectures

- Multiferroic and magnetoelectric materials: Phenomenology and microscopic mechanisms of magnetoelectric coupling.

- Ferroelectric properties of magnetic defects. Toroidal magnetoelectrics. Electromagnons.

Outline

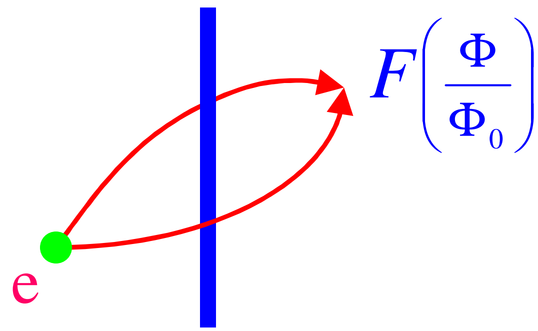
- Broken symmetries
- Linear magnetielectric effect and magnetically –induced ferroelectricity
- Phenomenological description
- Microscopic mechanisms of magnetoelectric coupling

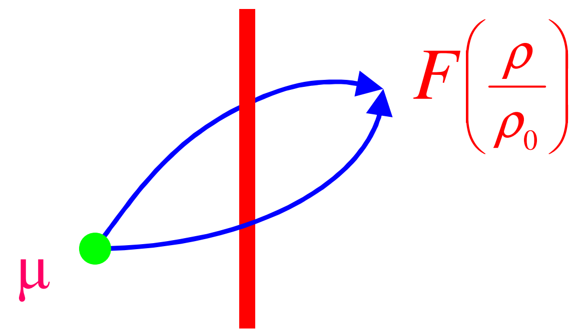
Electric ↔ Magnetic

- Duality of Maxwell equations

$$\begin{cases} \nabla \times \mathbf{E} = -\dfrac{1}{c}\dfrac{\partial \mathbf{H}}{\partial t} \\ \nabla \times \mathbf{H} = +\dfrac{1}{c}\dfrac{\partial \mathbf{E}}{\partial t} \end{cases} \qquad \begin{cases} \mathbf{E} \to \mathbf{H} \\ \mathbf{H} \to -\mathbf{E} \end{cases}$$

- Aharonov-Bohm
  Aharonov-Casher

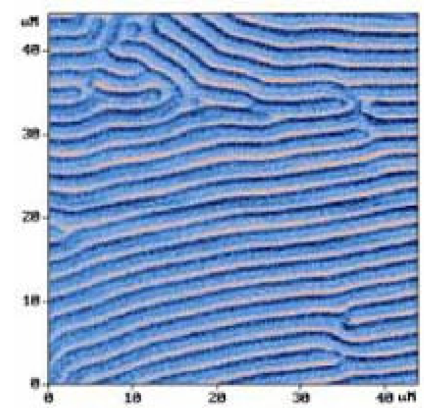




- Thermodynamics of ferroelectrics and ferromagnets

$$\begin{cases} \Phi_{FE} = aP^2 + bP^4 - PE \\ \Phi_{FM} = aM^2 + bM^4 - MH \end{cases}$$

$$\begin{cases} \nabla \times \mathbf{E} = 0 \\ \nabla \cdot (\mathbf{E} + 4\pi\mathbf{P}) = 0 \end{cases} \qquad \begin{cases} \nabla \times \mathbf{H} = 0 \\ \nabla \cdot (\mathbf{H} + 4\pi\mathbf{M}) = 0 \end{cases}$$



Transformation properties

polar vectors **axial vectors**

$$\mathbf{E} = -\nabla\varphi \qquad \mathbf{P} = -\nabla\rho \qquad \mathbf{H} = \nabla\times\mathbf{A} \qquad \mathbf{L} = \mathbf{x}\times\mathbf{p}$$

inversion *I* $(x, y, z) \rightarrow (-x, -y, -z)$

$$\mathbf{E} \rightarrow -\mathbf{E} \qquad \mathbf{P} \rightarrow -\mathbf{P} \qquad \mathbf{H} \rightarrow \mathbf{H} \qquad \mathbf{M} \rightarrow \mathbf{M}$$

time reversal *T* $t \rightarrow -t$

$$\mathbf{E} \rightarrow \mathbf{E} \qquad \mathbf{P} \rightarrow \mathbf{P} \qquad \mathbf{H} \rightarrow -\mathbf{H} \qquad \mathbf{M} \rightarrow -\mathbf{M}$$

mirror $m_{yz} = m_x$ $(x, y, z) \rightarrow (-x, y, z)$

$$(P_x, P_y, P_z) \rightarrow (-P_x, P_y, P_z) \qquad (M_x, M_y, M_z) \rightarrow (M_x, -M_y, -M_z)$$

180°-rotation 2_x $(x, y, z) \rightarrow (x, -y, -z)$

$$(P_x, P_y, P_z) \rightarrow (P_x, -P_y, -P_z) \qquad (M_x, M_y, M_z) \rightarrow (M_x, -M_y, -M_z)$$

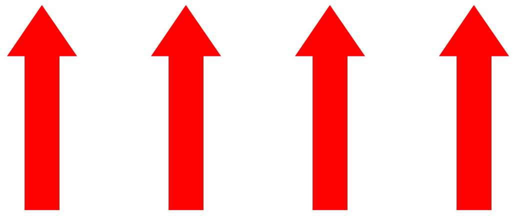
Time-reversal symmetry breaking in magnets

$$< \mathbf{S} > \neq 0$$

$$\mathbf{S}(-t) = -\mathbf{S}(t)$$

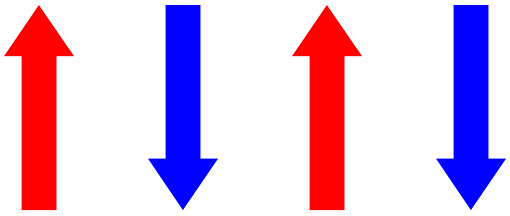
Ferromagnets

$$\mathbf{M} \neq 0$$

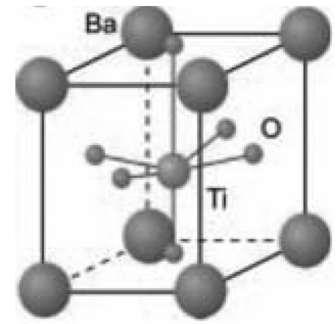


Antiferromagnets

$$\mathbf{M} = 0$$



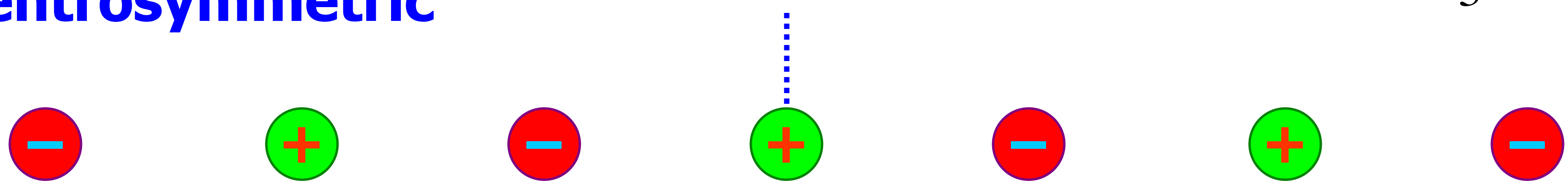
Inversion symmetry breaking in ferroelectrics



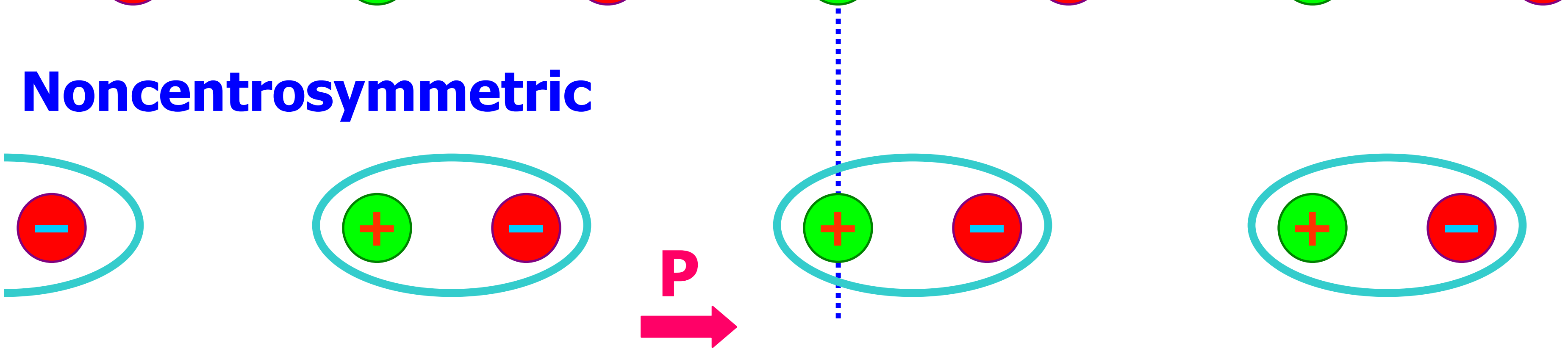
$$\mathbf{P}(-\mathbf{x}) = -\mathbf{P}(\mathbf{x})$$

$BaTiO_3$

Centrosymmetric



Noncentrosymmetric



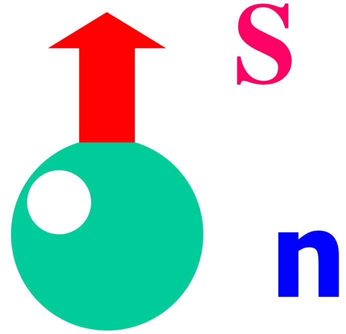
Electric dipole moment of neutron

inversion

$\mathbf{x} \rightarrow -\mathbf{x}$

$\mathbf{d} \rightarrow -\mathbf{d}$

$\mathbf{S} \rightarrow +\mathbf{S}$



time reversal

$t \rightarrow -t$

$\mathbf{d} \rightarrow +\mathbf{d}$

$\mathbf{S} \rightarrow -\mathbf{S}$

$$\mathbf{d} \propto \mathbf{S}$$

Electric dipole moment is only nonzero if both spatial parity and time reversal symmetry are broken

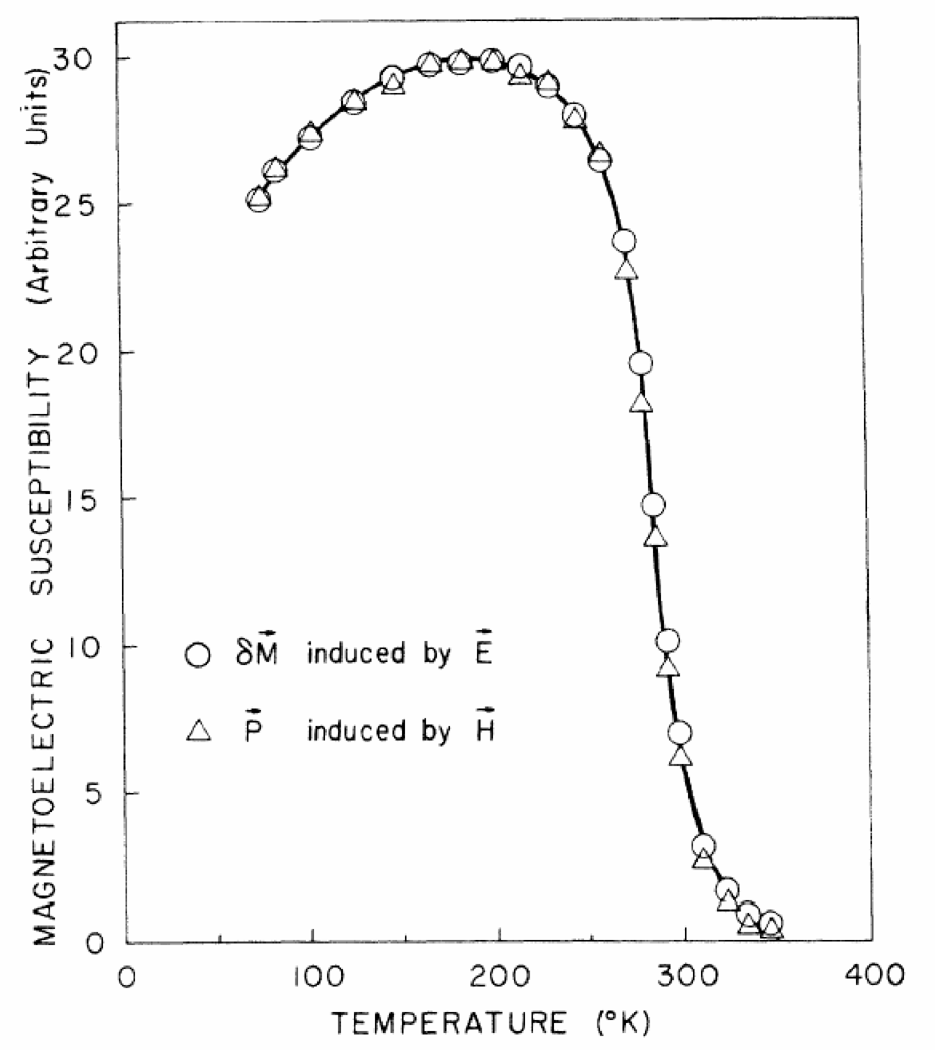
Outline

- Broken symmetries
- Linear magnetielectric effect and magnetically –induced ferroelectricity
- Phenomenological description
- Microscopic mechanisms of magnetoelectric coupling

Linear magnetoelectric effect

Cr_2O_3

*I. E. Dzyaloshinskii JETP **10** 628 (1959),*
*D. N. Astrov, JETP **11** 708 (1960)*



$$P = \chi_e E + \alpha H$$

$$M = \alpha E + \chi_m H$$

*G.T. Rado PRL **13** 335 (1964)*

Multiferroics

- Both ferroelectric and magnetic
- Coupling between **P** and **M**

$Pb(Fe_{2/3}W_{1/3})O_3$ $BiFeO_3$

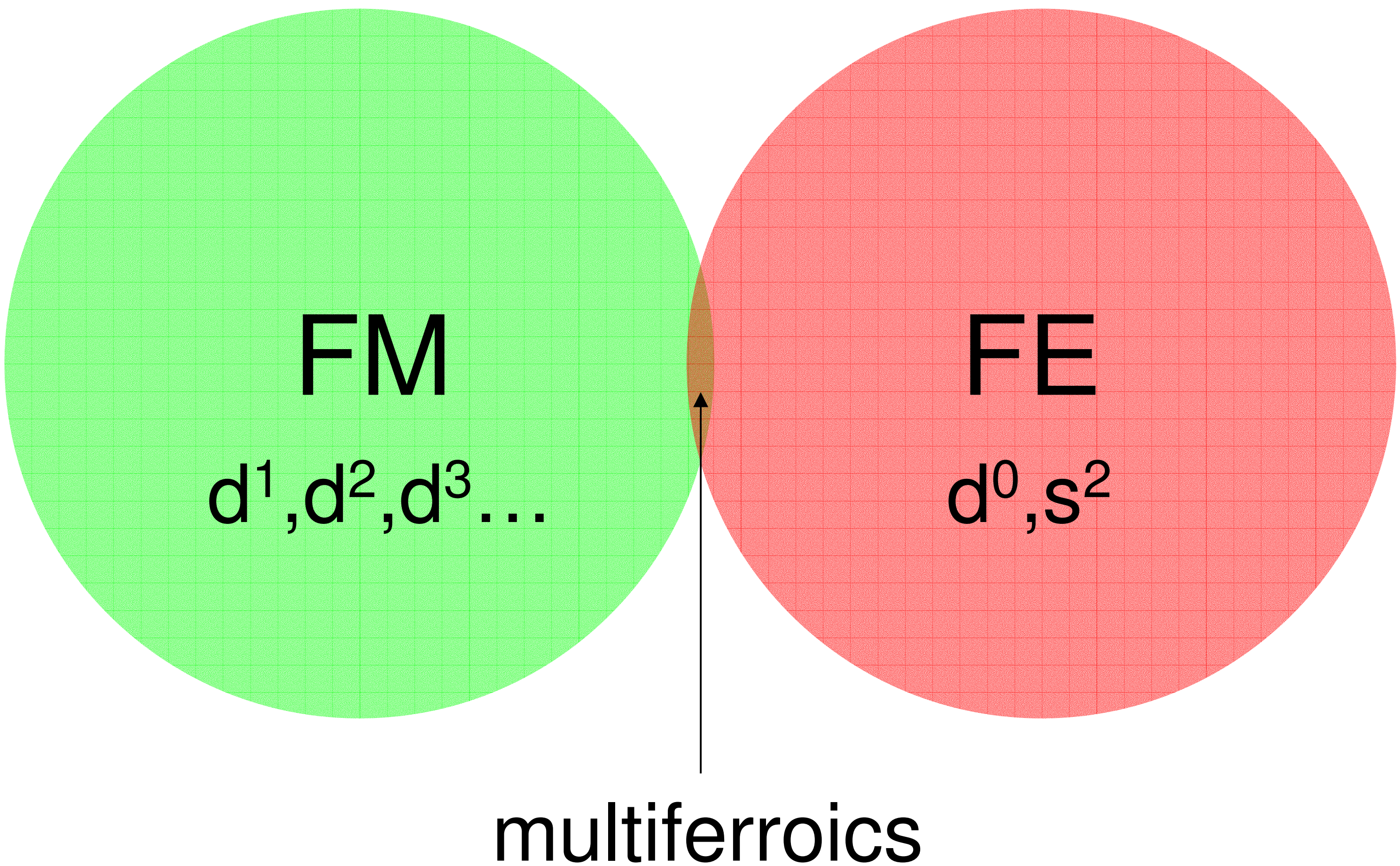
$Pb(Fe_{1/2}Ta_{1/2})O_3$ $BiMnO_3$

$Ni_3B_2O_{13}I$ $YMnO_3$

G. A. Smolenskii

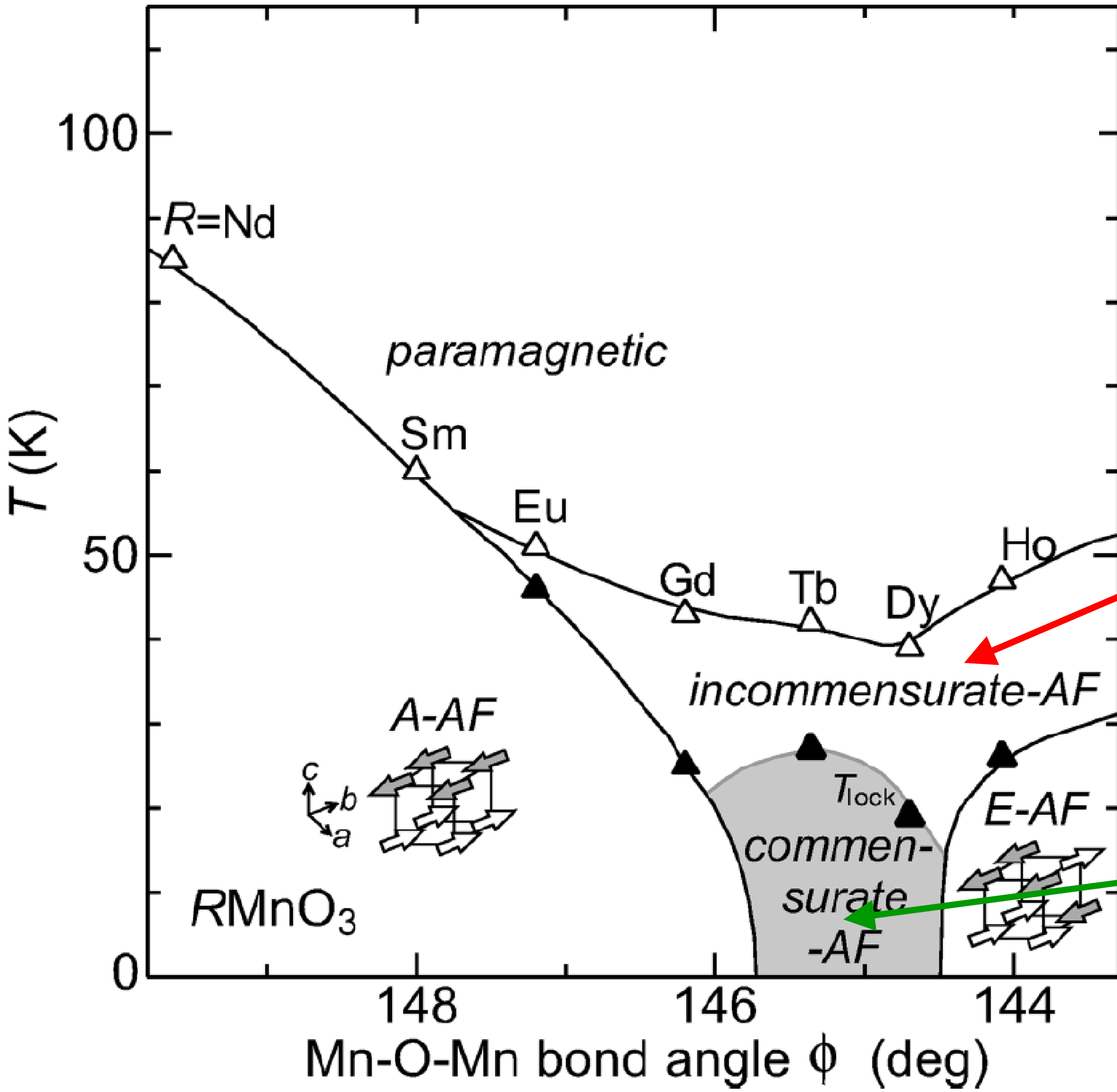
*G.A. Smolenskii & I.E. Chupis, Sov. Phys. Usp. **25**, 475 (1982)*

No chemistry between magnetism and ferroelectricity

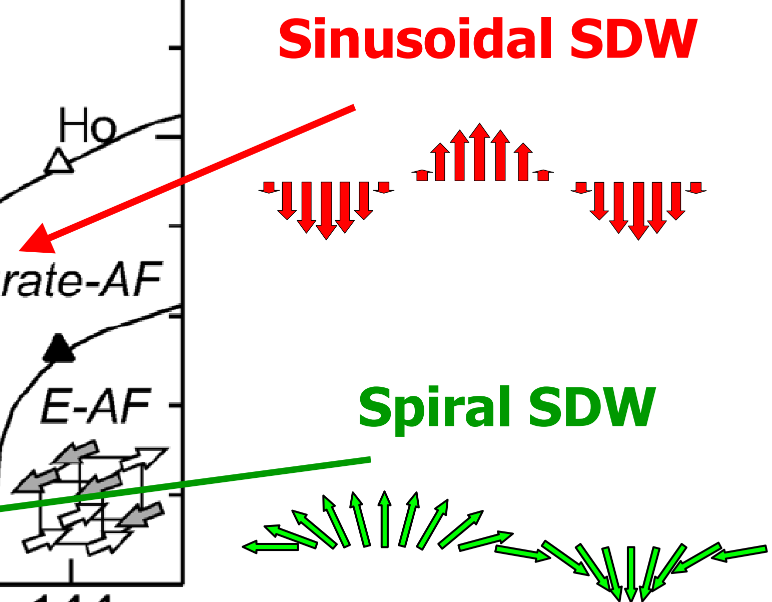


N. A. Hill, J. Phys. Chem. B ***104****, 6694 (2000)*

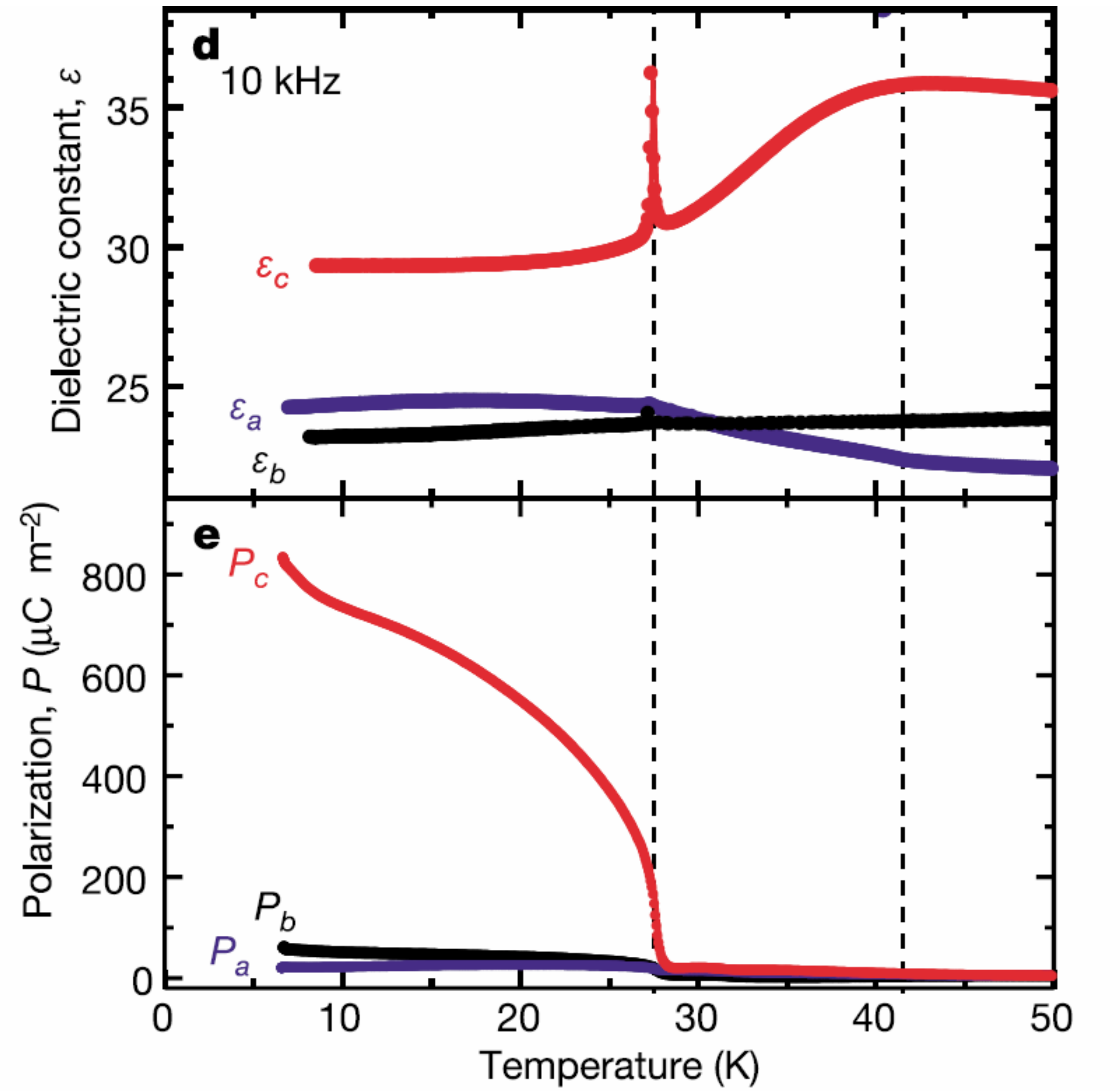
Orthorombic $RMnO_3$



T. Kimura et al
*PRB **68**,060403 (2003)*

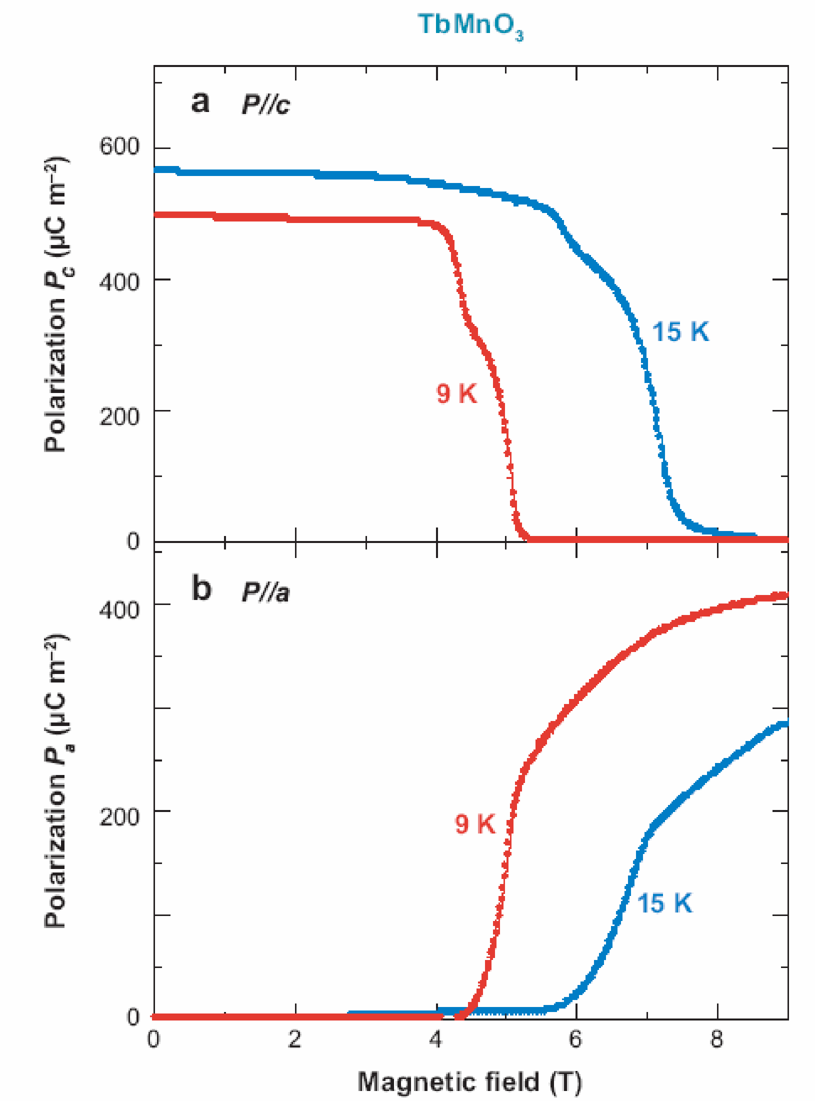


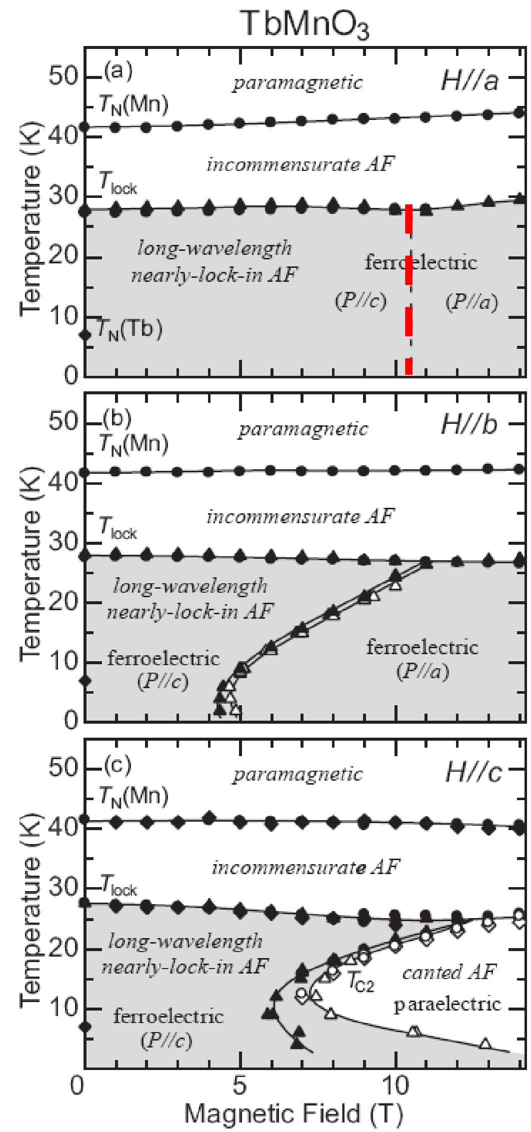
Dielectric constant anomaly at the transition to spiral state



T. Kimura et al , Nature ***426****, 55 (2003)*

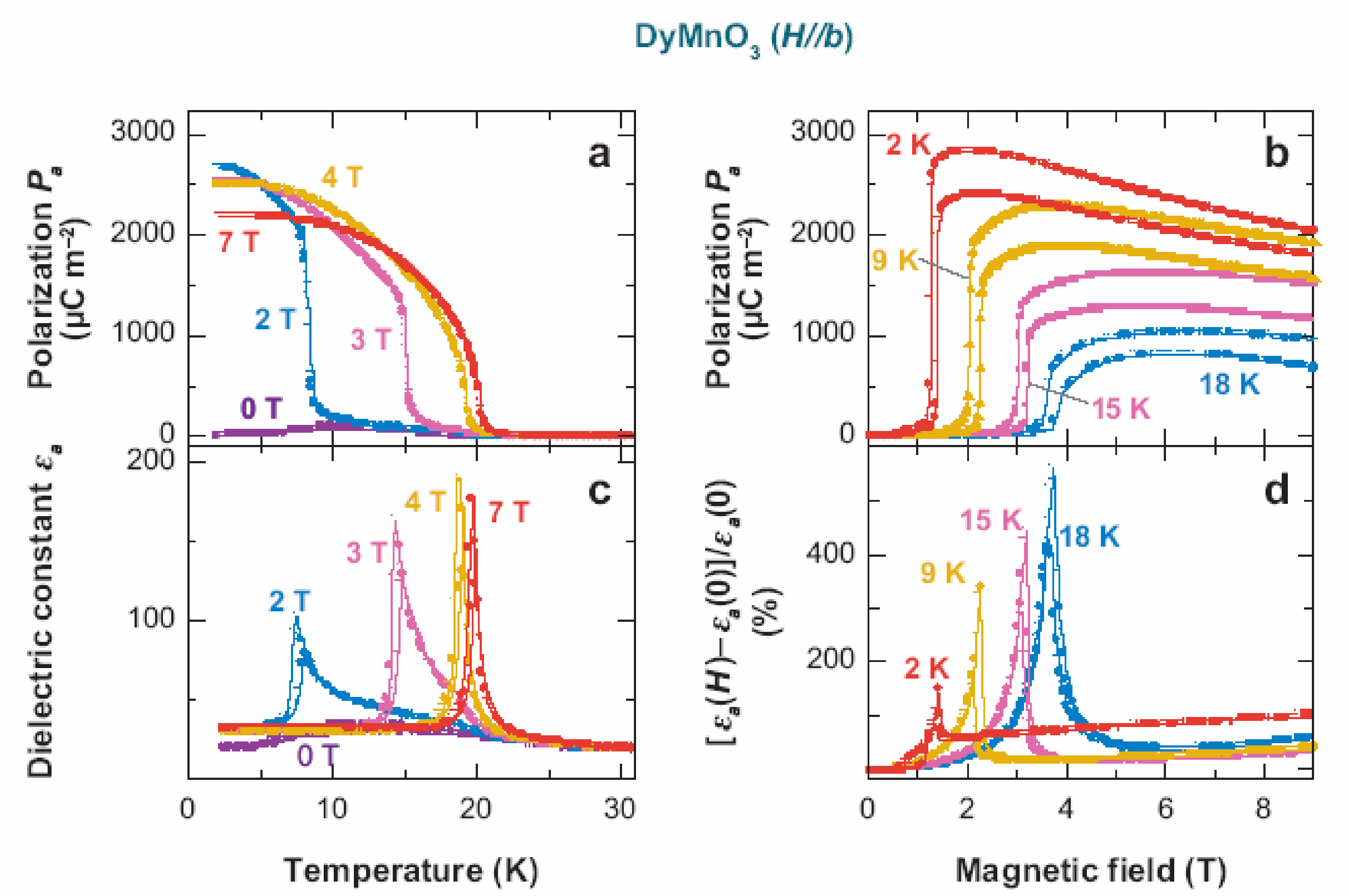
Polarization switching by magnetic field





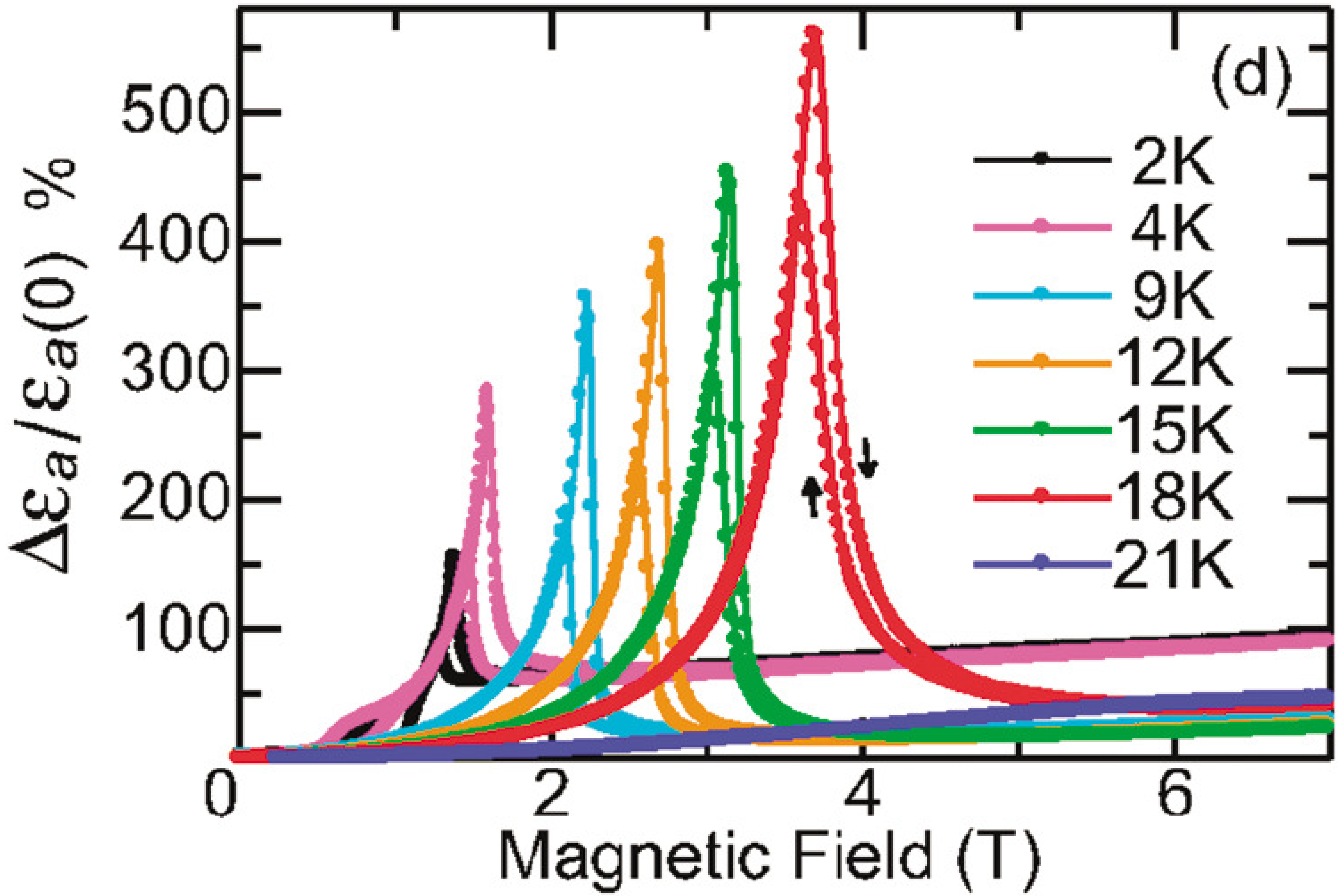
T. Kimura Annu. Rev. Mater. Res. ***37*** *387(2007)*

Magnetic control of dielectric properties



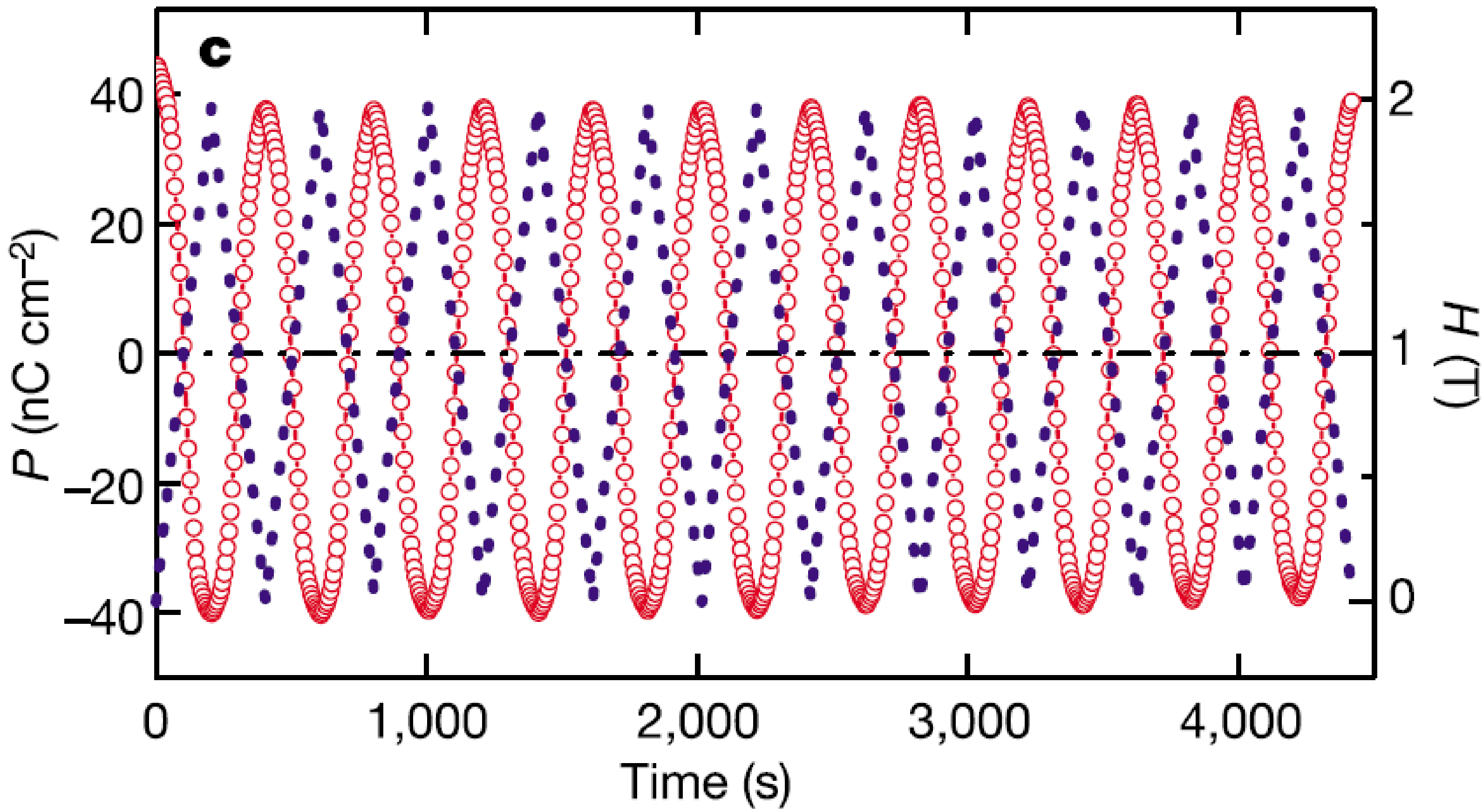
T. Kimura Annu. Rev. Mater. Res. ***37*** *387(2007)*

Giant magnetocapacitance effect in $DyMnO_3$



*T. Goto et al PRL **92**, 257201 (2004)*

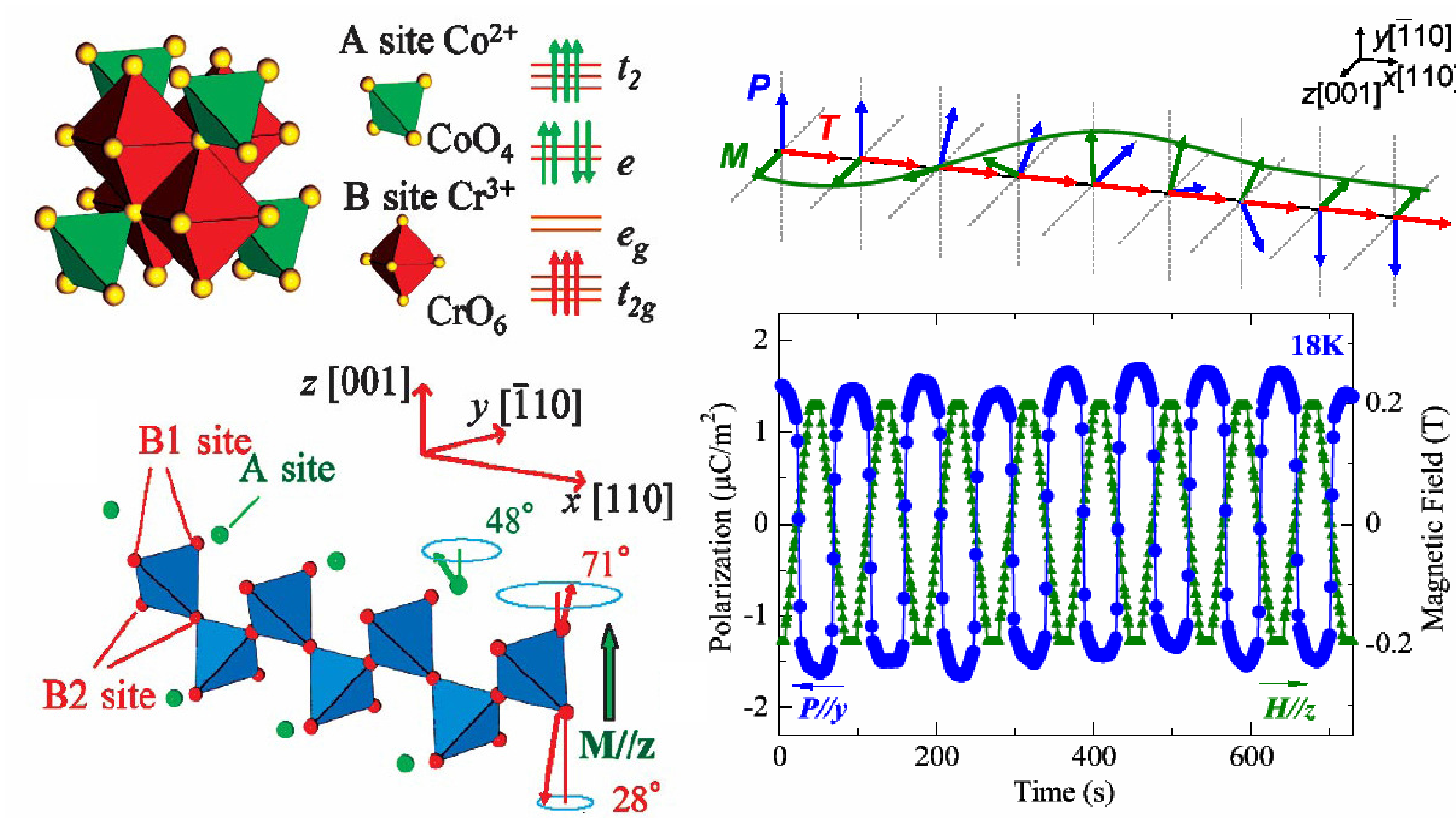
Electric polarization reversals in $TbMn_2O_5$



*N. Hur et al Nature **429**, 392 (2004)*

$CoCr_2O_4$

$\mathbf{P} \times \mathbf{M}$ is conserved



*Y. Yamasaki et al, PRL **96,** 207204 (2006)*

Outline

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Linear magnetoelectric effect

Cr_2O_3 *I.E. Dzyaloshinskii (1959), D.N. Astrov (1960)*

$$\Phi_{\mathrm{me}} = -\alpha_{ij} E_i H_j$$

$$P_i = -\frac{\partial \Phi}{\partial E_i} = \alpha_{ij} H_j$$

$$M_i = -\frac{\partial \Phi}{\partial H_i} = \alpha_{ji} E_j$$

Time-reversal symmetry T ($t \rightarrow -t$)
and inversion I ($\mathbf{r} \rightarrow -\mathbf{r}$) are broken

Symmetric under time reversal
combined with inversion, IT: ($t \rightarrow -t$, $\mathbf{r} \rightarrow -\mathbf{r}$),
or mirror, e.g. ($t \rightarrow -t$, $x \rightarrow -x$)

Cr_2O_3

magnetic point group

$\bar{3}'m'$

Symmetries of low-T phase: $1,\ 3(2_\perp),\ \pm 3_z,\ \bar{1}',\ 3(m'_\perp),\ \pm \bar{3}'_z$

	I'	2_x	3_z
$\begin{pmatrix} E_x \\ E_y \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$R_{2\pi/3}$
E_z	-1	-1	$+1$
$\begin{pmatrix} H_x \\ H_y \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$R_{2\pi/3}$
H_z	-1	-1	$+1$

Inversion combined with time reversal

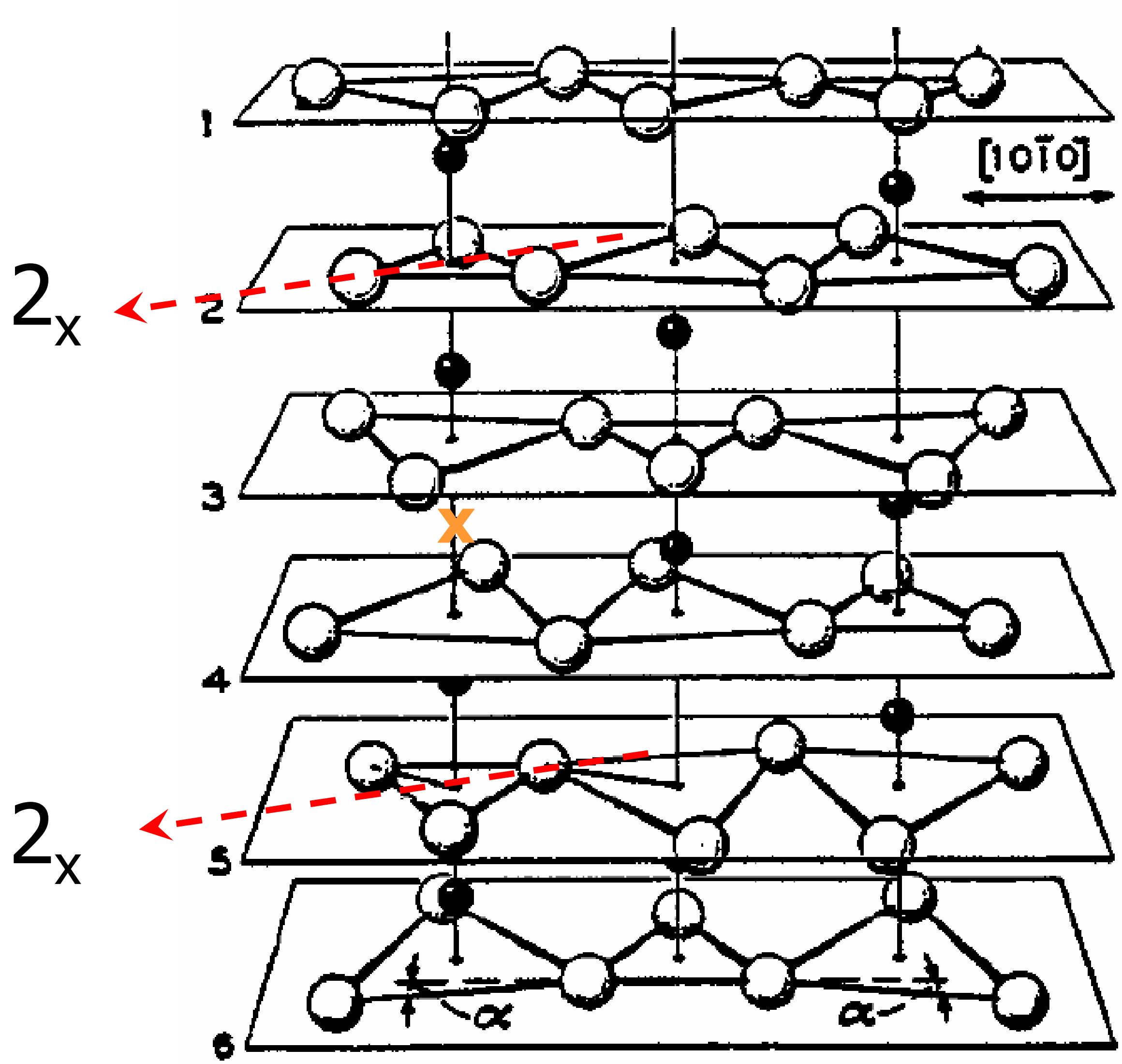
$$I' = IT$$

120°-rotation

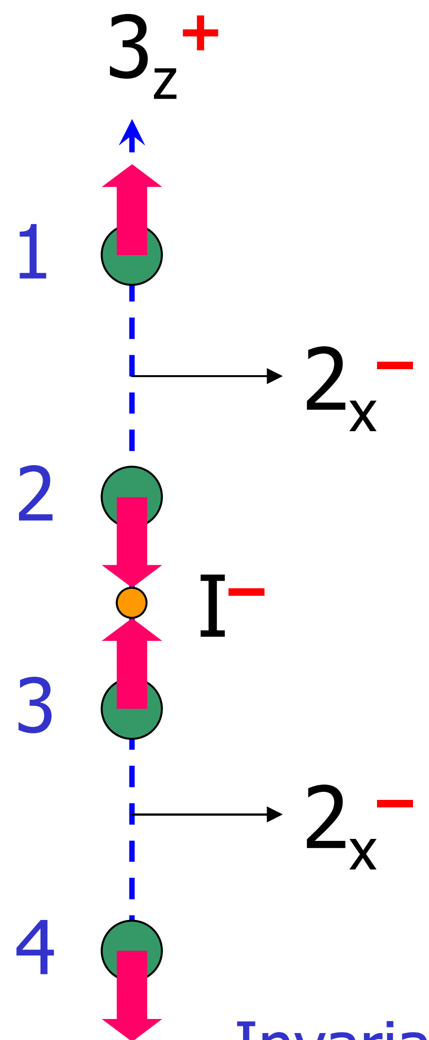
$$R_{2\pi/3} = \frac{1}{2}\begin{pmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}$$

Invariants: $F_{\mathrm{me}} = -\alpha_{\parallel} E_z H_z - \alpha_{\perp}\left(E_x H_x + E_y H_y\right)$

Crystal structure of Cr_2O_3



Cr_2O_3



AFM order parameter $T_N = 306K$

$$\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2 + \mathbf{M}_3 - \mathbf{M}_4 \qquad L_z \neq 0$$

symmetries of paramagnetic phase

	I	2_x	3_z
L_z	−	+	+
E_z	−	−	+
H_z	+	−	+

point group

$$\bar{3}m$$

$$1,\ 3(2_\perp),\ \pm 3_z$$

$$\bar{1},\ 3(m_\perp),\ \pm \bar{3}_z$$

Invariants:

$$\lambda L_z E_z H_z = \alpha_\parallel E_z H_z$$

$$L_z\left(E_x H_x + E_y H_y\right)$$

$$\alpha_\parallel, \alpha_\perp \propto L_z$$

Ferroelectrics

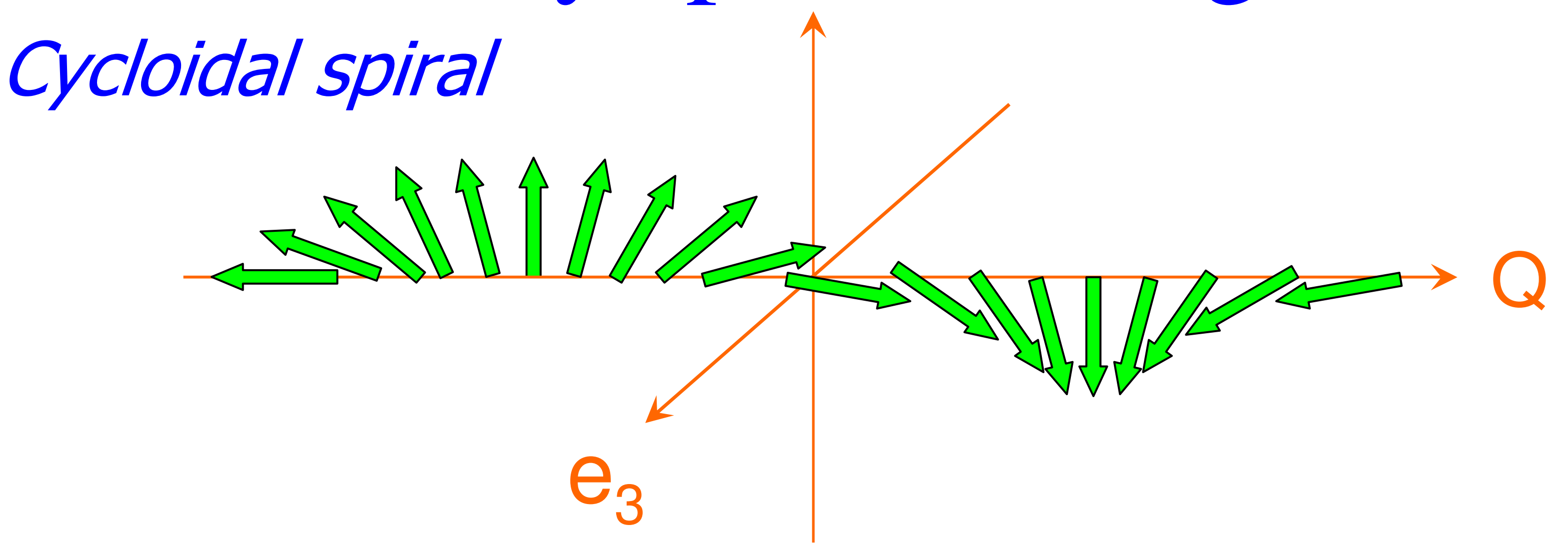
	Mechanism of inversion symmetry breaking	Materials
Proper	covalent bonding between $3d^0$ transition metal (Ti) and oxygen	$BaTiO_3$
	polarizability of $6s^2$ lone pair	$BiMnO_3$, $BiFeO_3$
Improper	structural transition 'Geometric ferroelectrics'	K_2SeO_4, Cs_2CdI_4 h-$RMnO_3$
	charge ordering 'Electronic ferroelectrics'	$LuFe_2O_4$
	magnetic ordering 'Magnetic ferroelectrics'	o-$RMnO_3$, RMn_2O_5, $CoCr_2O_4$, $MnWO_4$

*S.-W. Cheong & M. M. Nature Materials **6**, 13 (2007)*

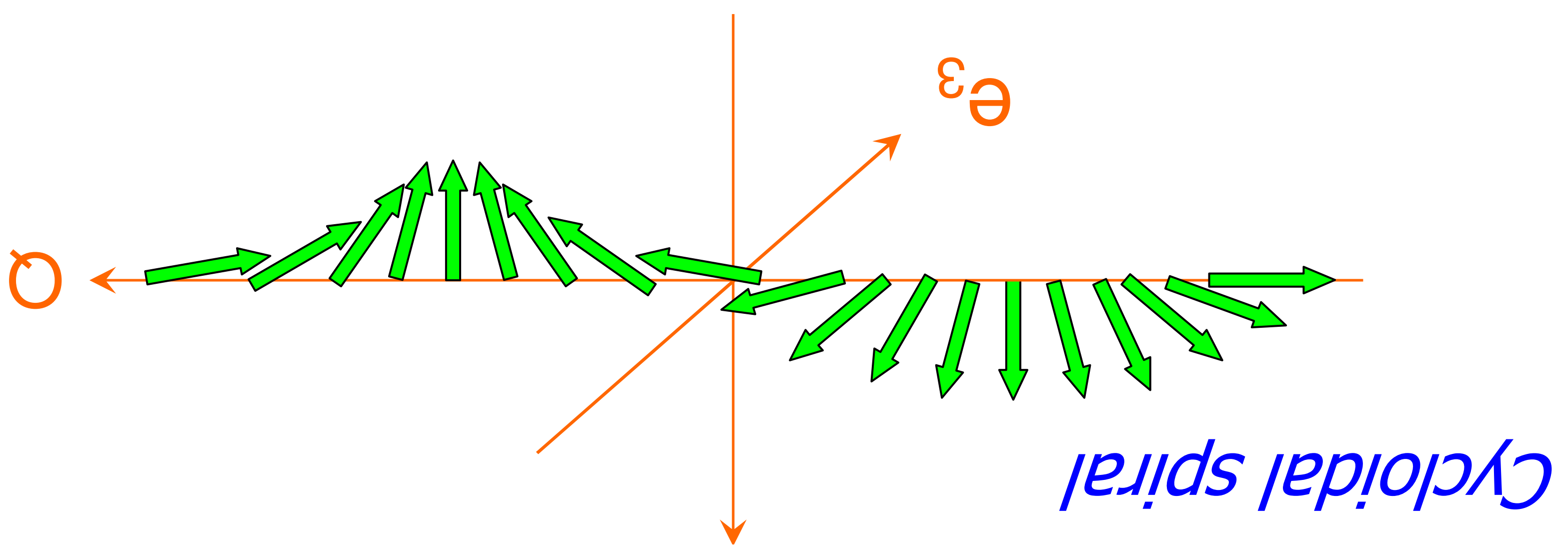
Novel Multiferroics

material	T_{FE} (K)	T_M (K)	P(μC m^{-2})
$TbMnO_3$	28	41	600
$TbMn_2O_5$	38	43	400
$Ni_3V_2O_8$	6.3	9.1	100
$MnWO_4$	8	13.5	60
$CoCr_2O_4$	26	93	2
$CuFeO_2$	11	14	300
$LiCu_2O_2$	23	23	5
CuO	230	230	100

Breaking of inversion symmetry by spin ordering



Inversion I: $(x,y,z) \longrightarrow (-x,-y,-z)$



Induced Polarization

Energy (cubic lattice)

$$F_P = \frac{\mathbf{P}^2}{2\chi_e} - \lambda \mathbf{P} \cdot \left[(\mathbf{M} \cdot \nabla)\mathbf{M} - \mathbf{M}(\nabla \cdot \mathbf{M}) \right]$$

Induced electric polarization

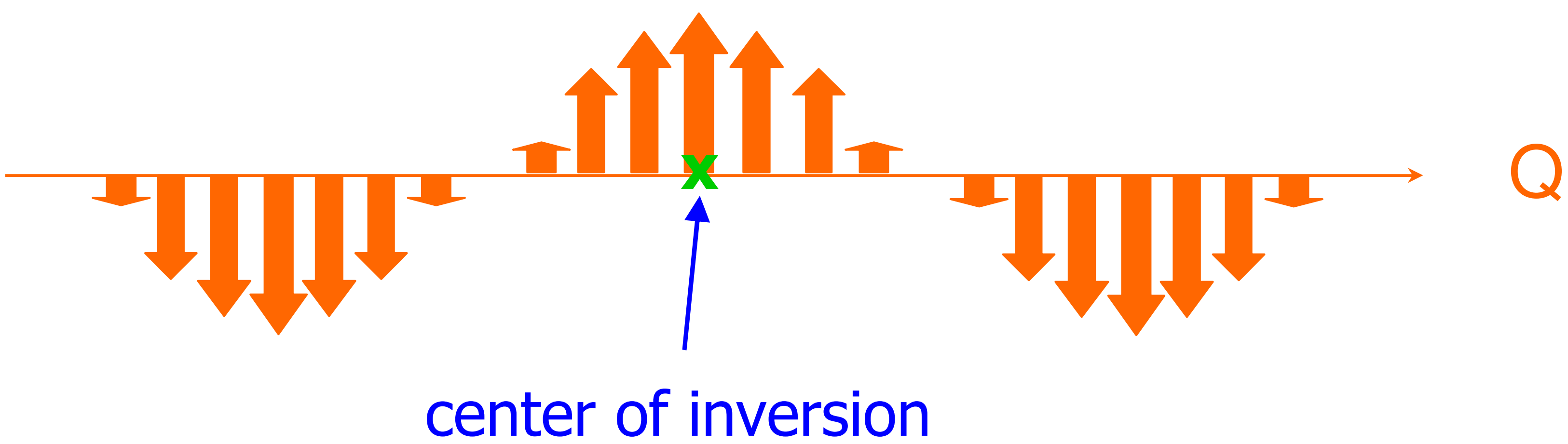
$$\mathbf{P} = \lambda \chi_e \left[(\mathbf{M} \cdot \nabla)\mathbf{M} - \mathbf{M}(\nabla \cdot \mathbf{M}) \right]$$

Bary'akhtar et al, JETP Lett ***37****, 673 (1983); Stefanovskii et al, Sov. J. Low Temp. Phys.* ***12****, 478(1986), M.M. PRL* ***96****, 067601 (2006)*

Sinusoidal SDW

$$\mathbf{M} = \mathbf{A} \sin Qx$$

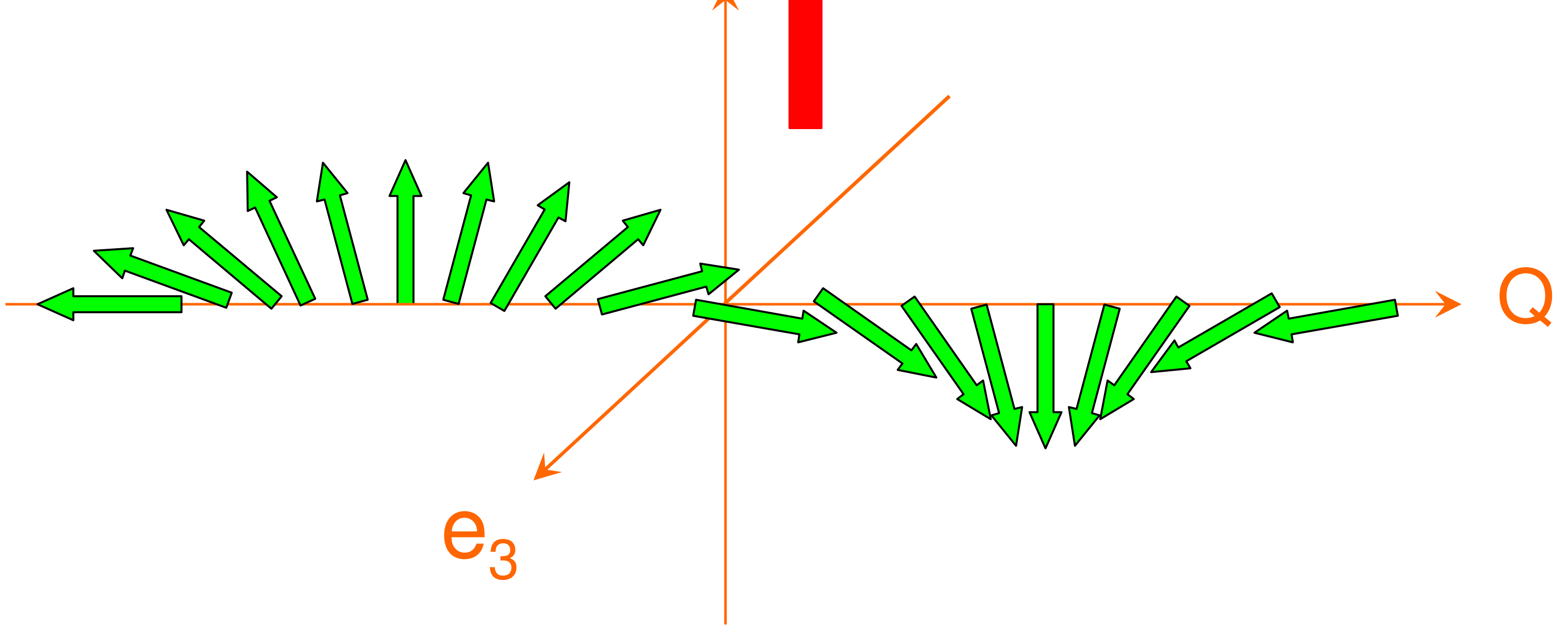
$$\overline{\mathbf{P}} = 0$$



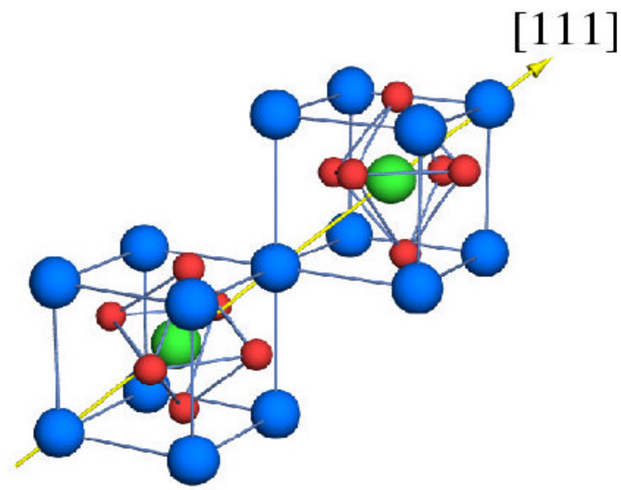
Spiral SDW

$$\mathbf{M} = M_0\left(\mathbf{e}_1 \cos \mathbf{Qx} + \mathbf{e}_2 \sin \mathbf{Qx}\right)$$

$$\overline{\mathbf{P}} \propto \left[\mathbf{e}_3 \times \mathbf{Q}\right]$$



$BiFeO_3$



Ferroelectric $T_{FE} = 1100$ K

Antiferromagnetic $T_N = 640$ K

Free energy

$$F = \varphi(L) + (\partial L)^2 - \lambda PL\partial L$$

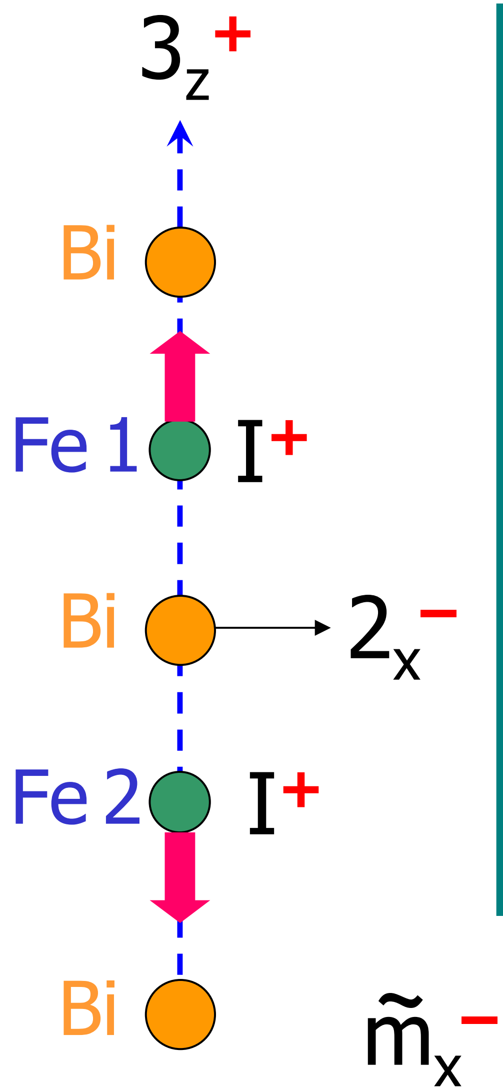
A.M. Kadomtseva et al. JETP Lett. ***79****, 571 (2004)*

Periodic modulation of AFM ordering: $Q \propto \lambda P$

Low-pitch spiral $\lambda = 620$ Å

$BiFeO_3$

$$\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2$$



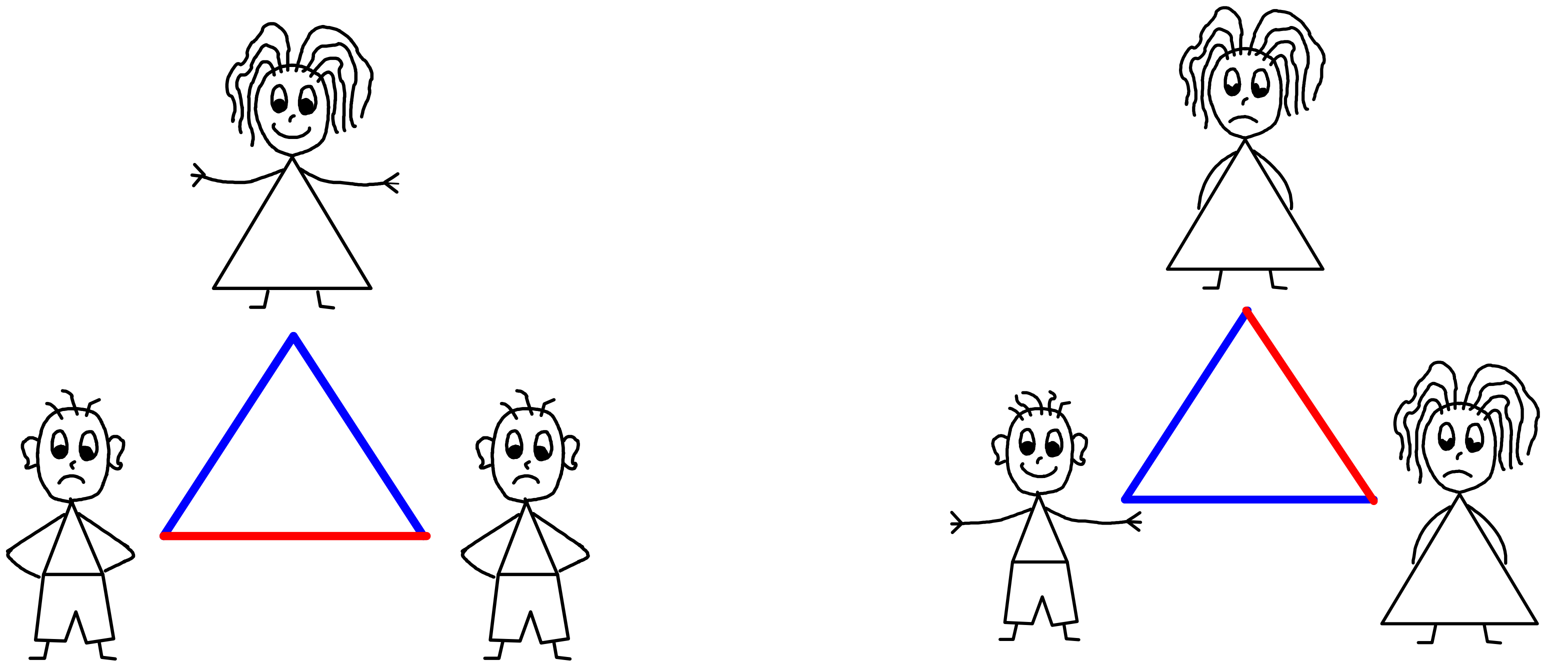
$$(x, y, z) \rightarrow (-x, y, z + 1/2)$$

	I^+	2_x^-	$\tilde{m}_x^-$	3_z
$\begin{pmatrix} L_x \\ L_y \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$R_{2\pi/3}$
L_z	-1	$+1$	$+1$	$+1$
$\begin{pmatrix} \partial_x \\ \partial_y \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$R_{2\pi/3}$
P_z	-1	-1	$+1$	$+1$

invariant

$$P_z \left(L_x \overleftrightarrow{\partial}_x L_z + L_y \overleftrightarrow{\partial}_y L_z \right)$$

Geometrical Frustration

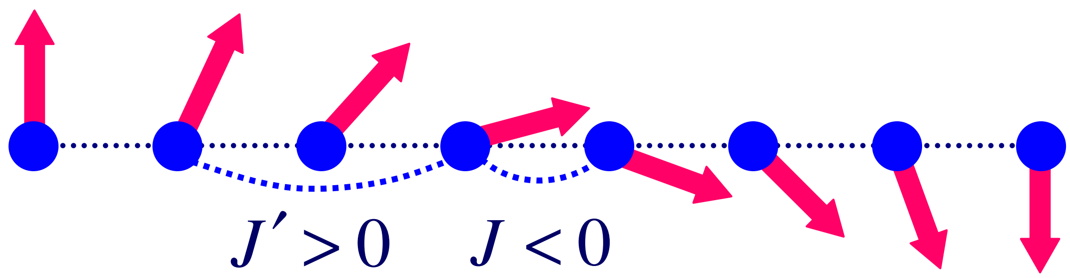


Competing interactions

Frustrated Heisenberg chain

$$E = \sum_n \left[J\,\mathbf{S}_n \cdot \mathbf{S}_{n+1} + J'\,\mathbf{S}_n \cdot \mathbf{S}_{n+2} \right]$$

$$J' > \frac{|J|}{4}$$



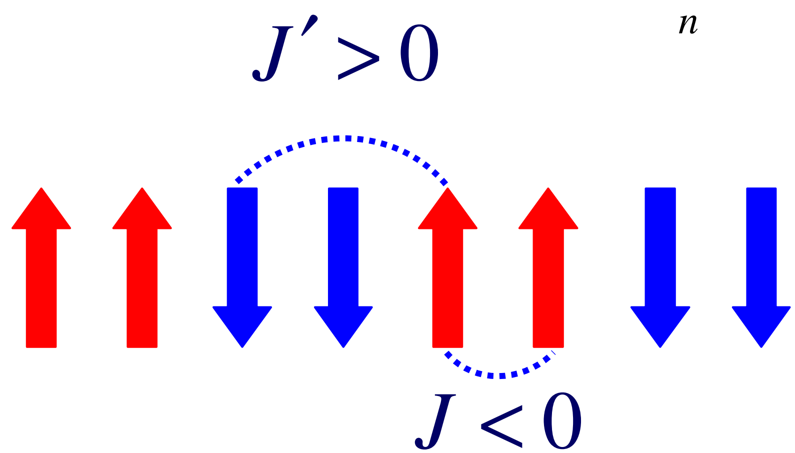
$$\cos Q = \frac{|J|}{4J'}$$

Frustrated Ising chain

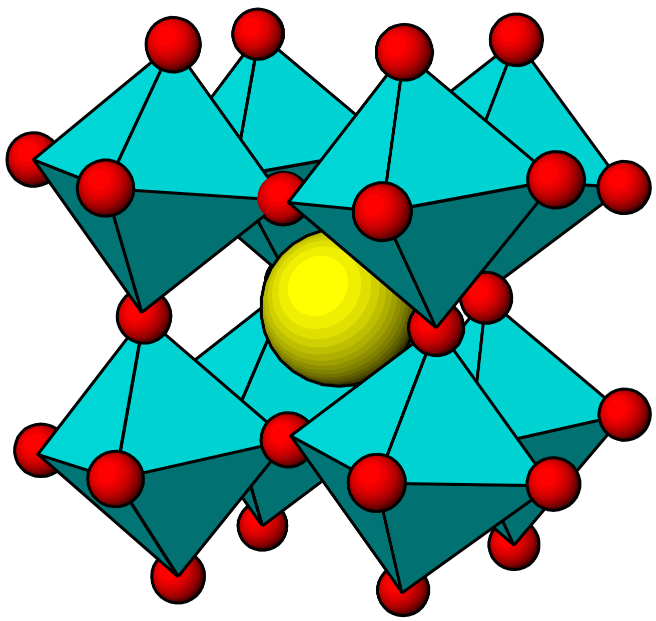
$$E = \sum_n \left[J\,\sigma_n \sigma_{n+1} + J'\,\sigma_n \sigma_{n+2} \right]$$

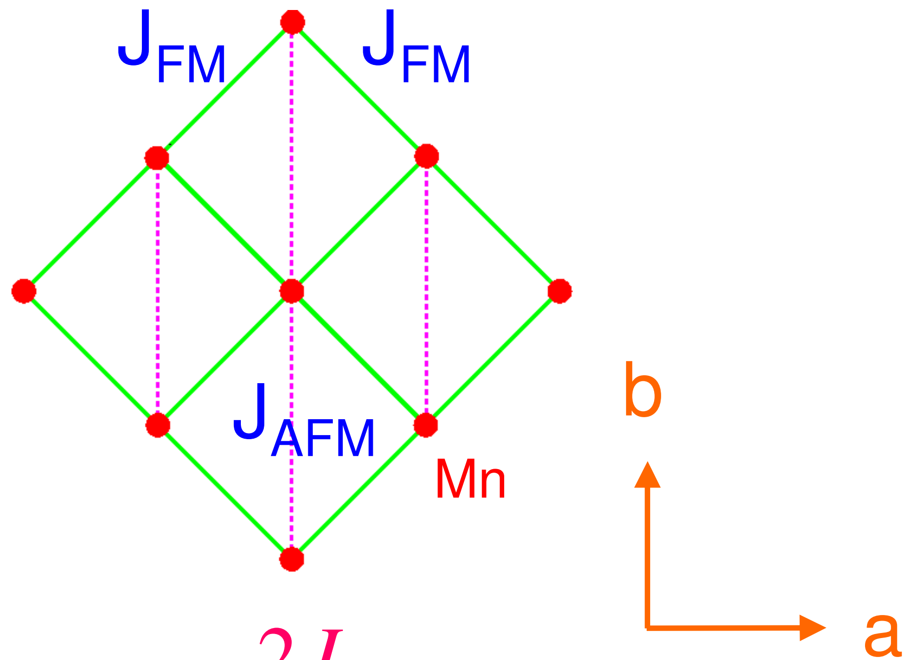
$$\sigma_n = \pm 1$$

$$J' > \frac{|J|}{2}$$



Magnetic frustration in $RMnO_3$





$$\kappa = \frac{2J_{AFM}}{J_{FM}}$$

$\kappa < 1$ **Ferromagnetic**

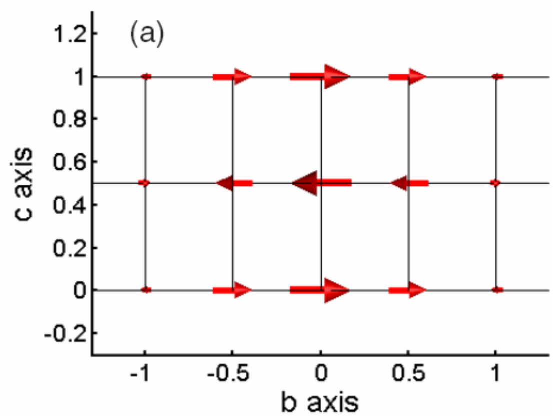
$\kappa > 1$ **Incommensurate SDW**

$$\cos\frac{Q_b}{2} = \frac{1}{\kappa}$$

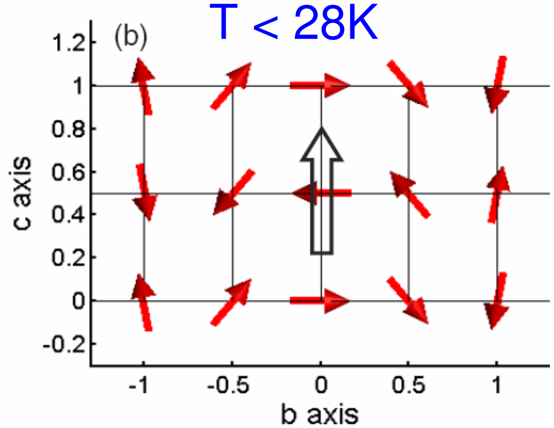
Why T_{FE} is lower than T_M?

$TbMnO_3$

28K < T < 41K



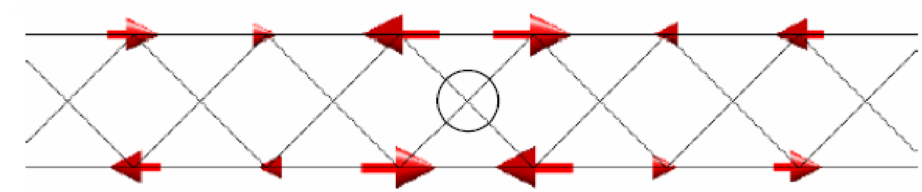
T < 28K

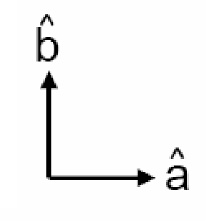


*M. Kenzelmann et al PRL **95**, 087206 (2005)*

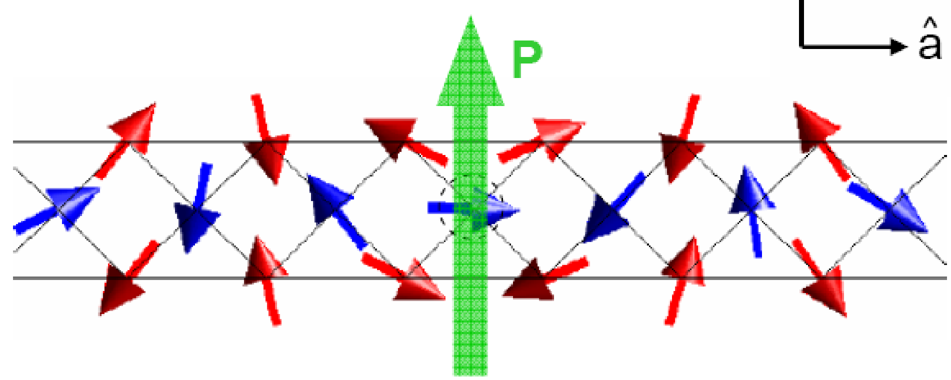
$Ni_3V_2O_8$

6.3K < T < 9.1K





3.9K < T < 6.3K



*G. Lawes et al PRL **95**, 087205 (2005)*

Sinusoidal-helicoidal transition

Ginzburg-Landau expansion

$$\Phi_m = a_x (M^x)^2 + a_y (M^y)^2 + a_z (M^z)^2 + \frac{b}{2} M^4 + c\mathbf{M}\left(\frac{d^2}{dx^2} + Q^2\right)^2 \mathbf{M}$$

Anisotropy:

$$a_x < a_y = a_x + \Delta < a_z$$

1st transition: Sinusoidal SDW $\mathbf{M} = M^x \hat{\mathbf{x}} \cos Qx$

$$a_x = \alpha(T - T_{SDW}) = 0$$

P = 0

2nd transition: Helicoidal SDW $\mathbf{M} = M^x \hat{\mathbf{x}} \cos Qx + M^y \hat{\mathbf{y}} \sin Qx$

$$a_y = \frac{a_x}{3}$$

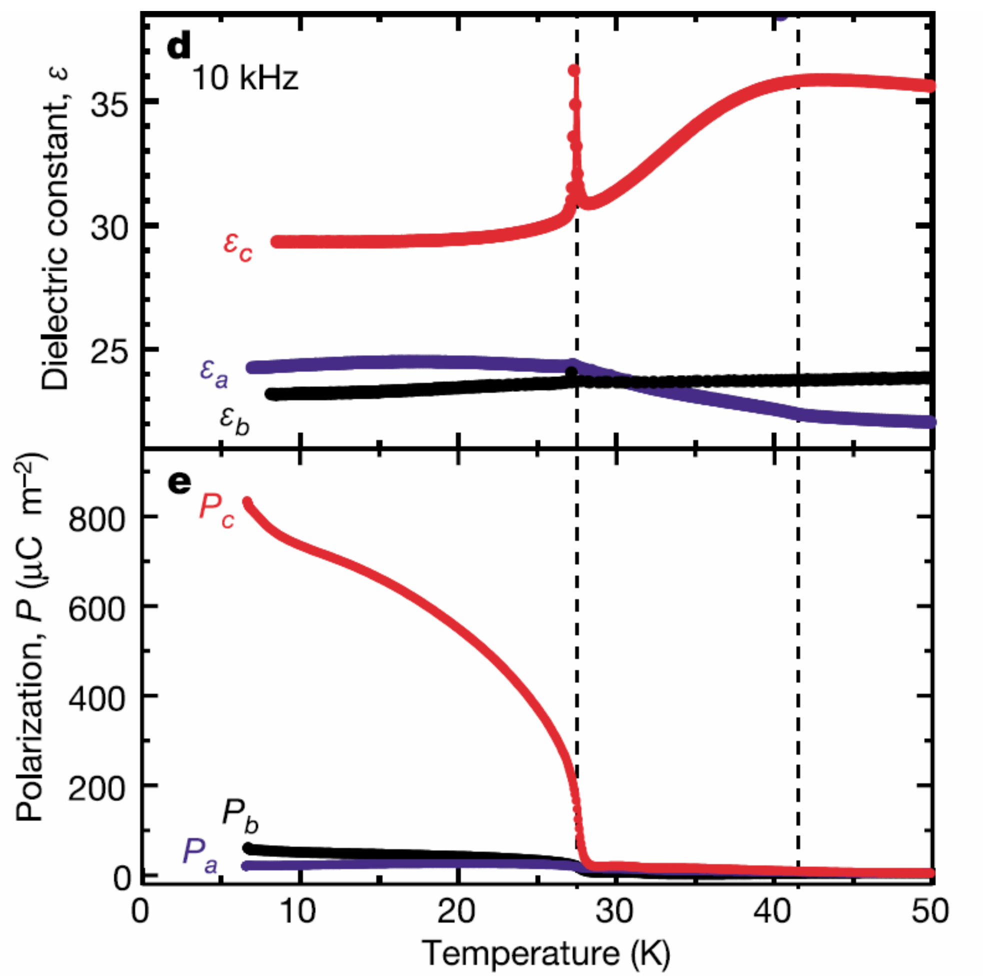
$$T_{SP} = T_{SDW} - \frac{3}{2}\frac{\Delta}{\alpha}$$

P || y

Dielectric constant anomaly at the transition to spiral state

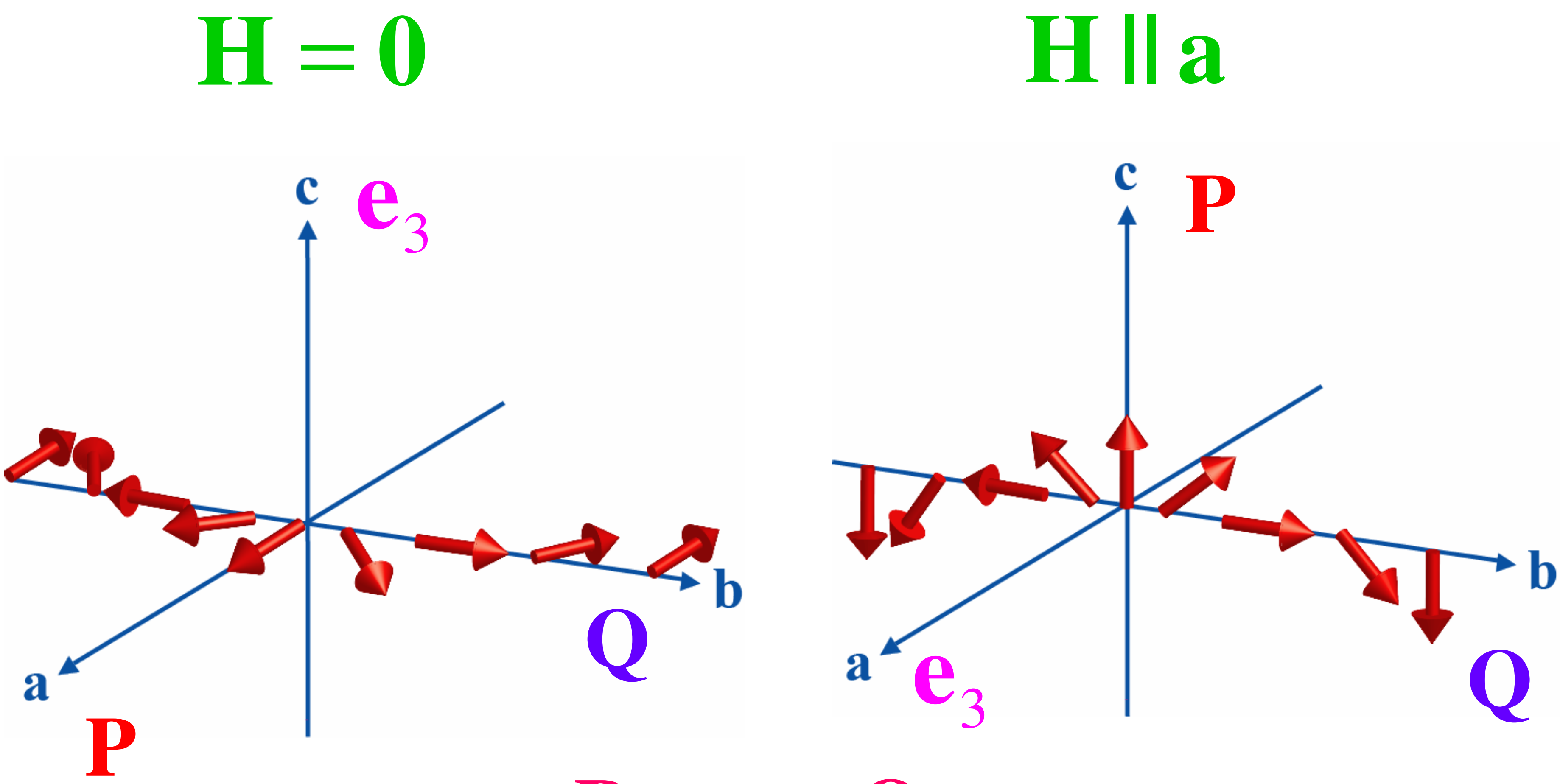
$$\varepsilon_{yy} = \begin{cases} \dfrac{A}{T - T_{SP}}, & T > T_{SP} \\ \dfrac{1}{2}\dfrac{A}{T_{SP} - T}, & T < T_{SP} \end{cases}$$

$$P^y \propto M^x M^y \propto \sqrt{T_{SP} - T}$$



T. Kimura et al , Nature ***426****, 55 (2003)*

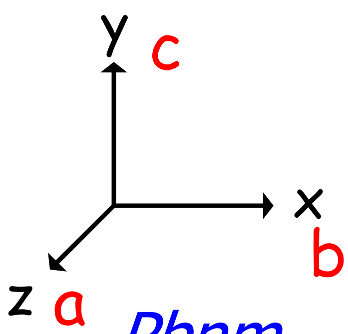
Polarization Flop in $Eu_{1-x}Y_xMnO_3$



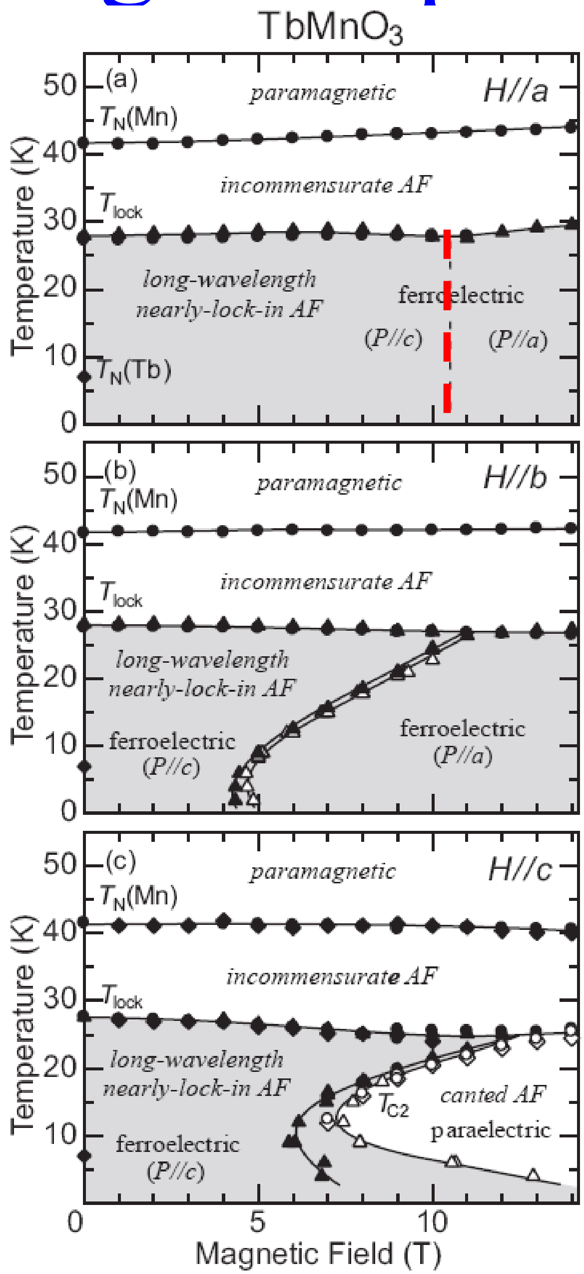
$$P \propto e_3 \times Q$$

Spin flops **Polarization flops**

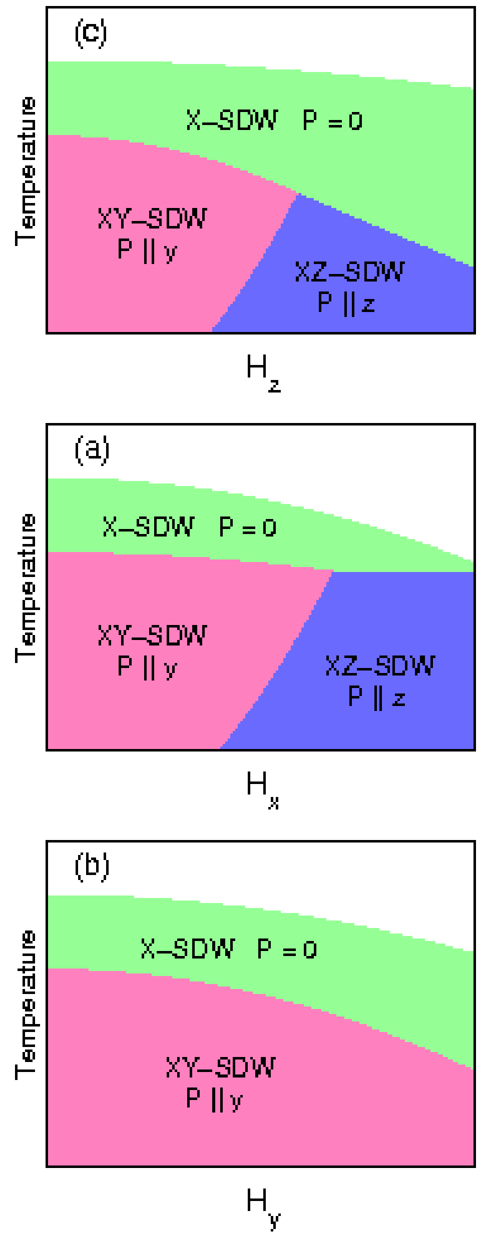
Magnetic phase diagrams



Pbnm



*T. Kimura et al PRB **71**,224425 (2005)*



*M.M. PRL **96**, 067601 (2006)*

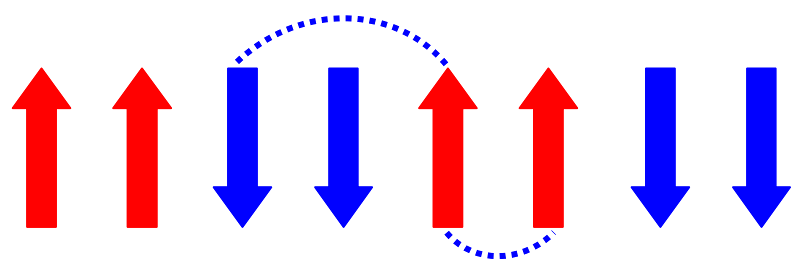
Non-spiral multiferroics

Frustrated Ising chain (ANNNI model)

$$E = \sum_n \left[J\,\sigma_n \sigma_{n+1} + J'\,\sigma_n \sigma_{n+2} \right] \qquad \sigma_n = \pm 1$$

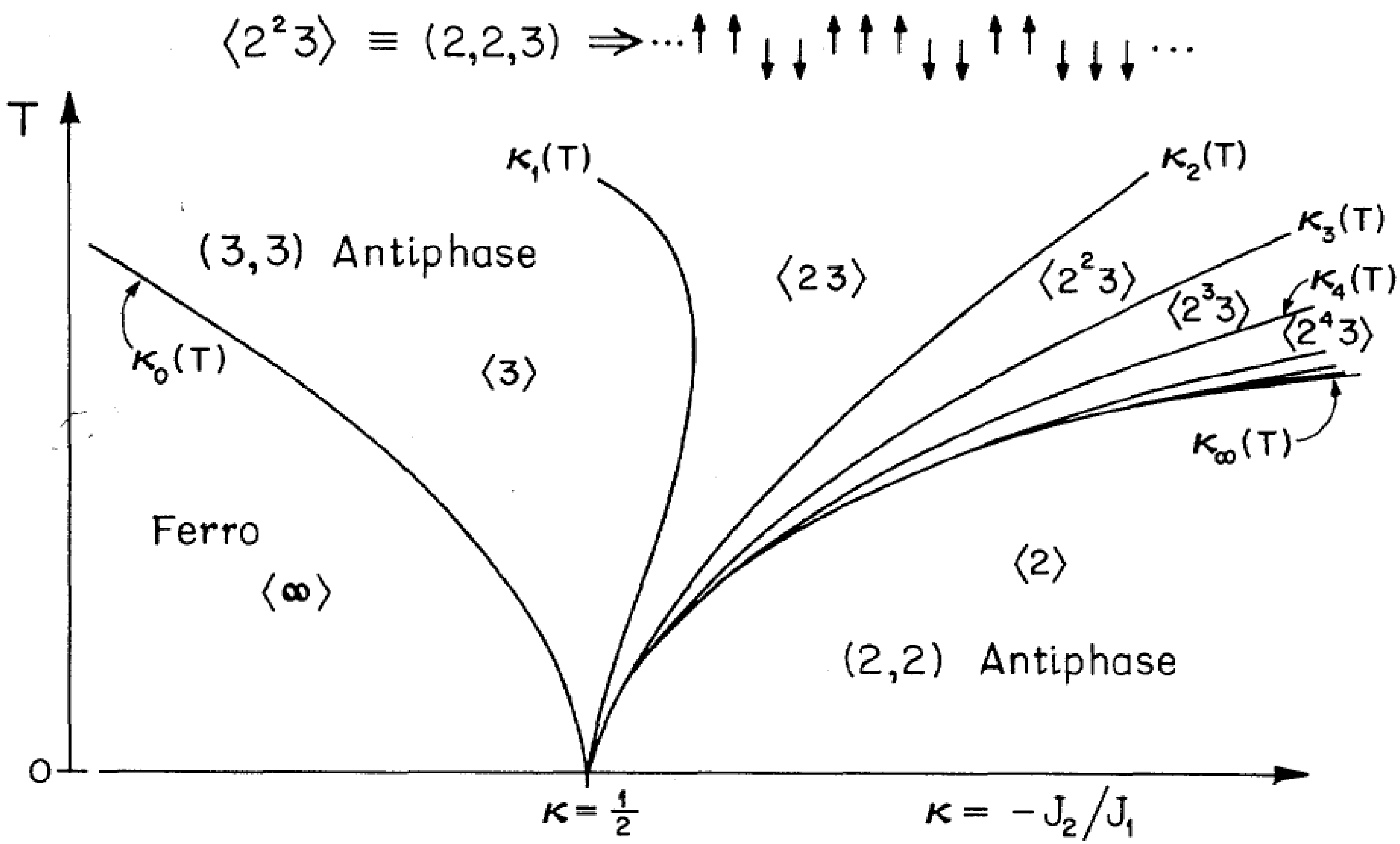
$J' > 0$

$J' > \frac{|J|}{2}$



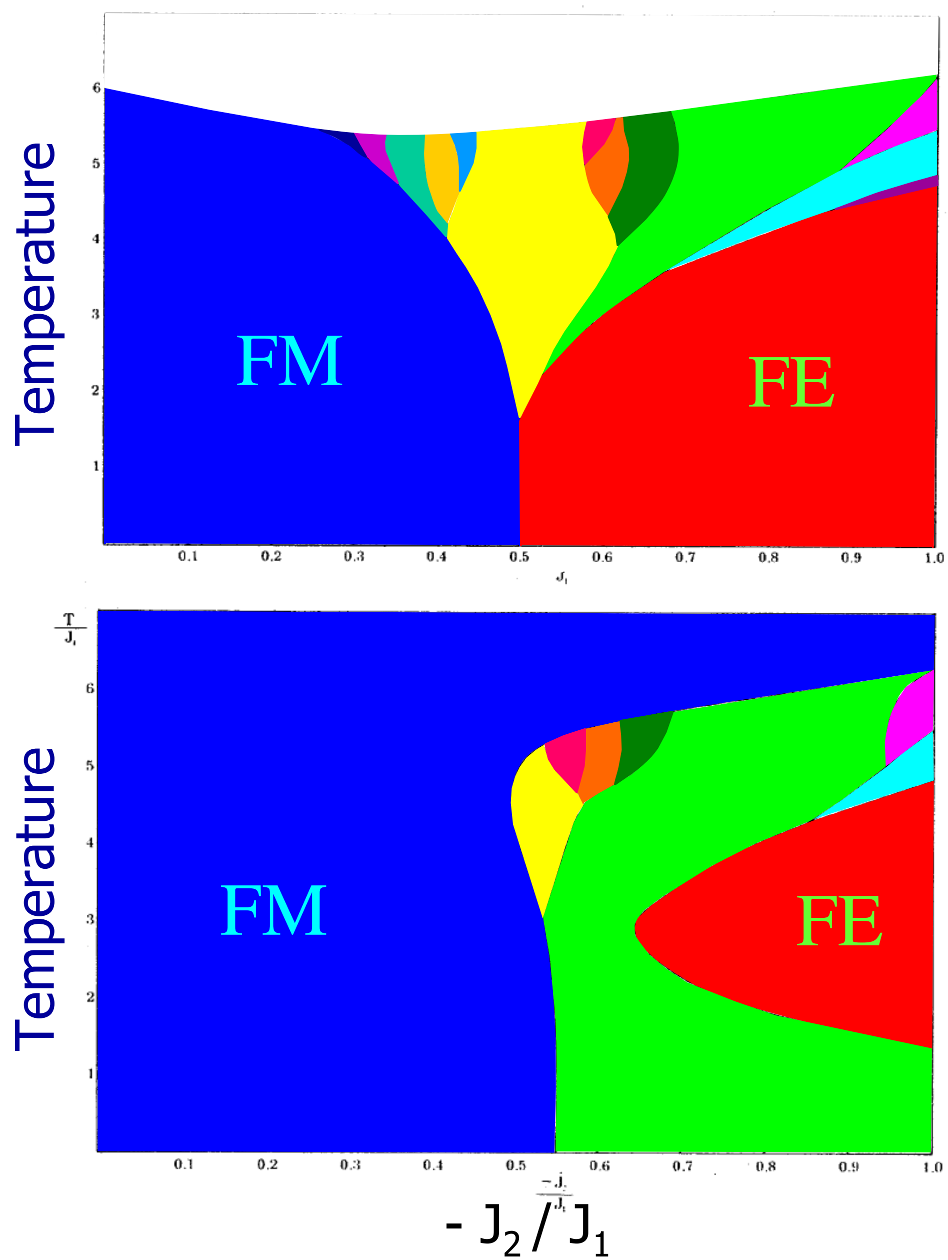
$J < 0$

Devil's flower



M.E. Fisher & W. Selke (1980)

Effect of magnetic field

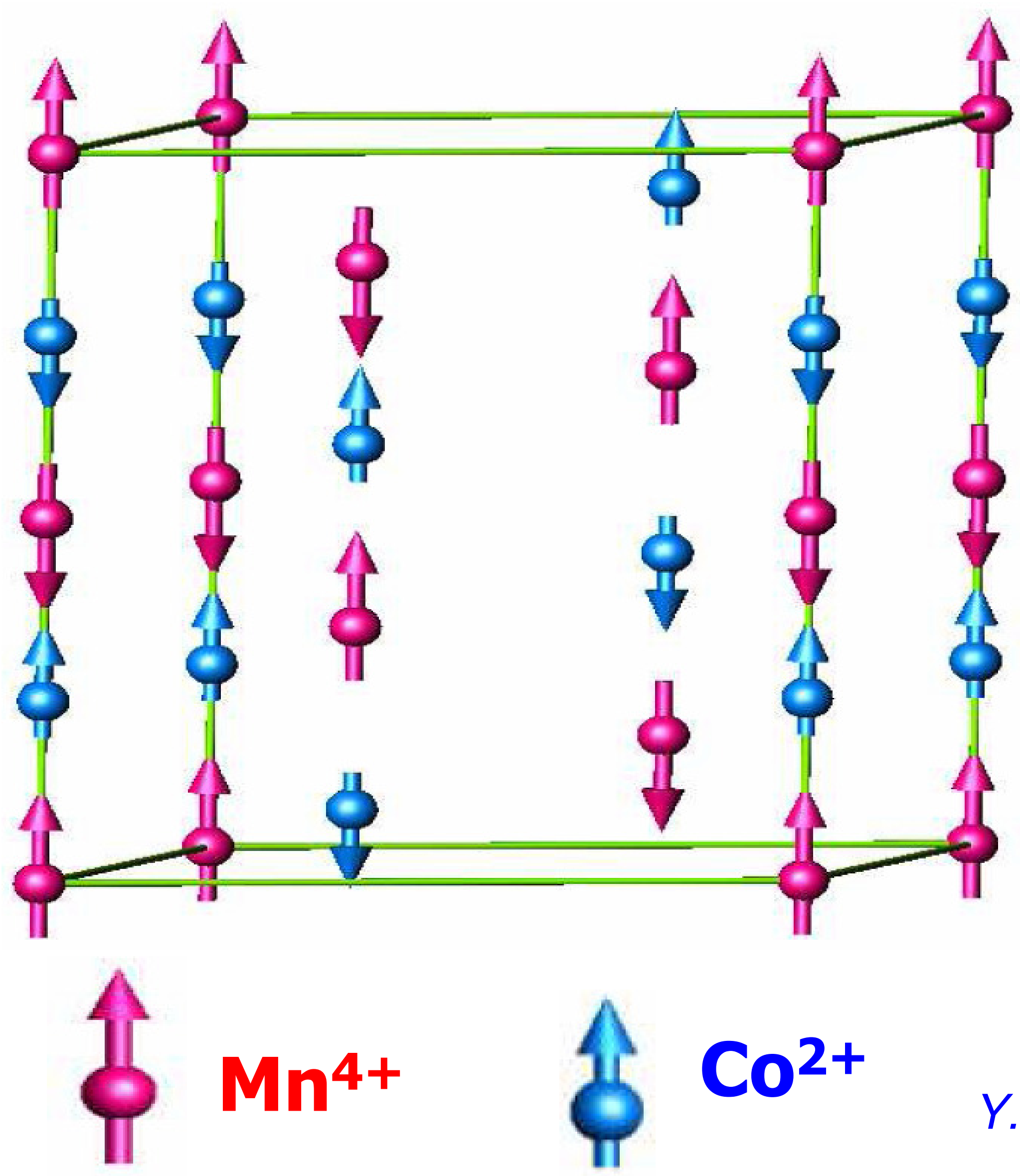


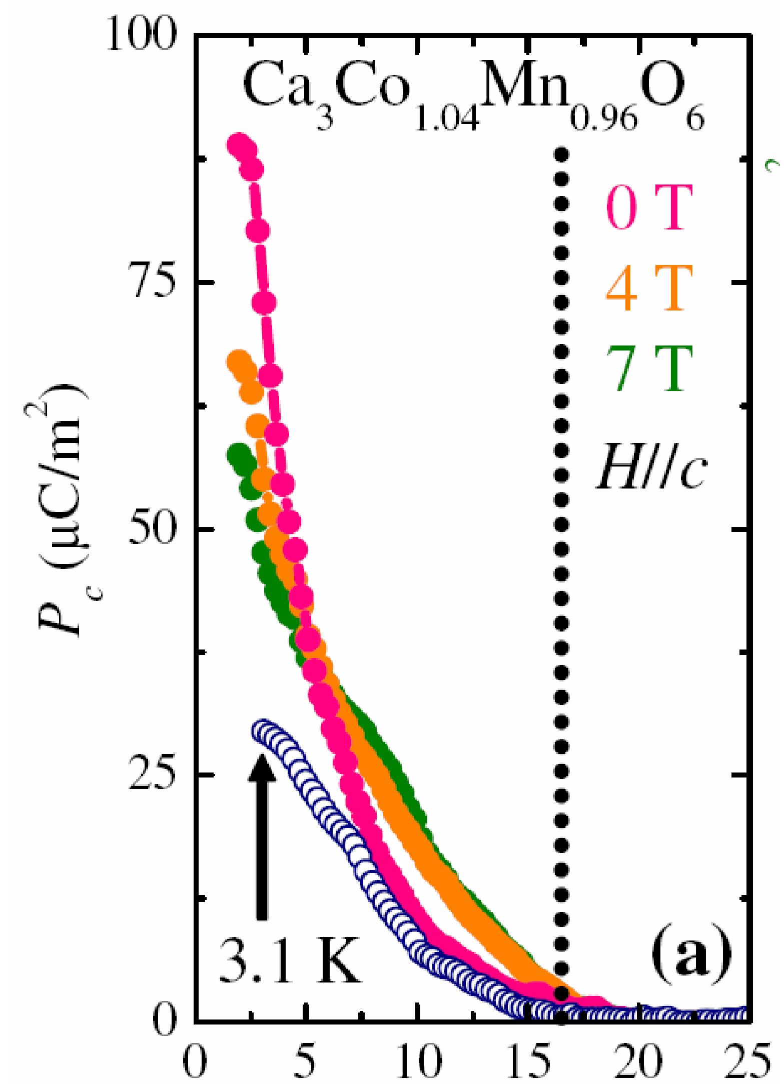
H = 0

H = 0.1 J_1

J. Randa (1985)

$Ca_3Co_{2-x}Mn_xO_6$





*Y.J. Choi et al PRL **100** 047601 (2008)*

Ferroelectricity induced by magnetostriction

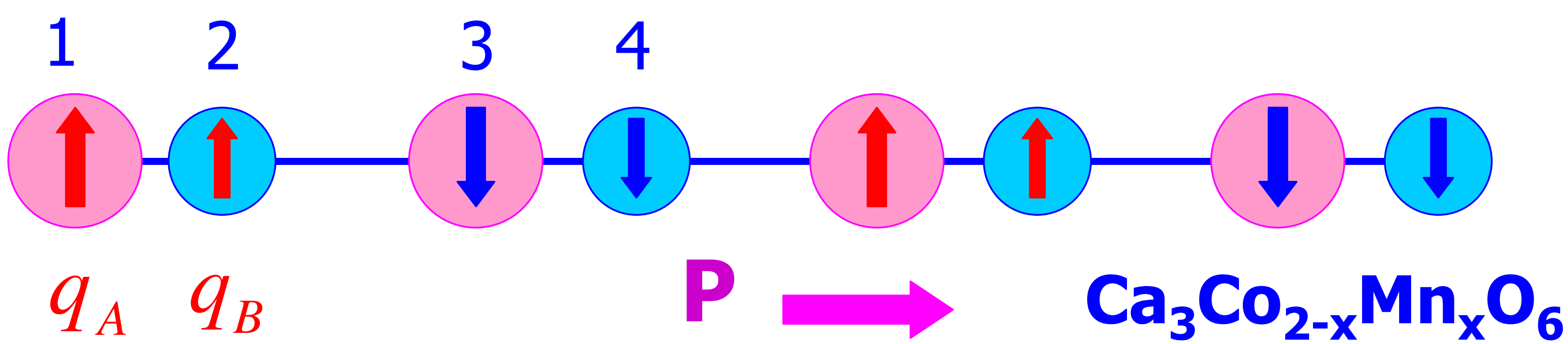
$$\Phi_{\text{int}} = -\lambda P\left(L_1^{\ 2} - L_2^{\ 2}\right)$$

$$L_1 \overset{I}{\leftrightarrow} L_2$$

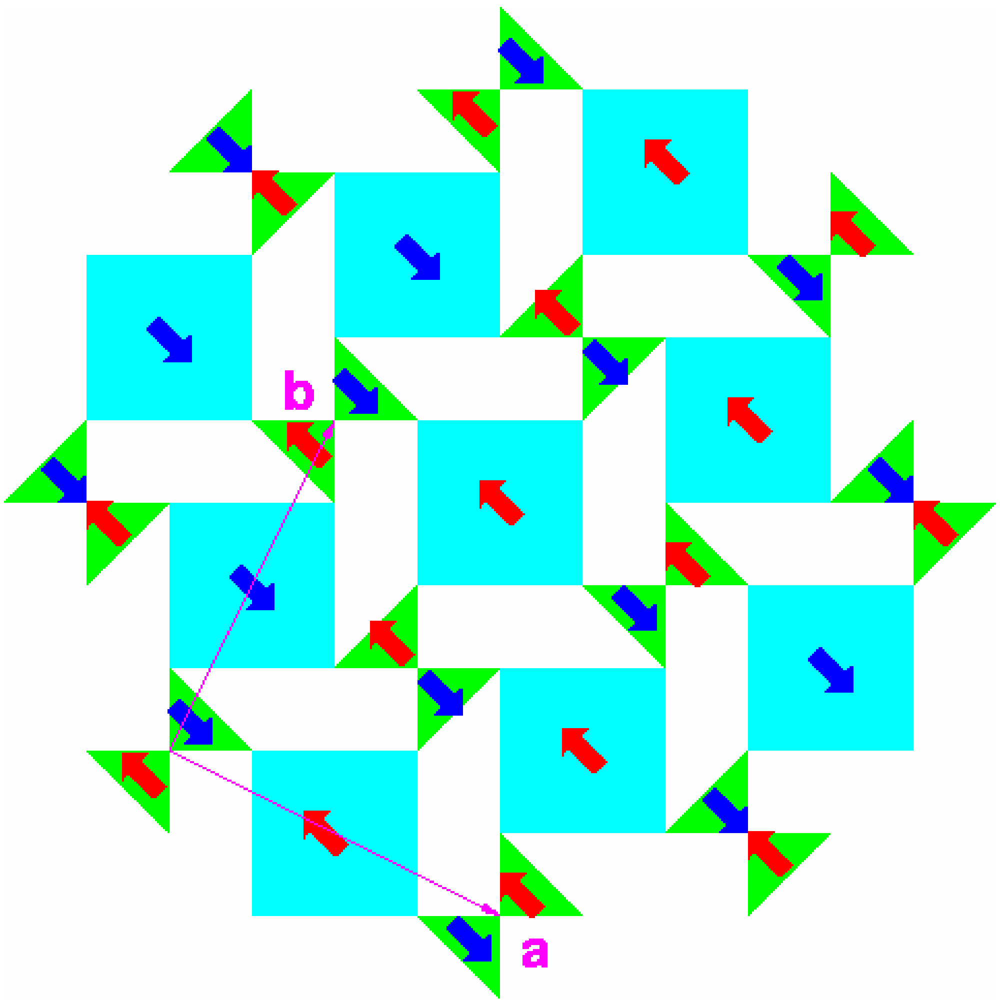
$$\mathbf{L}_1 = \mathbf{S}_1 + \mathbf{S}_2 - \mathbf{S}_3 - \mathbf{S}_4$$

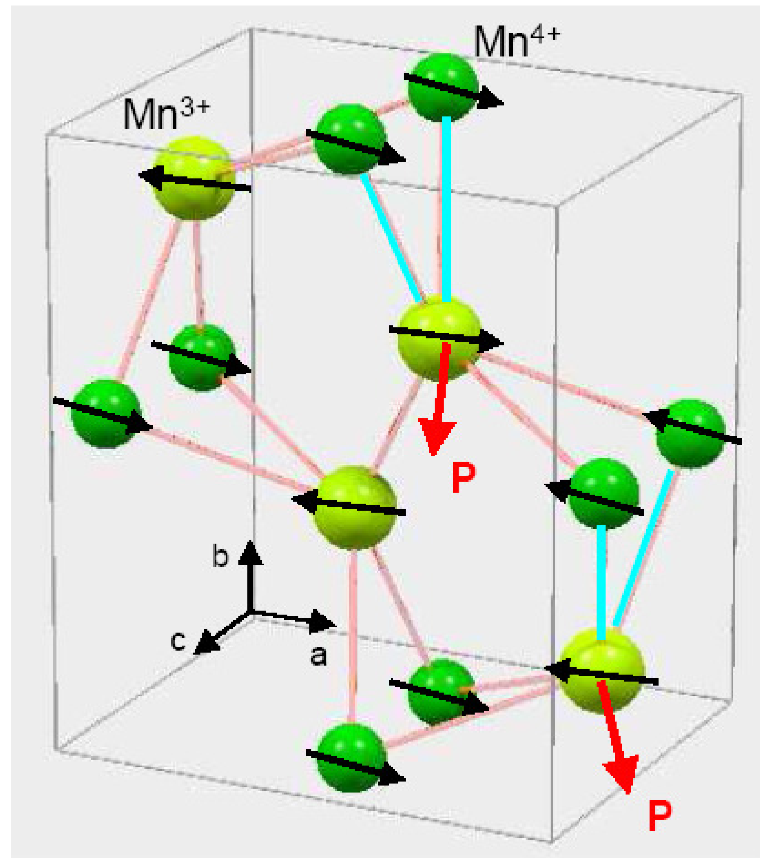
$$\mathbf{L}_2 = \mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3 + \mathbf{S}_4$$

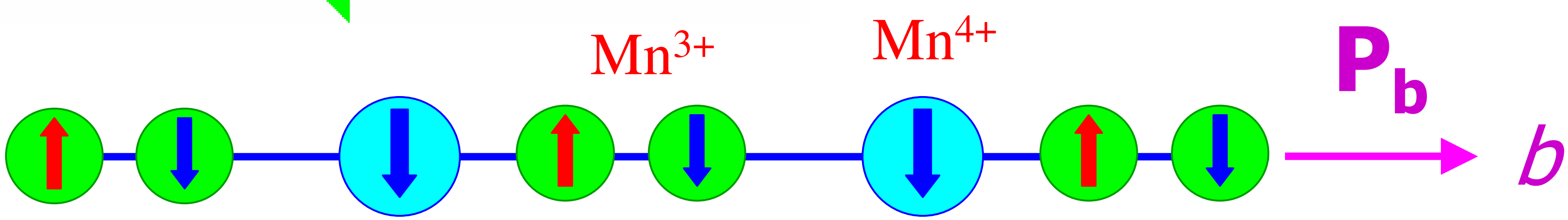
$$P \propto L_1^{\ 2} - L_2^{\ 2}$$



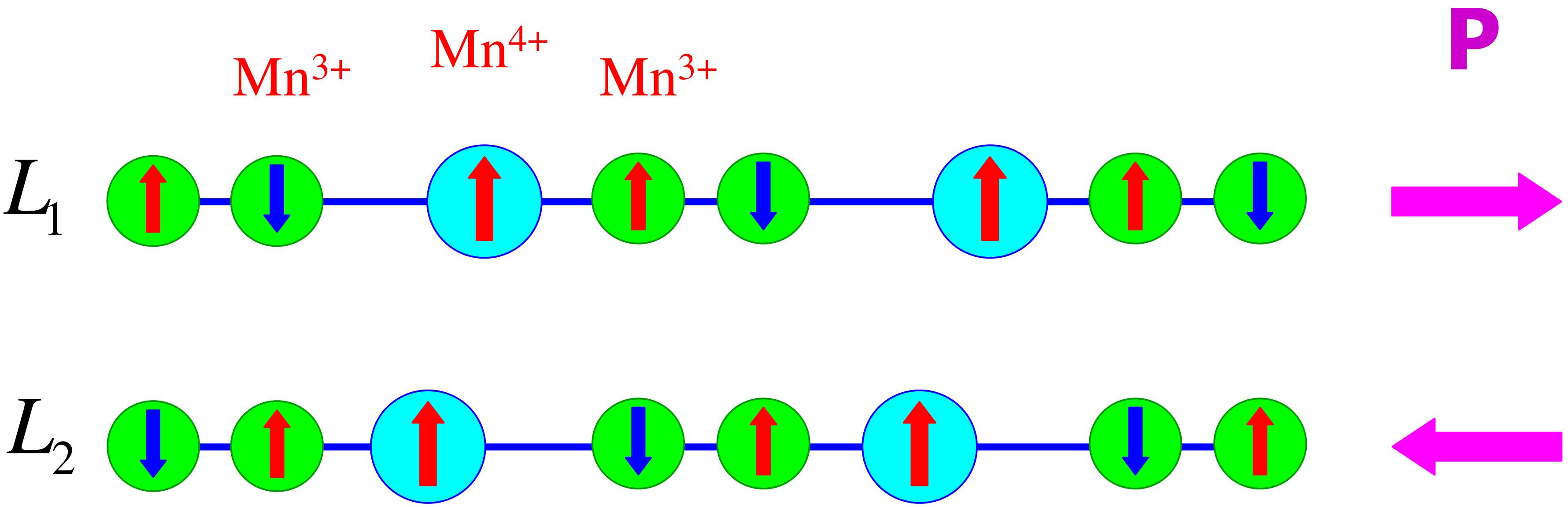
RMn_2O_5







Two-dimensional representation and induced polarization



A. B. Sushkov et al. J. Phys. Cond. Mat. (2008)

Outline

- Linear magnetoelectric effect, multiferroics
- Phenomenological description
- Microscopic mechanisms of magnetoelectric coupling

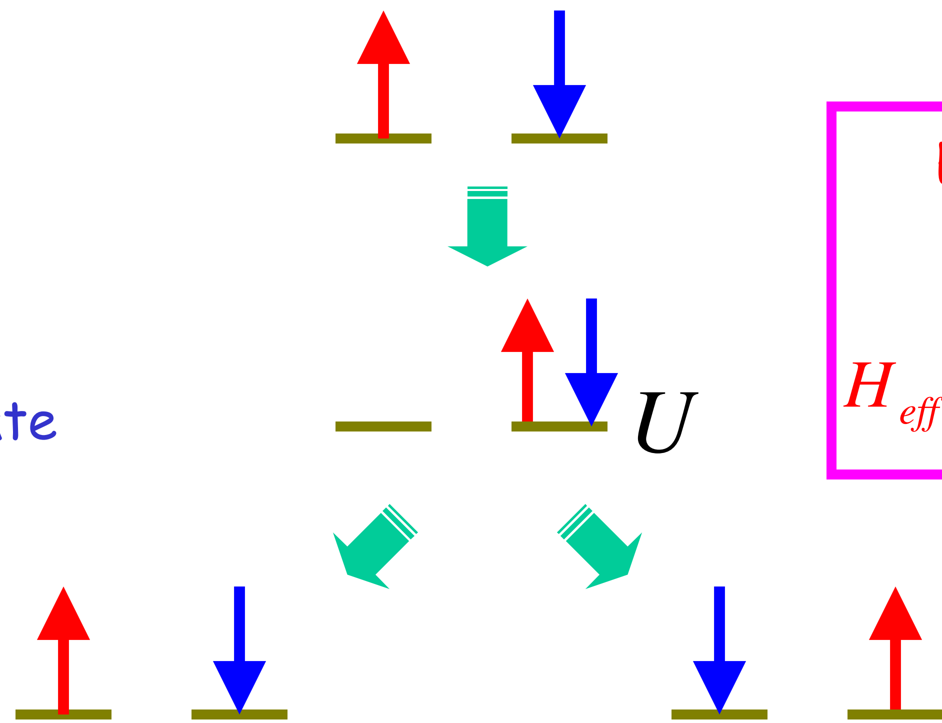
Spin exchange in Hubbard model

$$H = -t \sum_{\langle i,j \rangle \sigma} \left(c_{i\sigma}^{+} c_{j\sigma} + c_{j\sigma}^{+} c_{i\sigma} \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

$|i\rangle$

intermediate state

$|f\rangle$



$$-\frac{t^2}{U} \qquad\qquad +\frac{t^2}{U} S_{12}$$

Effective spin Hamiltonian:

$$H_{eff} = -\frac{2t^2}{U}\left(1 - S_{12}\right)$$

Spin-exchange operator: $S_{12} |\sigma_1\rangle |\sigma_2\rangle = |\sigma_2\rangle |\sigma_1\rangle$

Spin exchange in Hubbard model

Total spin $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = \begin{cases} -3/4, & S = 0 \\ +1/4, & S = 1 \end{cases}$$

projector operators

$$P_{S=0} = 1/4 - (\mathbf{S}_1 \cdot \mathbf{S}_2)$$

$$P_{S=1} = (\mathbf{S}_1 \cdot \mathbf{S}_2) + 3/4$$

$S = 1$ spin functions symmetric

$$|1+1\rangle = \uparrow\uparrow$$

$$|10\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \qquad S_{12}|1S^z\rangle = +|1S^z\rangle$$

$$|1-1\rangle = \downarrow\downarrow$$

$S = 0$ antisymmetric

$$|00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

$$S_{12}|00\rangle = -|00\rangle$$

Spin-exchange operator $S_{12} = P_{S=1} - P_{S=0} = 2(\mathbf{S}_1 \cdot \mathbf{S}_2) + \frac{1}{2}$

Effective Hamiltonian

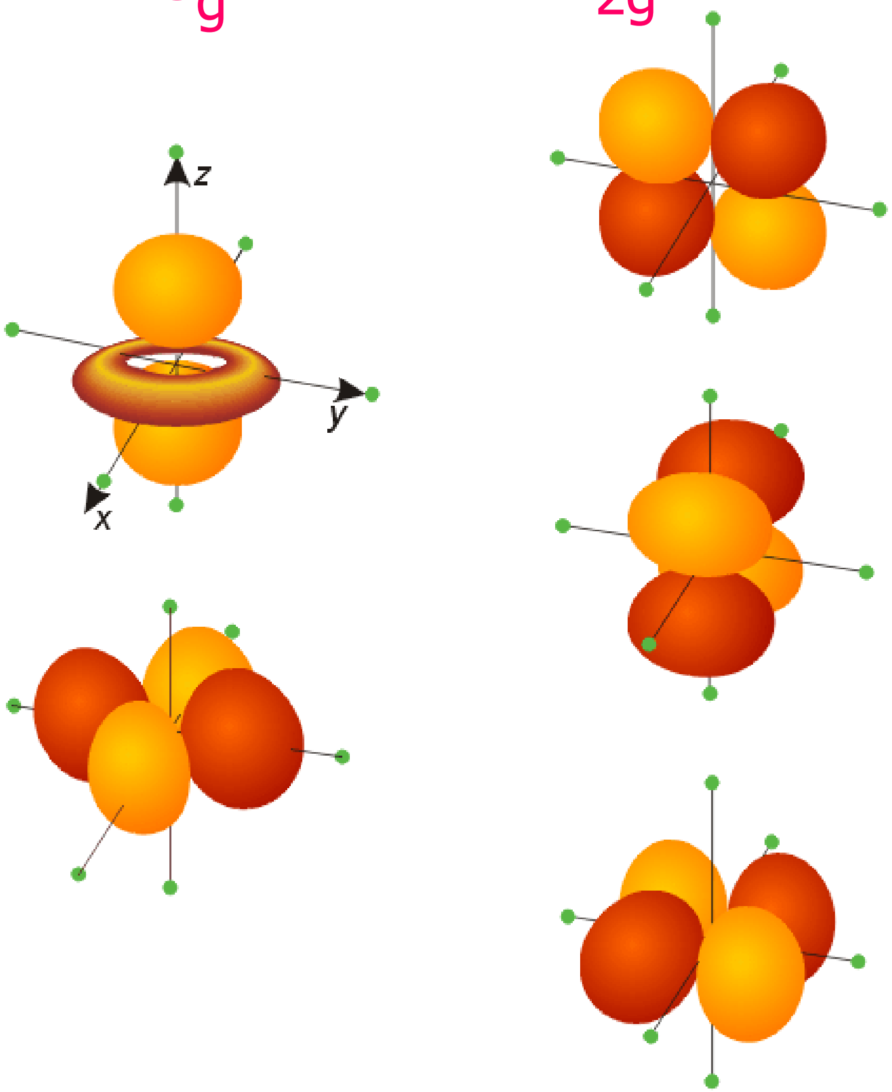
$$H_{eff} = -\frac{2t^2}{U}(1 - S_{12}) = -\frac{4t^2}{U} P_{S=0} = J\left(\mathbf{S}_1 \cdot \mathbf{S}_2 - \frac{1}{4}\right)$$

exchange constant

$$J = \frac{4t^2}{U} > 0$$

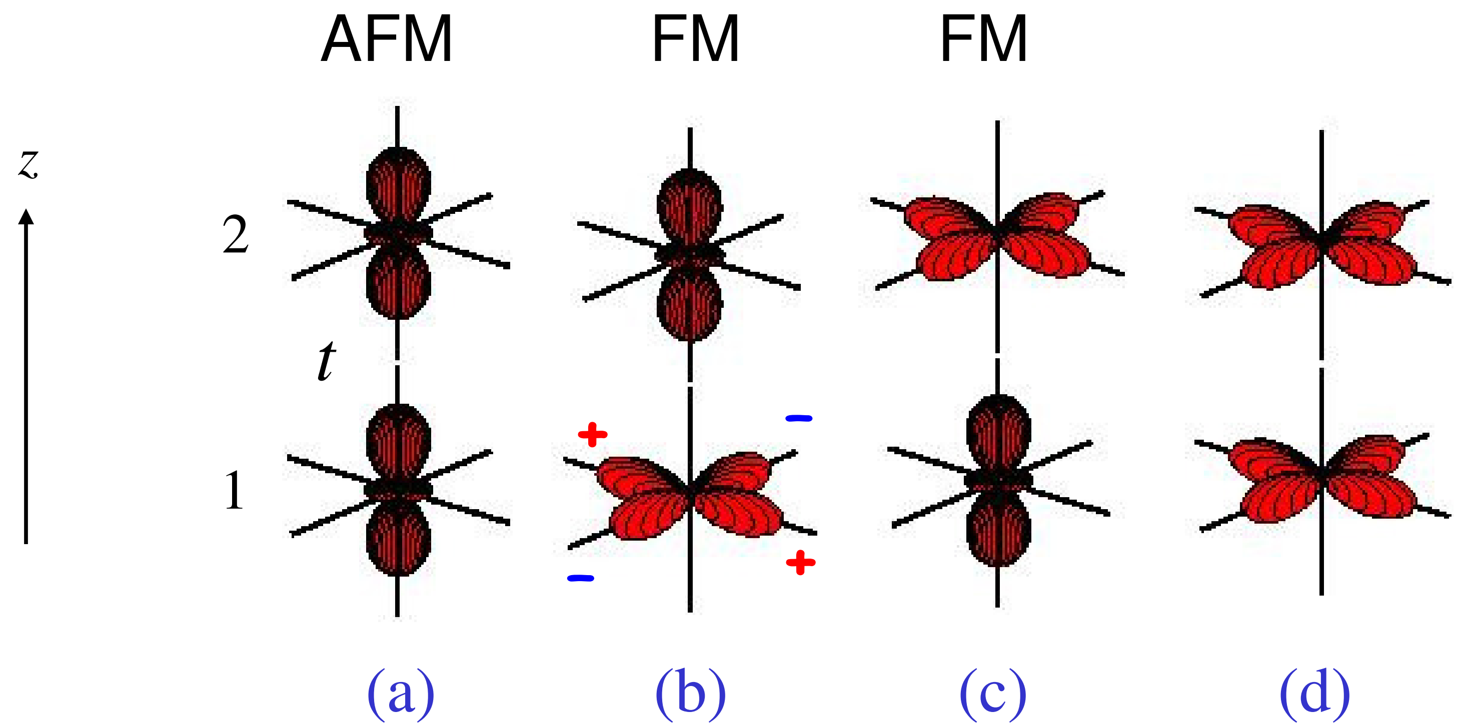
d-orbitals

e_g t_{2g}



octahedral crystal field	tetrahedral crystal field
e_g	t_{2g}
t_{2g}	e_g

Exchange along the *z*-axis

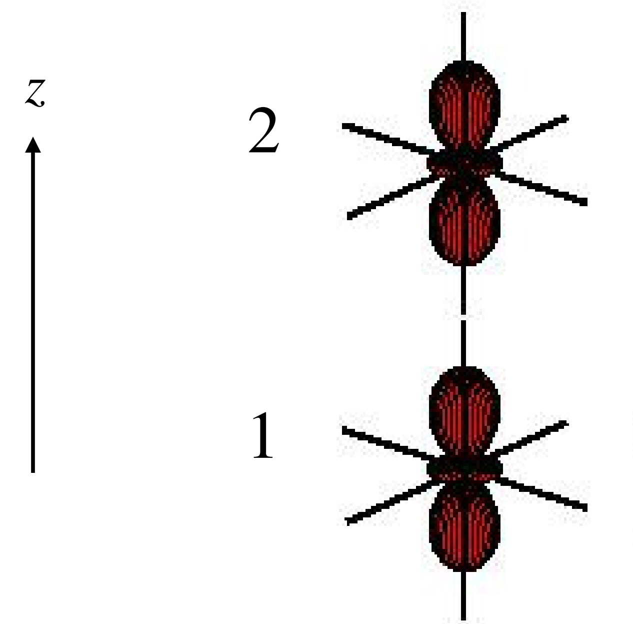


No hopping between $\left|3z^2 - r^2\right\rangle$ and $\left|x^2 - y^2\right\rangle$ orbitals

Exchange does not change orbital occupation

AFM interaction

(a)



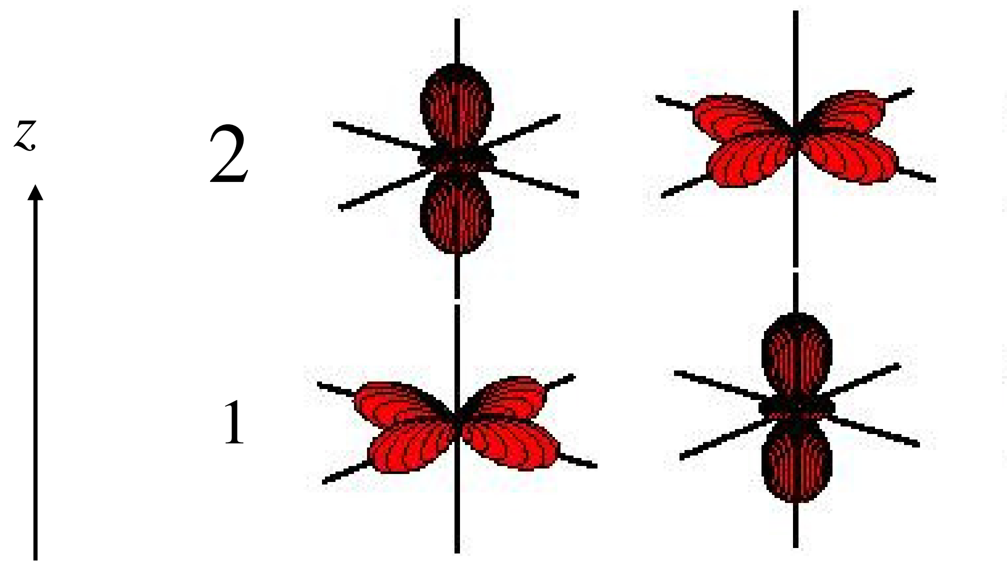
$$t = \frac{t_{pd}^2}{\Delta}$$

$$H_a = -\frac{4t^2}{U}\left(\frac{1}{4} - \mathbf{S}_1 \cdot \mathbf{S}_2\right)$$

$S = 0$

FM interaction

(b) + (c)



$$H = -\frac{t^2}{U - J_d\left(\frac{3}{4} + \mathbf{S}_1 \cdot \mathbf{S}_2\right)}$$

Hund's rule coupling

$$H_{FM} = -\frac{t^2 J_d}{U^2}\left(\frac{3}{4} + \mathbf{S}_1 \cdot \mathbf{S}_2\right)$$

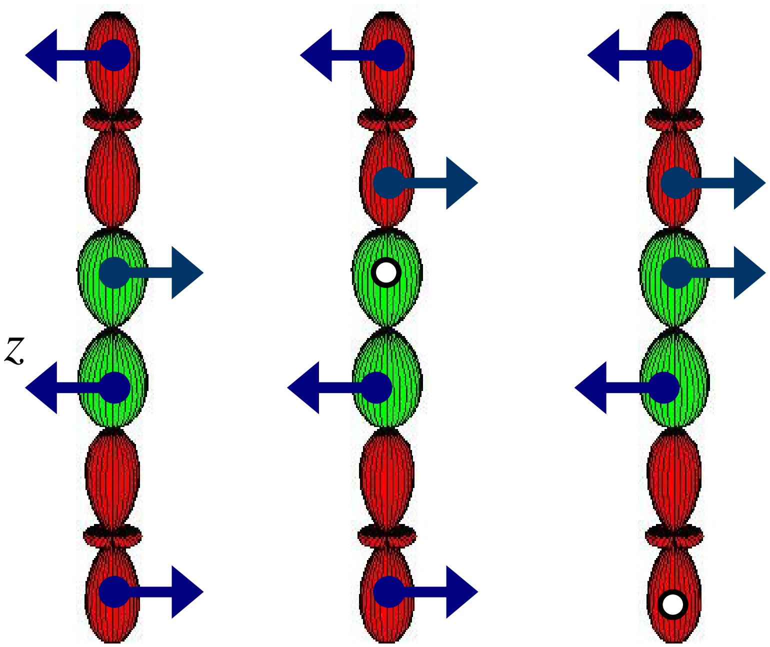
$S = 1$

Superexchange

Effective dd-hoping $t = \frac{t_{pd}^{2}}{\Delta}$

$d_{3z^2-r^2}$

p_z



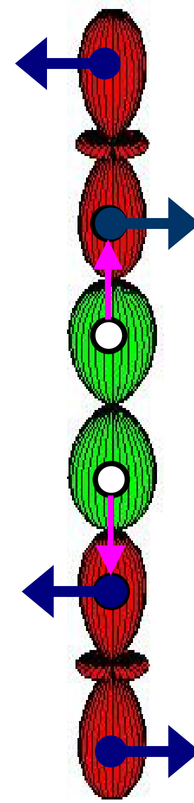
$d_{3z^2-r^2}$ charge transfer energy Δ

$d_{3z^2-r^2}$

Intermediate state with 2 oxygen holes

correction to exchange constant

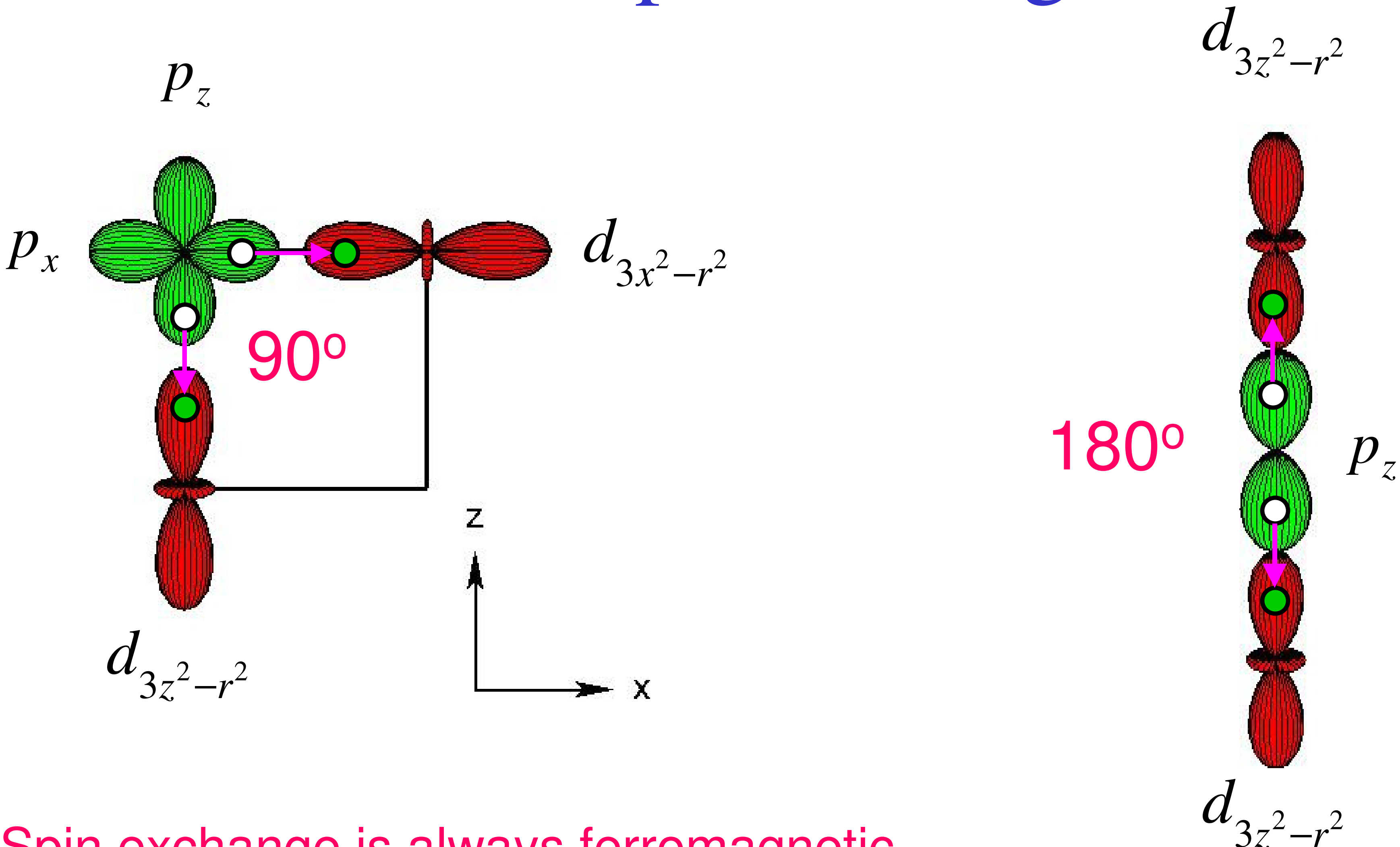
$$\delta J = \frac{8t_{pd}^{4}}{\Delta^{2}(2\Delta + U_{p})}$$



p_z

$d_{3z^2-r^2}$

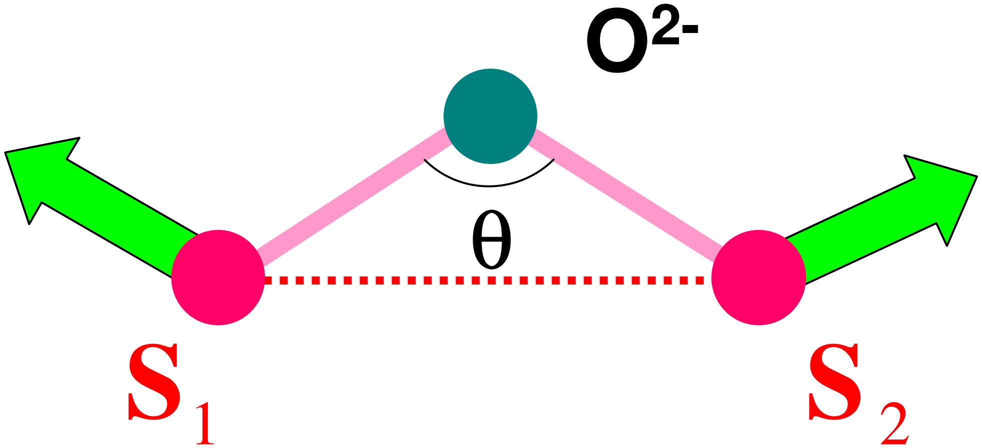
90^o superexchange



Spin exchange is always ferromagnetic

Spin exchange is weaker than orbital exchange

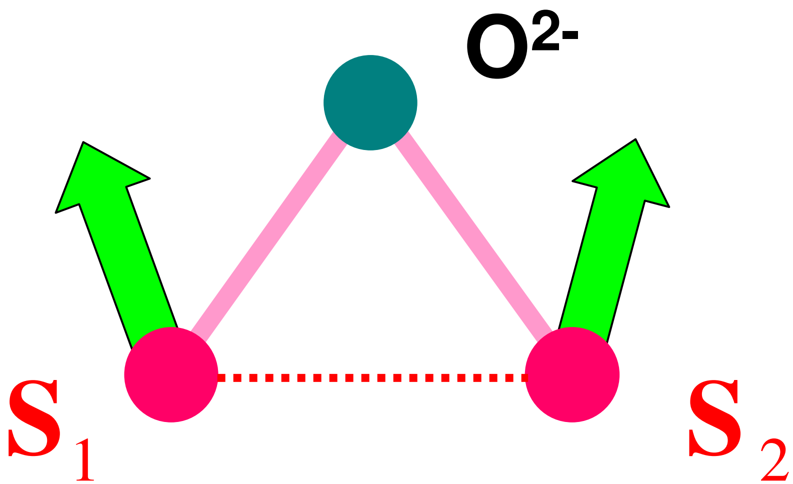
Exchange striction

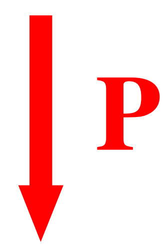


$$E = J\,(\mathbf{S}_1\mathbf{S}_2)$$

$$\theta = 180^o \quad J > 0$$

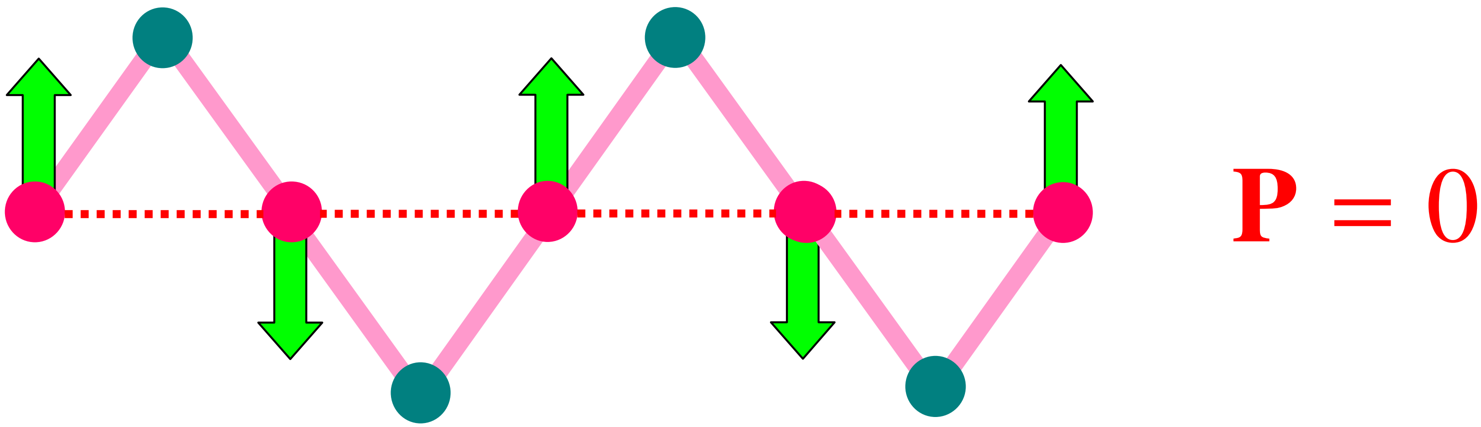
$$\theta = 90^o \quad J < 0$$



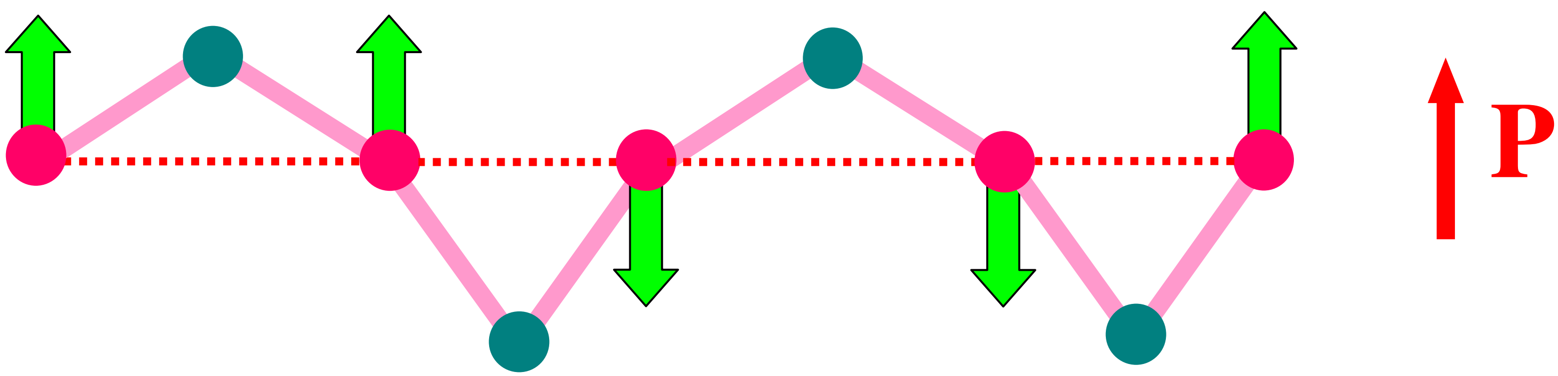


Role of frustration

Néel ordering: Inversion symmetry not broken



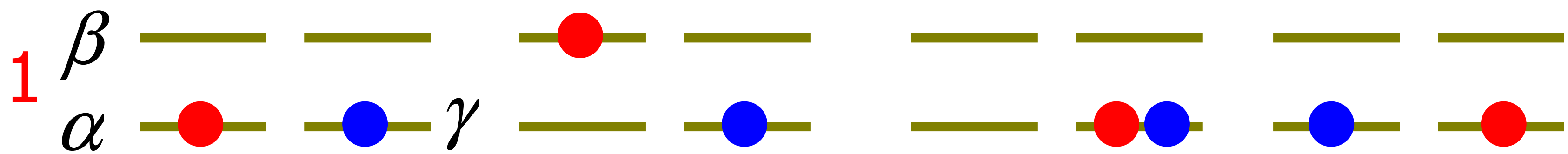
↑↑↓↓ ordering: Inversion symmetry is broken



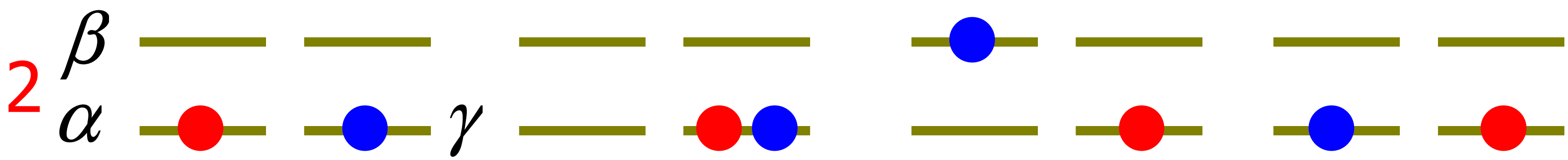
To induce P spin ordering must break inversion symmetry

Dzyaloshinskii-Moriya interaction

$$H_{SO} = \lambda(\mathbf{l}\cdot\mathbf{s}) \qquad \psi_\alpha|\sigma\rangle \rightarrow \left[\psi_\alpha + \lambda\sum_\beta \psi_\beta \frac{(\mathbf{l}_{\beta\alpha}\cdot\mathbf{s})}{\varepsilon_\alpha - \varepsilon_\beta}\right]|\sigma\rangle$$



$$(1)\quad S_{12}\frac{t_{\gamma\beta}t_{\alpha\gamma}}{U}\lambda\frac{(\mathbf{l}_{\beta\alpha}\cdot\mathbf{s}_1)}{\varepsilon_\alpha - \varepsilon_\beta} \qquad (2)\quad \lambda\frac{(\mathbf{l}_{\alpha\beta}\cdot\mathbf{s}_1)}{\varepsilon_\alpha - \varepsilon_\beta}S_{12}\frac{t_{\beta\gamma}t_{\gamma\alpha}}{U}$$



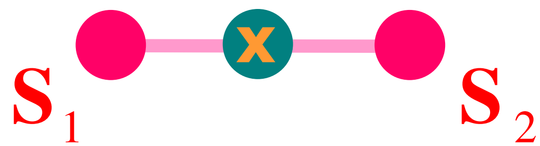
real wave functions

$$\mathbf{l} = \mathbf{r}\times\frac{\hbar}{i}\nabla \qquad \mathbf{l}_{\beta\alpha} = -\mathbf{l}_{\alpha\beta} \qquad t_{\alpha\gamma} = t_{\gamma\alpha}$$

$$\delta H_{ex} \propto [S_{12},\mathbf{s}_1] = \left[2\mathbf{s}_1\cdot\mathbf{s}_2 + \frac{1}{2},\mathbf{s}_1\right] \propto \mathbf{s}_1\times\mathbf{s}_2$$

Moriya rules

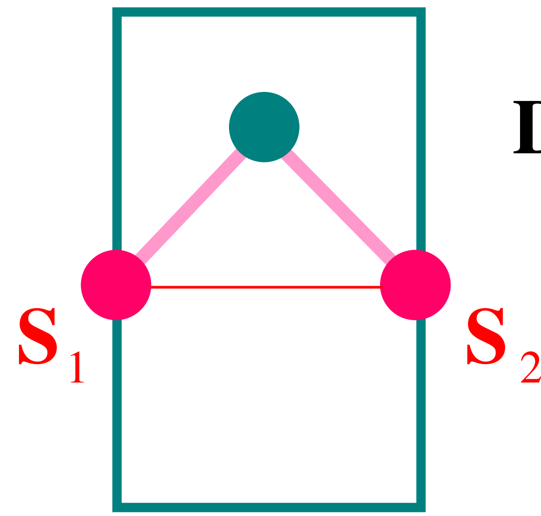
Inversion center



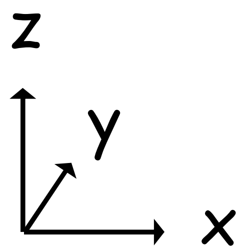
$$\mathbf{D}_{12} = 0$$

$$\mathbf{D}_{12} \propto \mathbf{l}_1 - \mathbf{l}_2$$

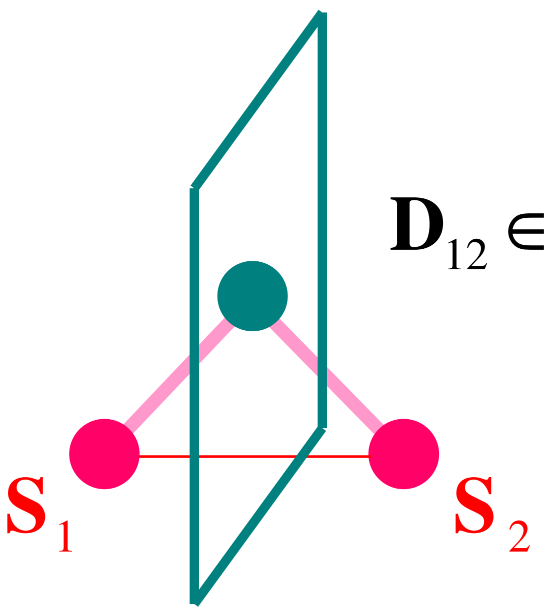
mirror xz plane



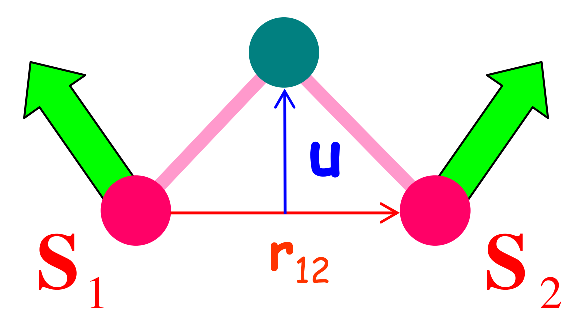
$$\mathbf{D}_{12} \perp xz$$



mirror yz plane

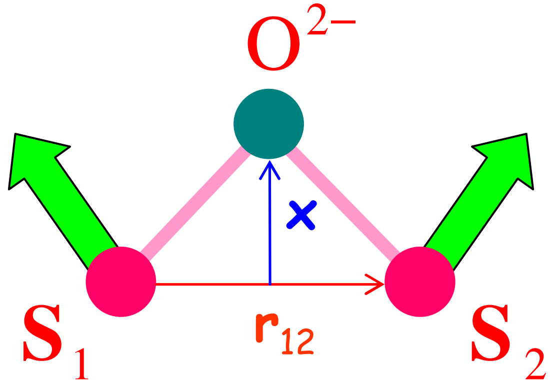


$$\mathbf{D}_{12} \in yz$$



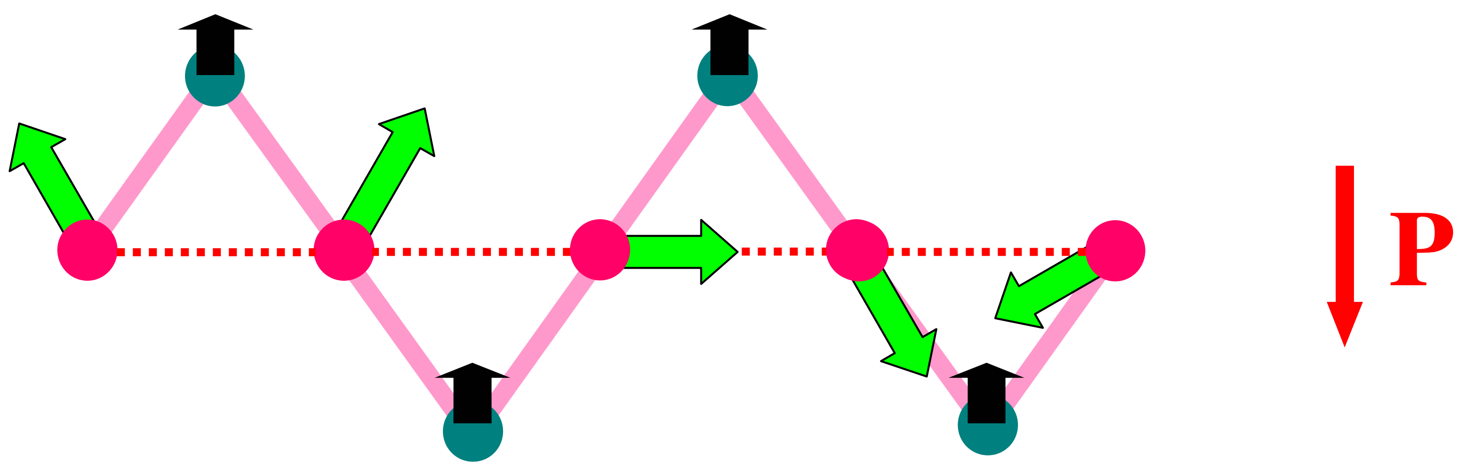
$$\mathbf{D}_{12} \propto \hat{\mathbf{r}}_{12} \times \mathbf{u}$$

Effects of Dzyaloshinskii-Moriya interaction



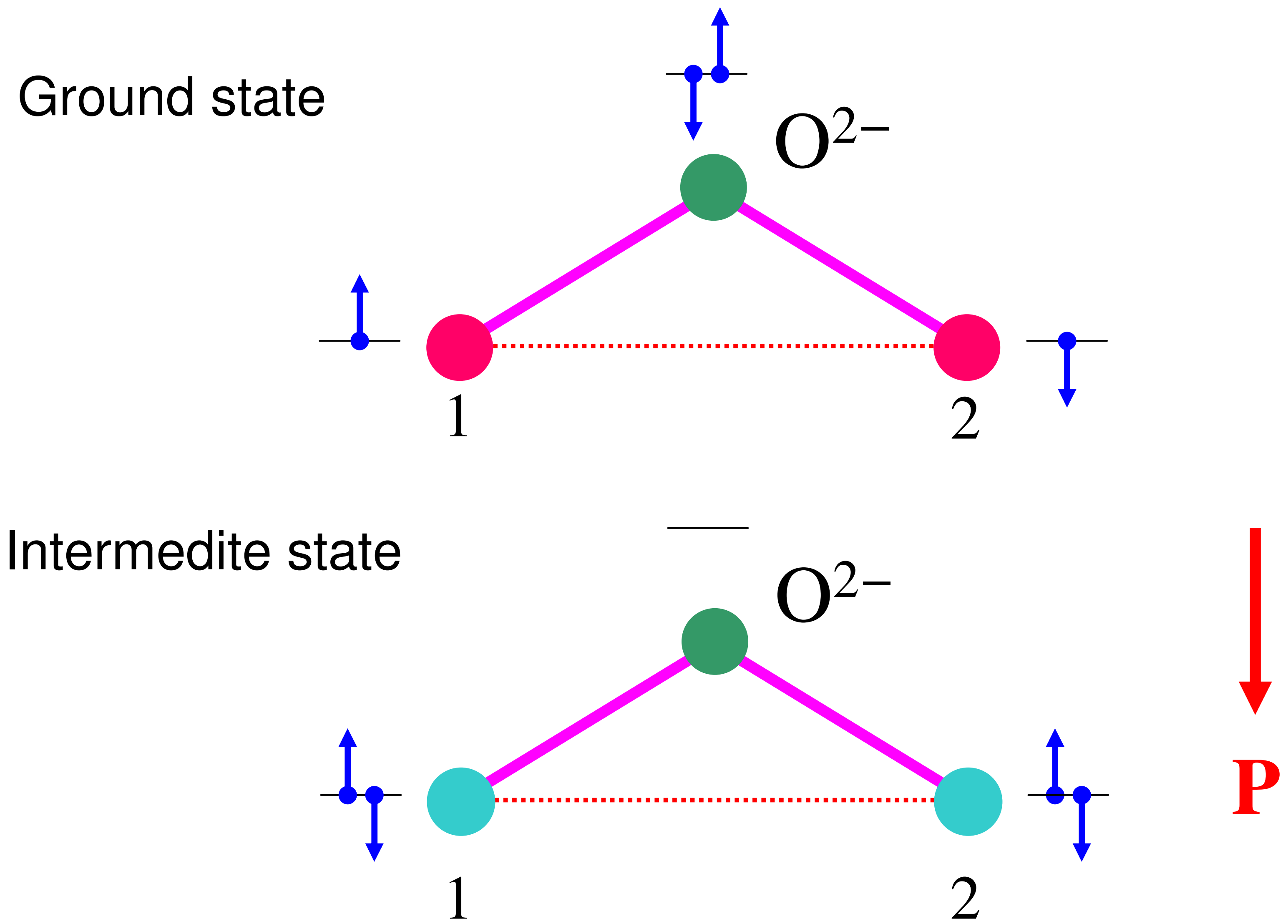
$$E_{DM} = \mathbf{D}_{12} \cdot [\mathbf{S}_1 \times \mathbf{S}_2]$$

$$\mathbf{D}_{12} \propto \mathbf{x} \times \hat{\mathbf{r}}_{12}$$



H. Katsura et al PRL ***95*** *057205 (2005),*
Sergienko & Dagotto PRB ***73*** *094434 (2006)*

Polarization of electronic orbitals



Higher-order terms in effective spin Hamiltonian

L.N. Bulaevskii, C.D. Batista, M. M., and D. Khomskii, arXiv:0709.0575

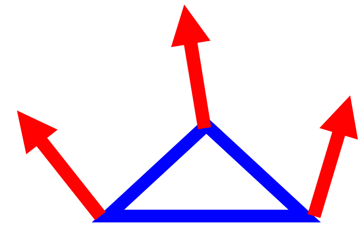
Hubbard model + coupling to external fields

$$H = \sum_{i\neq j,\sigma} t e^{-\frac{2\pi i}{\Phi_0}\int_{\mathbf{x}_i}^{\mathbf{x}_j} d\mathbf{x}\cdot\mathbf{A}} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U}{2}\sum_i (n_i - 1)^2$$
$$- \; e\sum_i \varphi_i n_i + \mu_B \sum_{i\alpha\beta} c_{i\alpha}^{\dagger} \mathbf{H}\cdot\sigma_{\alpha\beta} c_{i_\beta},$$

Effective spin Hamiltonian (2nd order)

$$H_{\mathrm{eff}}^{(2)} = \frac{4t^2}{U}\sum_{\langle i,j\rangle}\left(\mathbf{S}_i\cdot\mathbf{S}_j - \frac{1}{4}\right)$$

Effective spin Hamiltonian
(3$^{\text{d}}$ order)



Interaction with magnetic field

$$H_{\text{eff}}^{(3a)} = -48\pi \frac{t^3}{U^2} \sum_{\langle i,j,k \rangle} \frac{\Phi_{ijk}}{\Phi_0} \mathbf{S}_i \cdot [\mathbf{S}_j \times \mathbf{S}_k]$$

scalar spin chirality

Persistent electric current

$$I = -c \frac{\partial H_{\text{eff}}^{(3a)}}{\partial \Phi_{123}} = \frac{24e}{\hbar} \frac{t^3}{U^2} \mathbf{S}_1 \cdot [\mathbf{S}_2 \times \mathbf{S}_3]$$

Effective spin Hamiltonian
(3^d order)

Interaction with electric field

$$H_{\text{eff}}^{(3b)} = 8e\left(\frac{t}{U}\right)^3 \sum_{\langle i,j,k\rangle} \varphi_i \left[\mathbf{S}_i \cdot (\mathbf{S}_j + \mathbf{S}_k) - 2\mathbf{S}_j \cdot \mathbf{S}_k\right]$$

Spin-induced charge

$$\delta Q_1 = \frac{\partial H_{\text{eff}}^{(3b)}}{\partial \varphi_1} = 8e\left(\frac{t}{U}\right)^3 \left[\mathbf{S}_1 \cdot (\mathbf{S}_2 + \mathbf{S}_3) - 2\mathbf{S}_2 \cdot \mathbf{S}_3\right]$$