Multiferroic and magnetoelectric materials

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Lectures

- Spin-orbital exchange in Mott insulators

✓ Multiferroics and magnetoelectrics

Outline

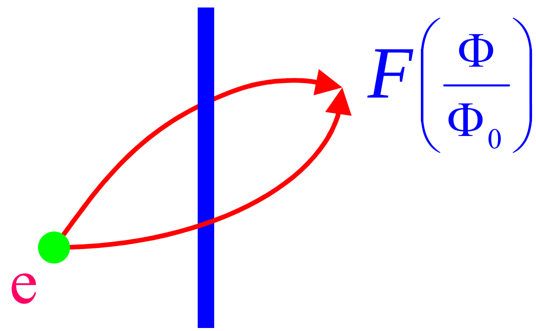
- Linear magnetoelectric effect, multiferroics
- Phenomenological description
- Microscopic mechanisms of magnetoelectric coupling
- Outlook

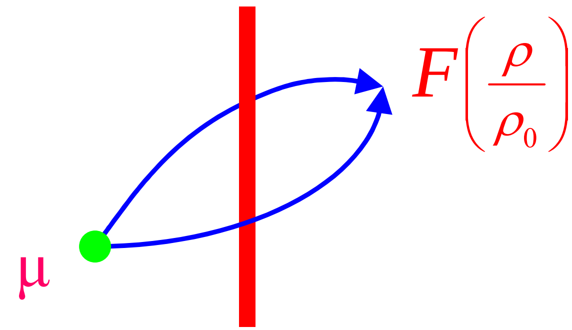
Electric ↔ Magnetic

- 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

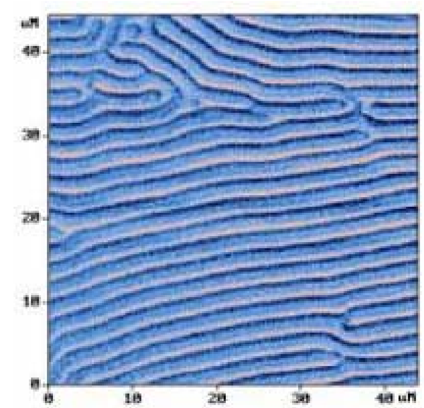




- Thermodynamics of ferroelectrics and ferromagnets

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

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



Multiferroics

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

G. A. Smolenskii

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

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

$Ni_3B_2O_{13}I$ $YMnO_3$

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

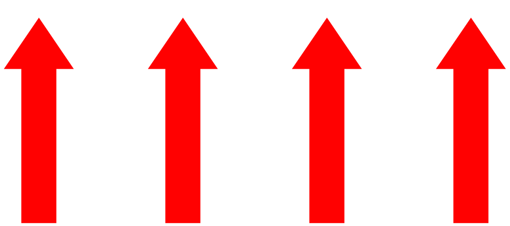
Time-reversal symmetry breaking in magnets

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

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

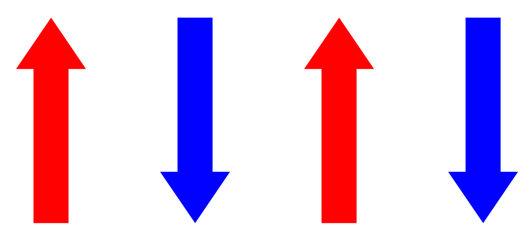
Ferromagnets

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

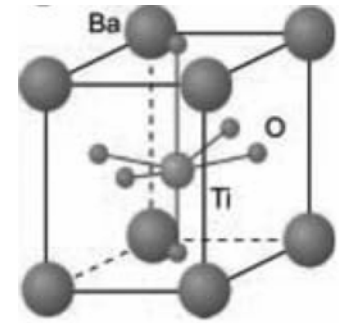


Antiferromagnets

$$\mathbf{M} = 0$$



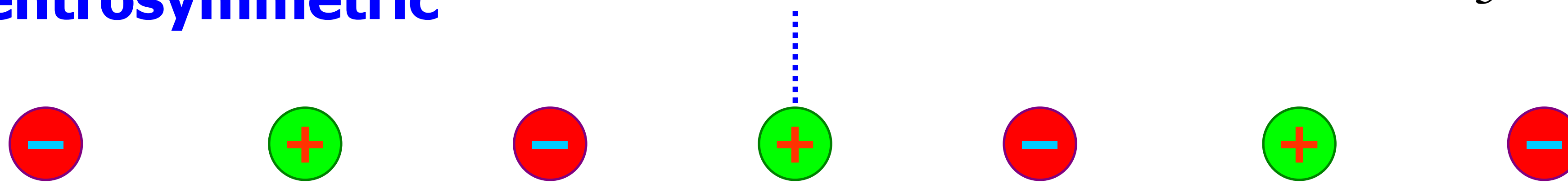
Inversion symmetry breaking in ferroelectrics



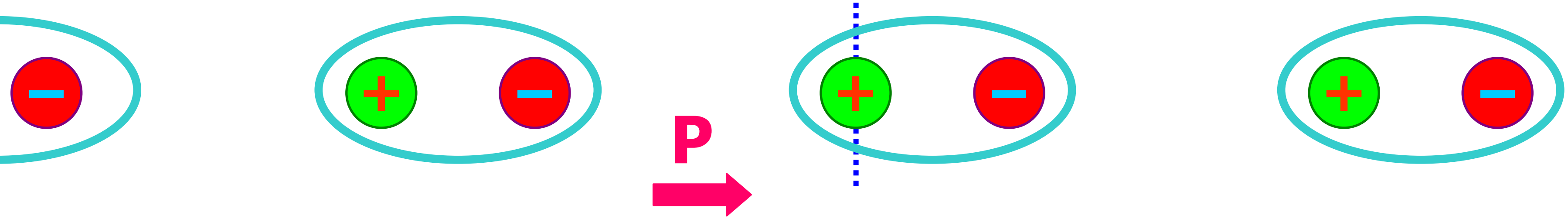
$$\mathbf{P}(-\mathbf{x}) = -\mathbf{P}(\mathbf{x})$$

$BaTiO_3$

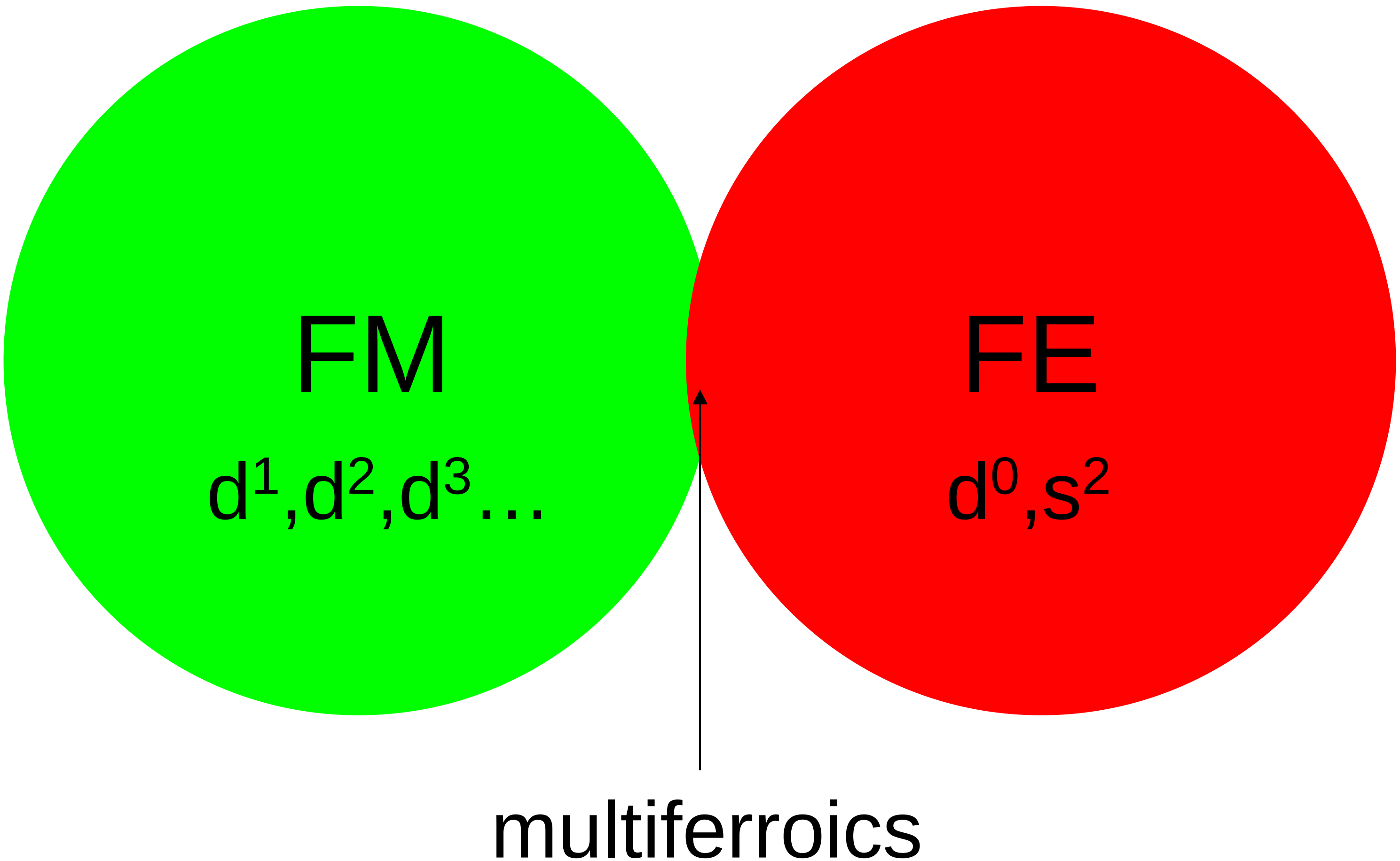
Centrosymmetric



Noncentrosymmetric



No chemistry between magnetism and ferroelectricity

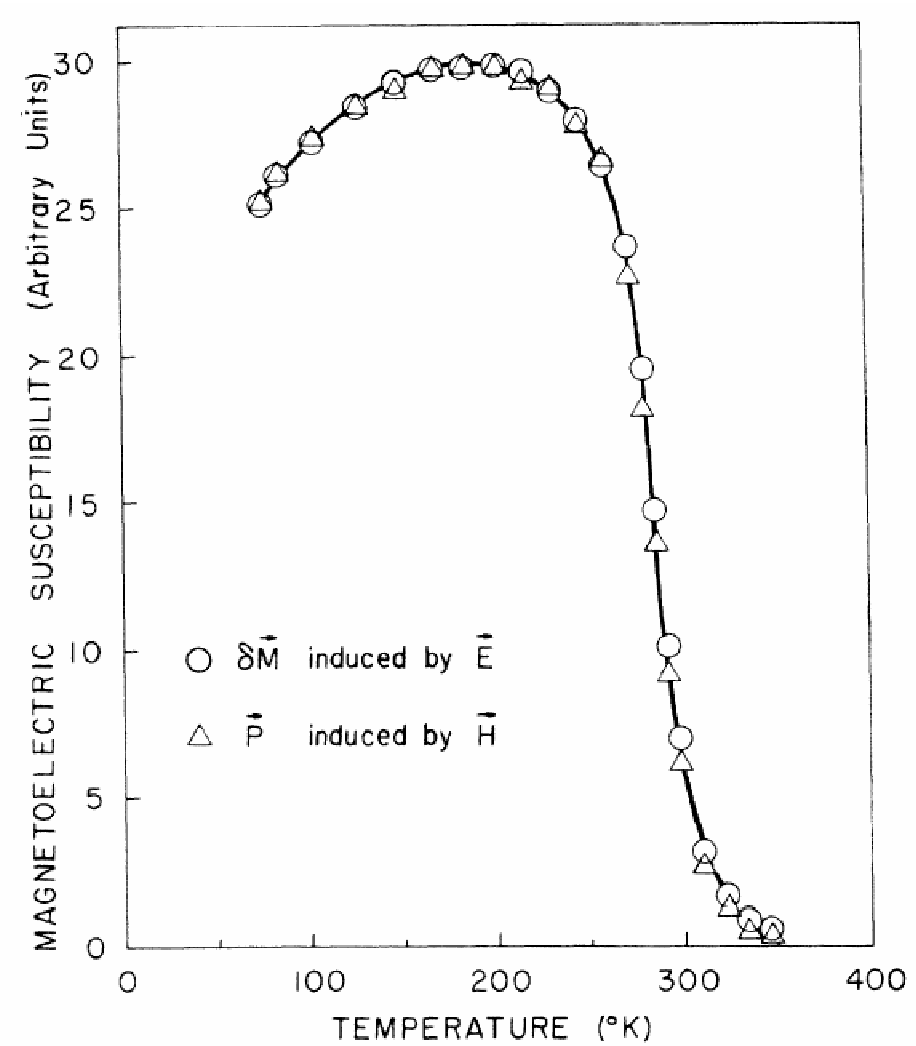


N. A. Hill, J. Phys. Chem. B ***104****, 6694 (2000)*

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)*

Anomalies of magnetoelectric constant in boracites

$M_3B_7O_{13}X$

M = Co^{2+}, Ni^{2+}

X = I, Br, Cl

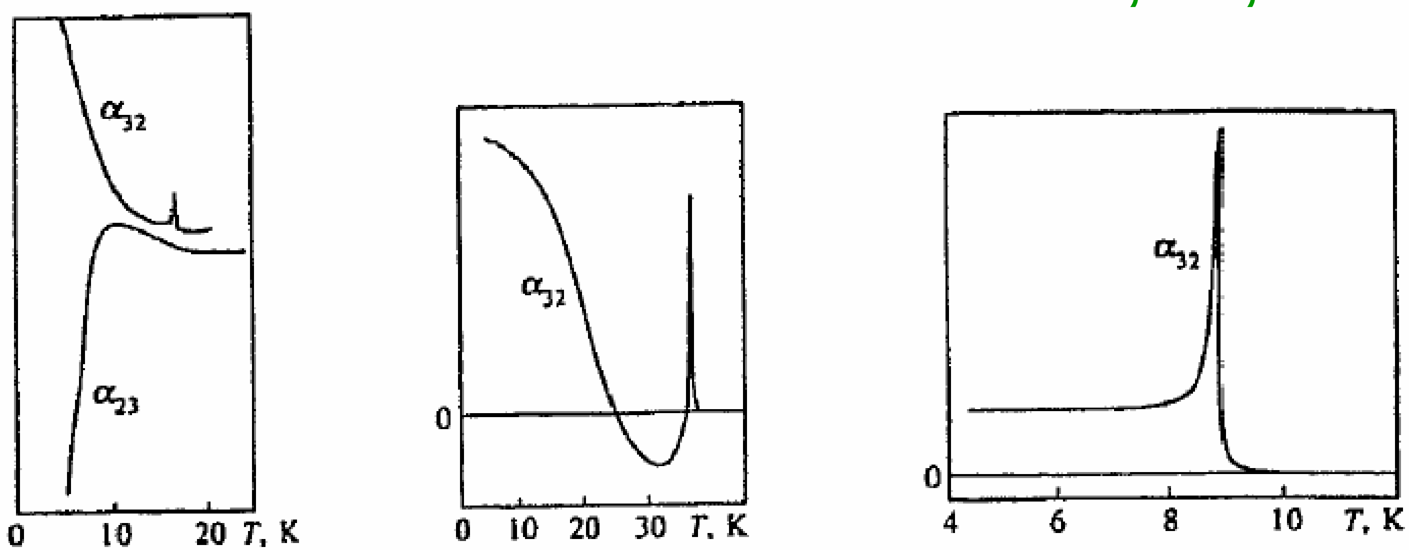
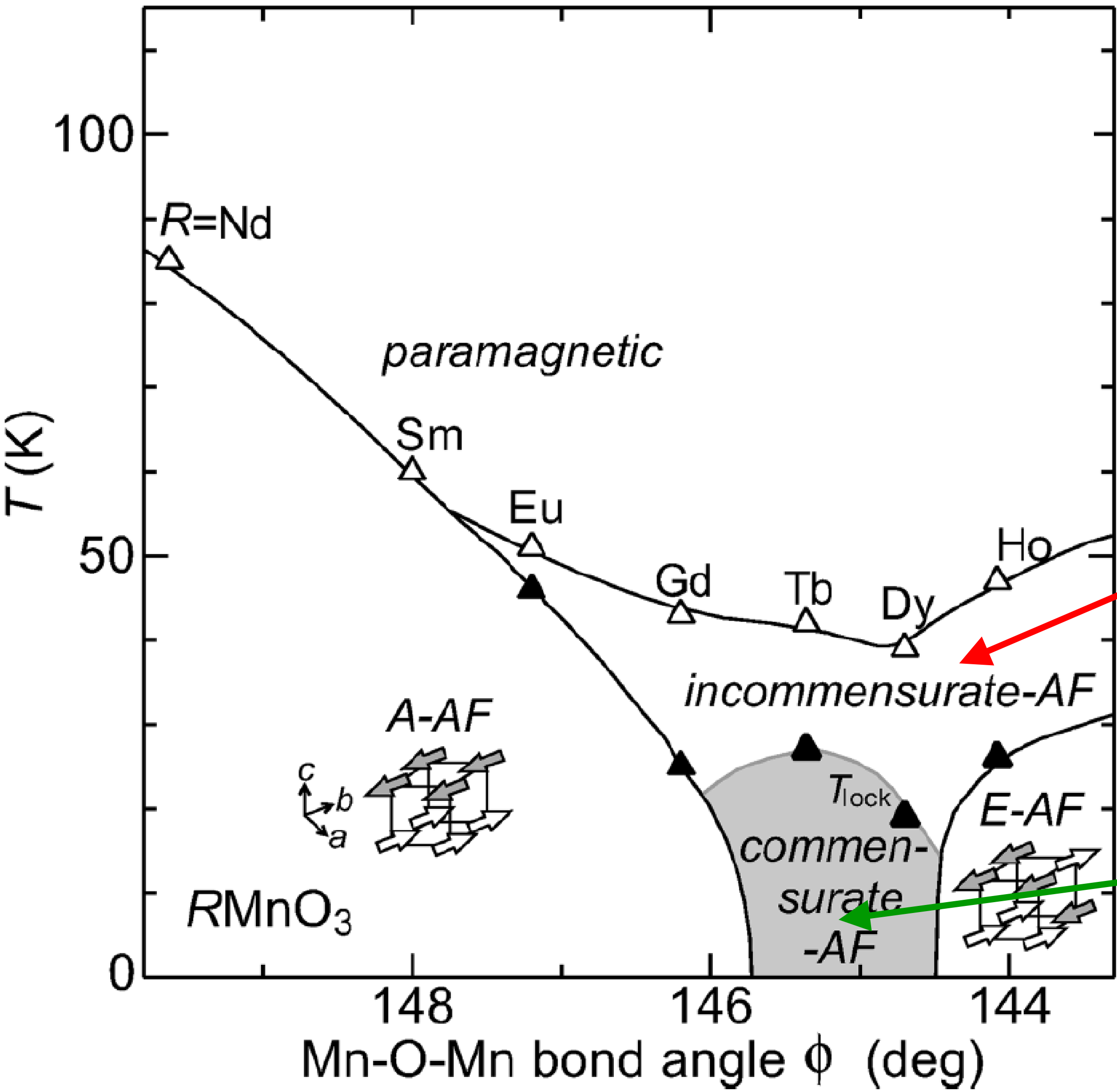


FIGURE 1 Temperature dependences of the components α_{32} and α_{23} of the magnetoelectric tensor in C_2 phase of Co – Br[1] (1), Co – I[2] (2), and Ni – Cl[3] (3) boracites.

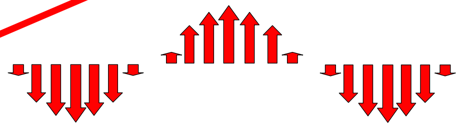
D. G. Sannikov, Ferroelectrics **219** 177 *(1998)*

Orthorombic $RMnO_3$

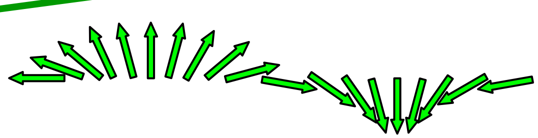


T. Kimura et al
*PRB **68**,060403 (2003)*

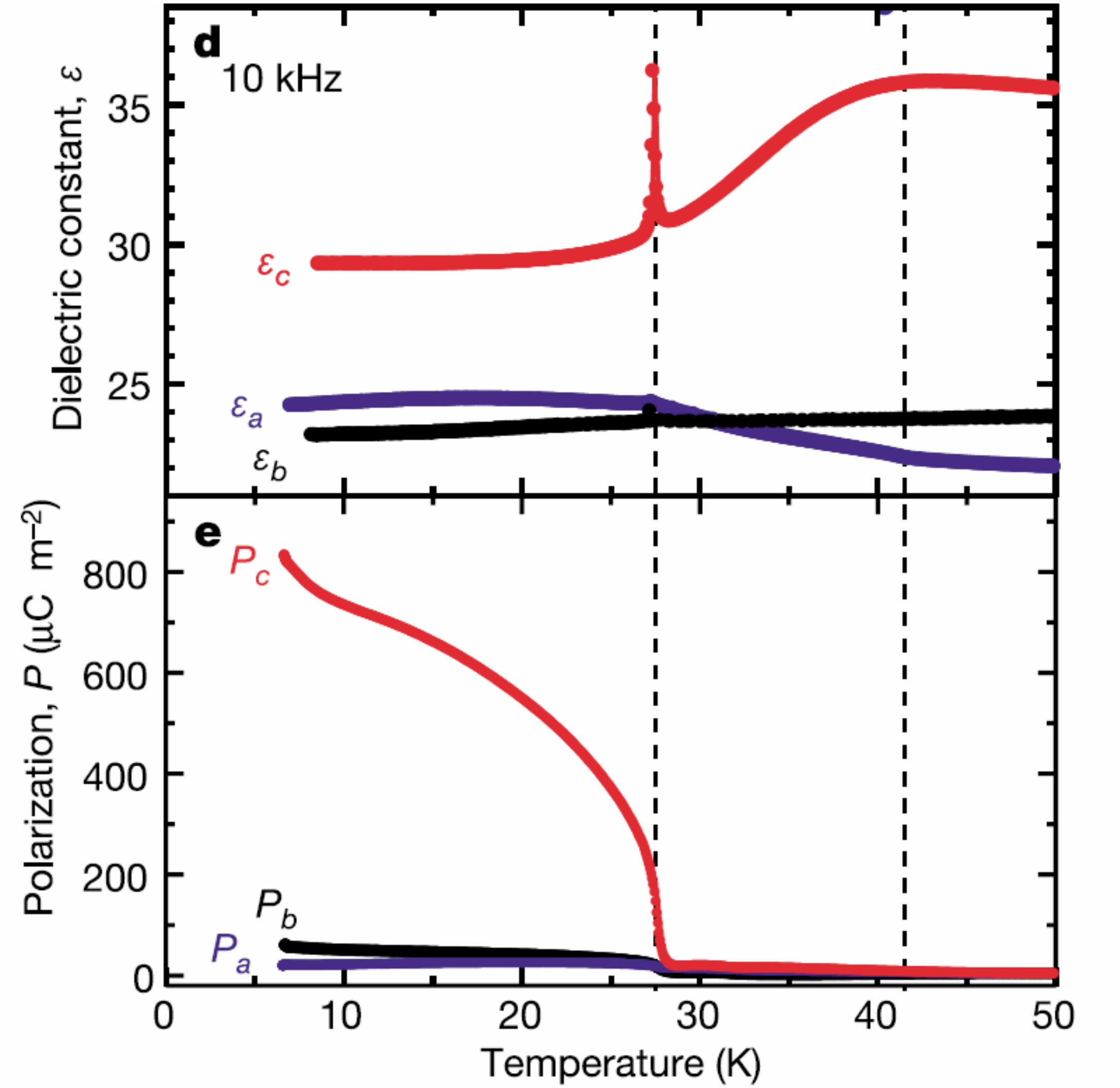
Sinusoidal SDW



Spiral SDW

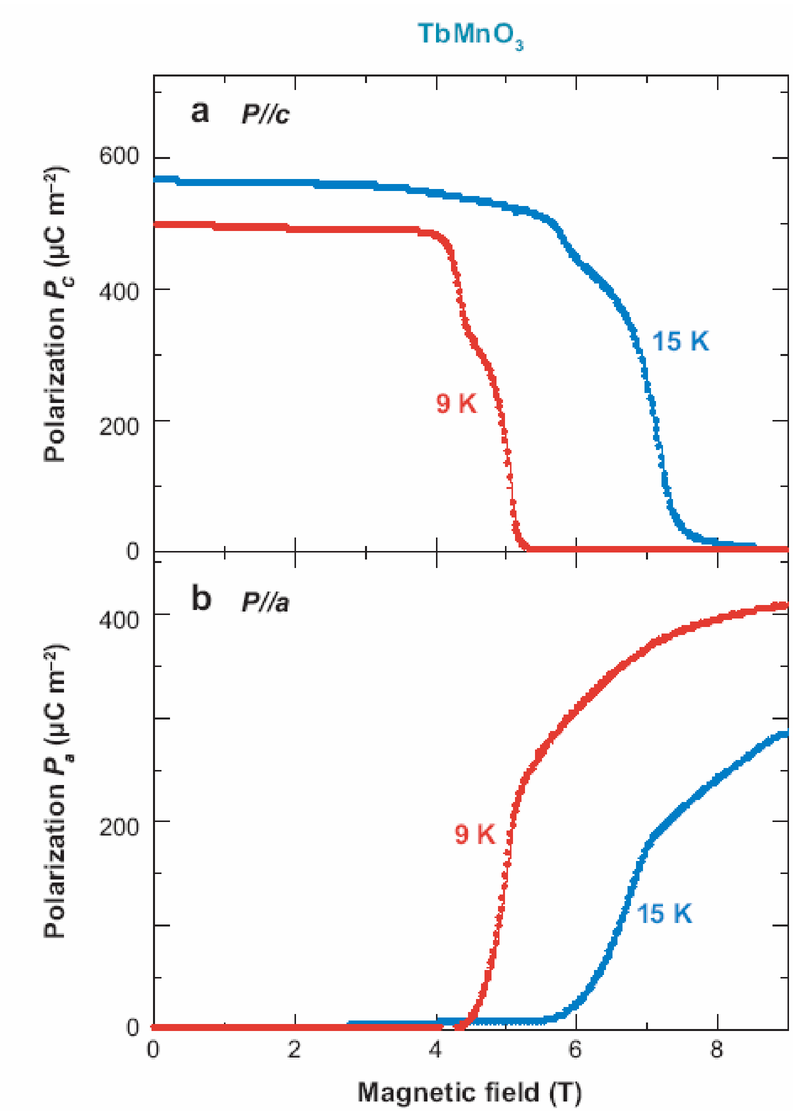


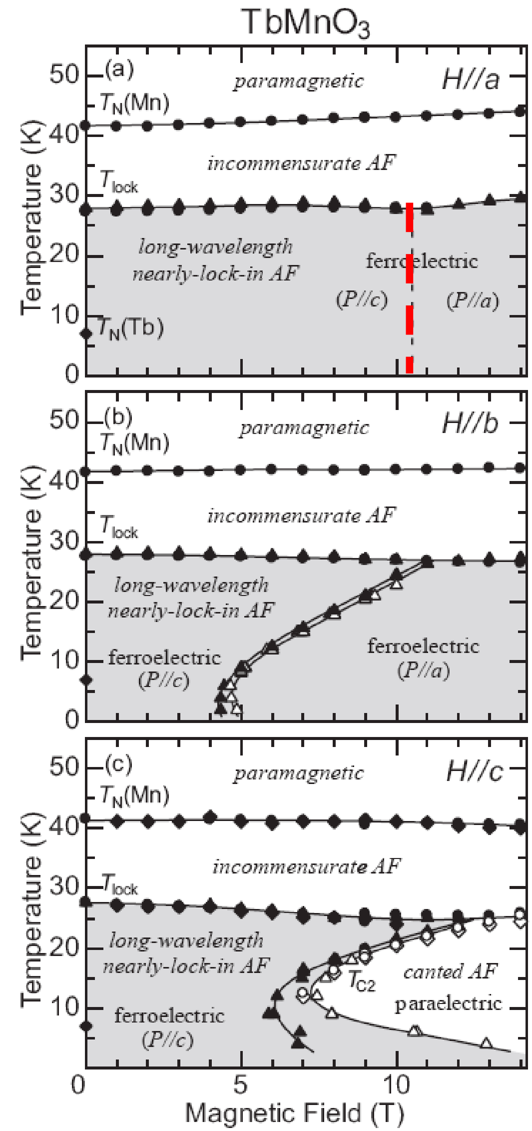
Dielectric constant anomaly at the transition to spiral state



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

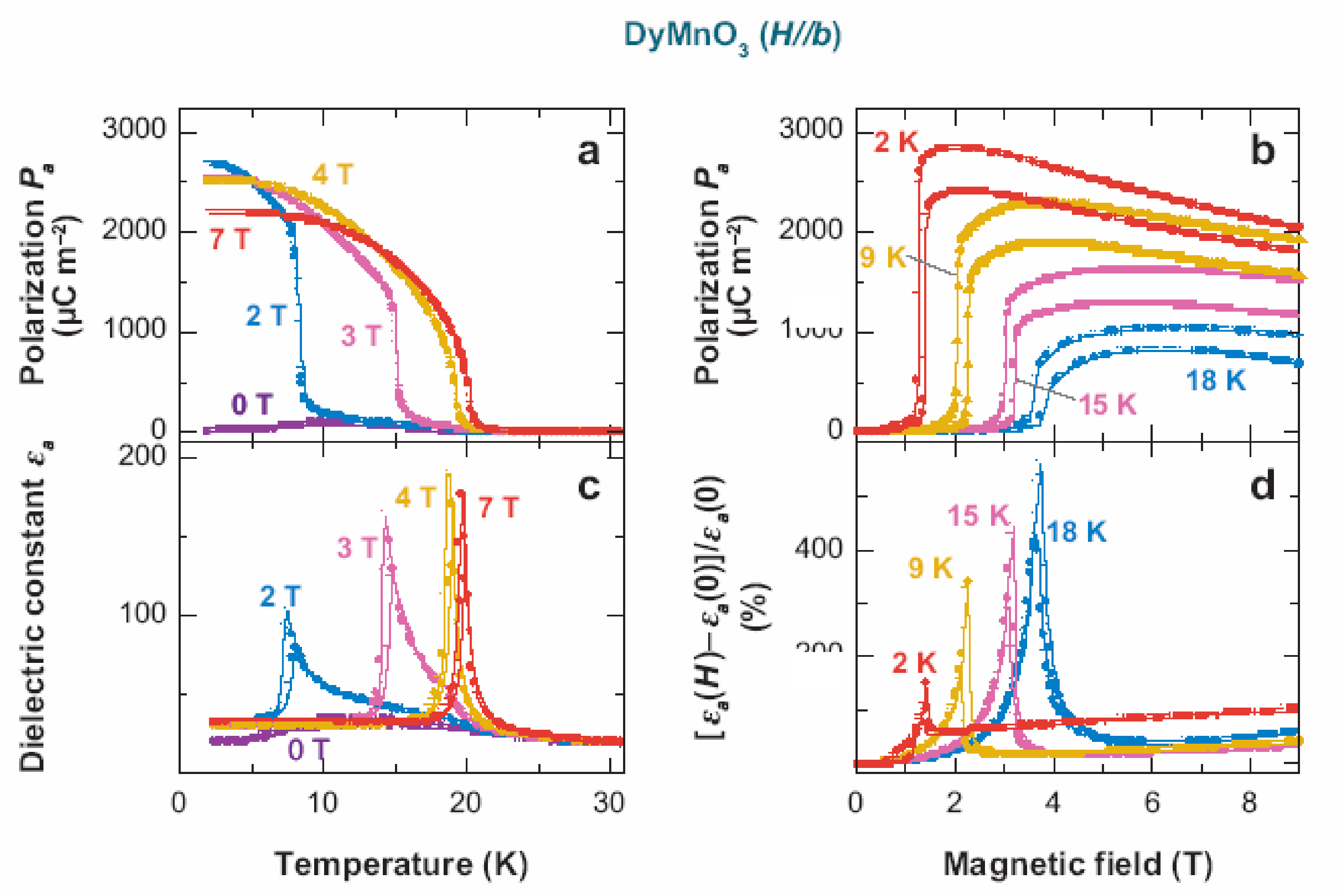
Polarization switching by magnetic field





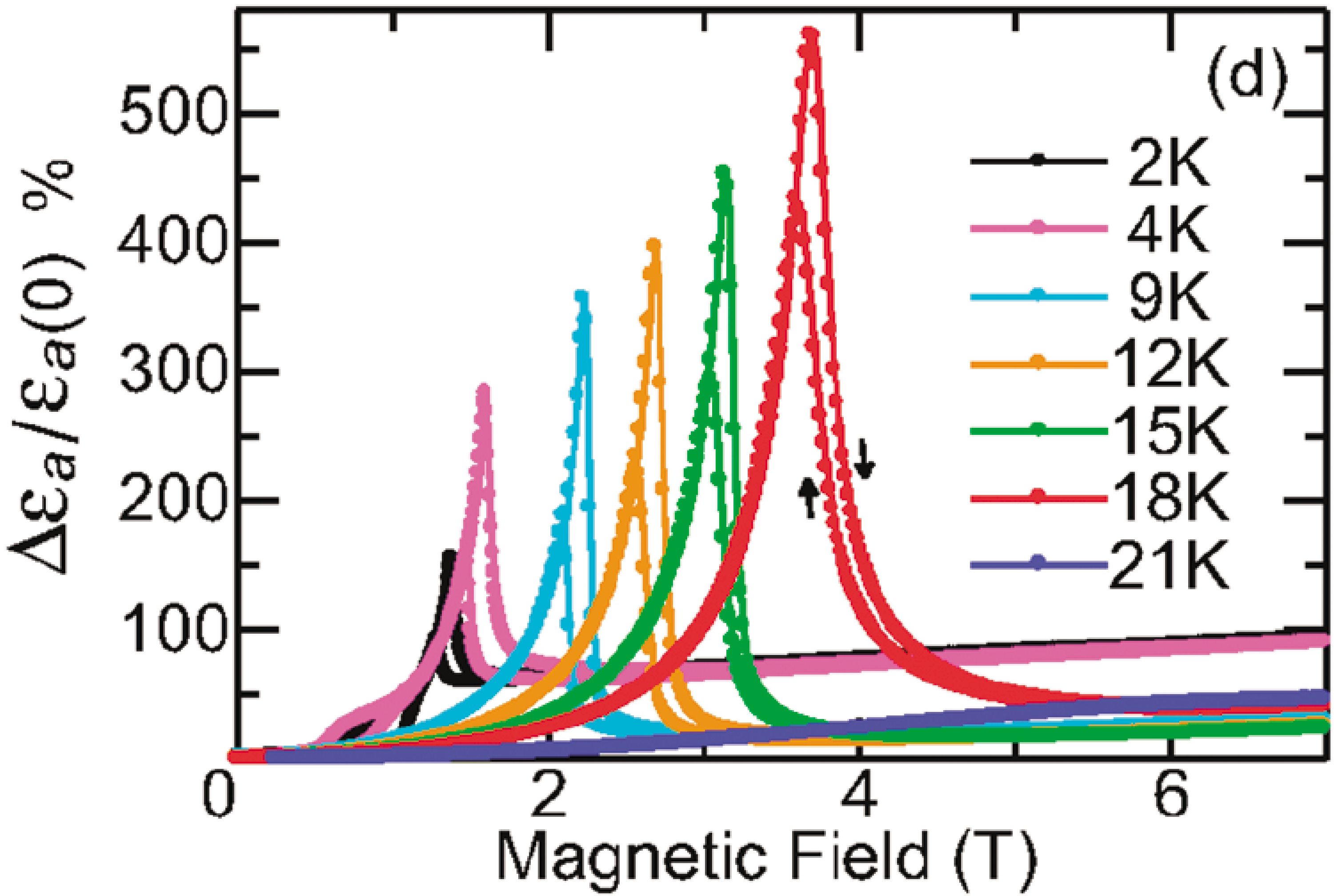
T. Kimura Annu. Rev. Mater. Res. ***37*** *387 (2007)*

Magnetic control of dielectric properties



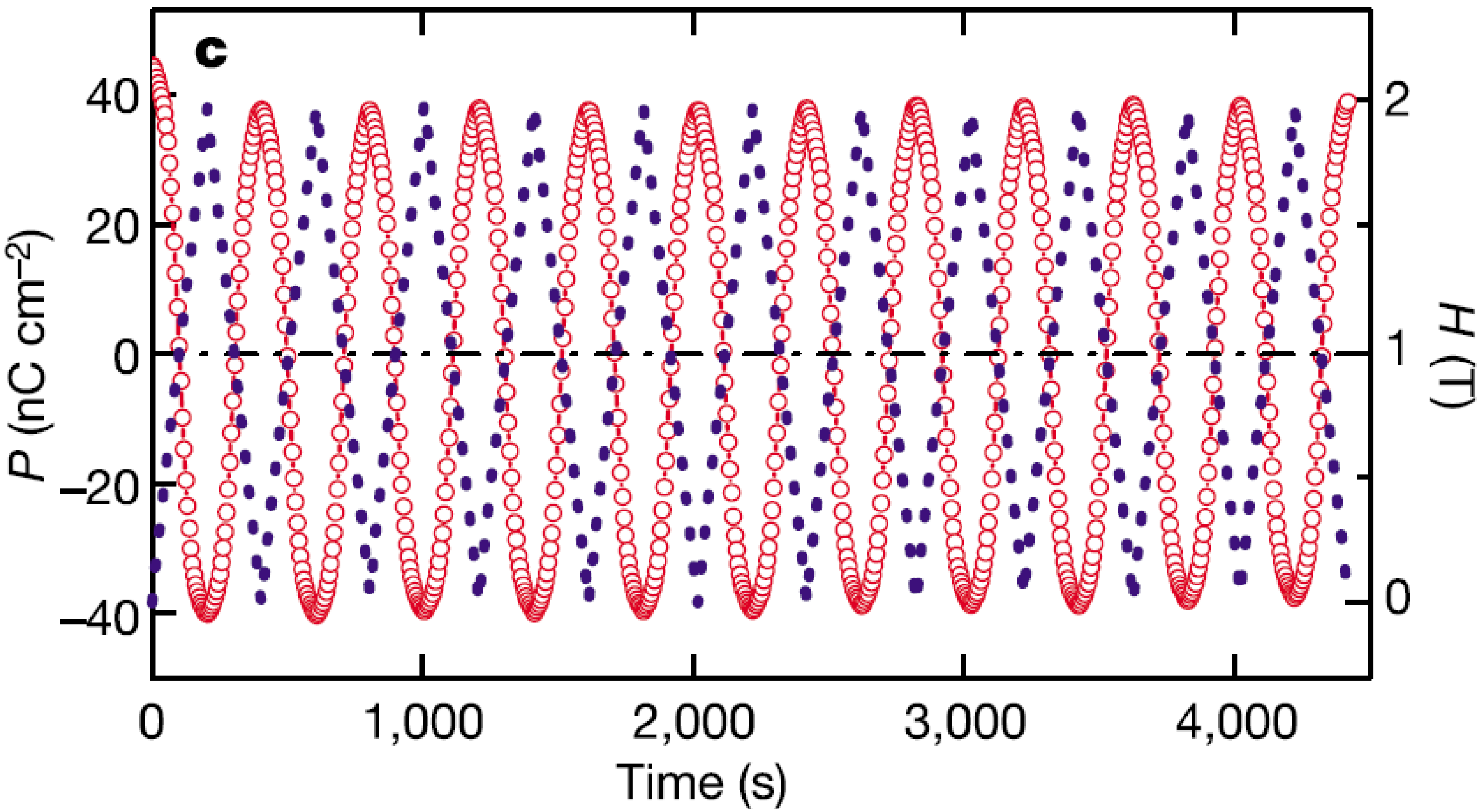
T. Kimura Annu. Rev. Mater. Res. ***37*** *387 (2007)*

Giant magnetocapacitance effect in $DyMnO_3$



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

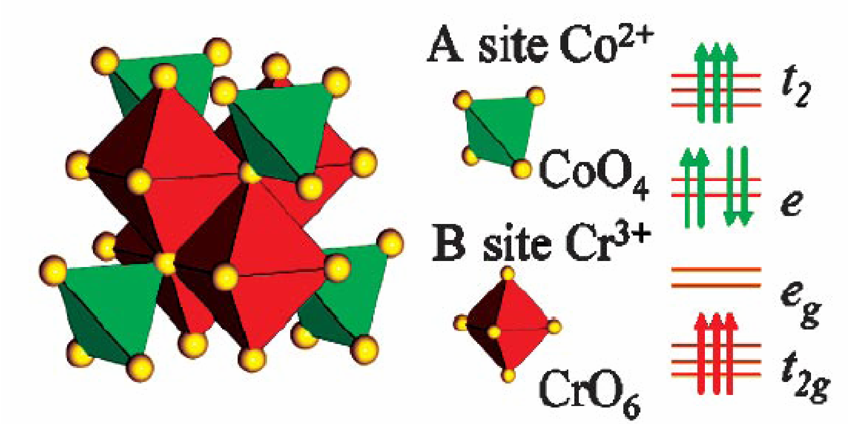
Electric polarization reversals in $TbMn_2O_5$

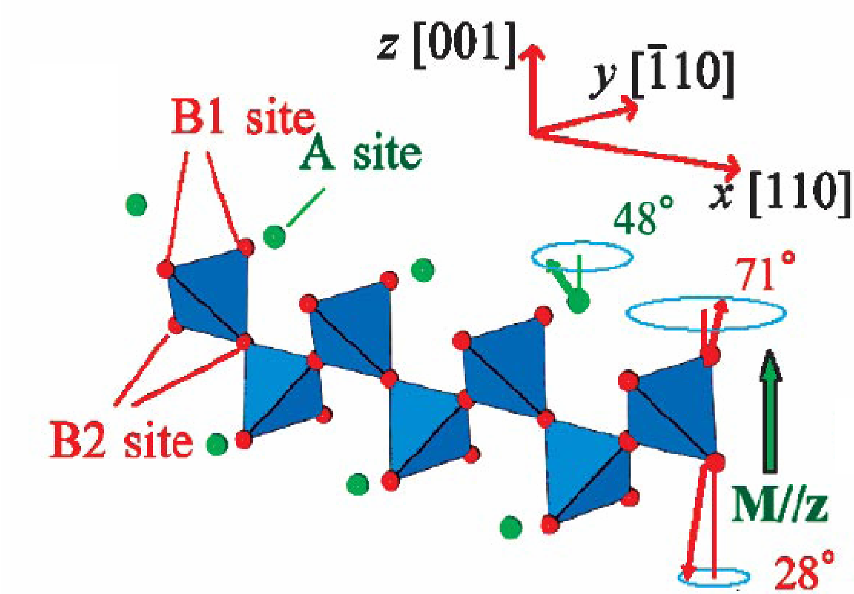


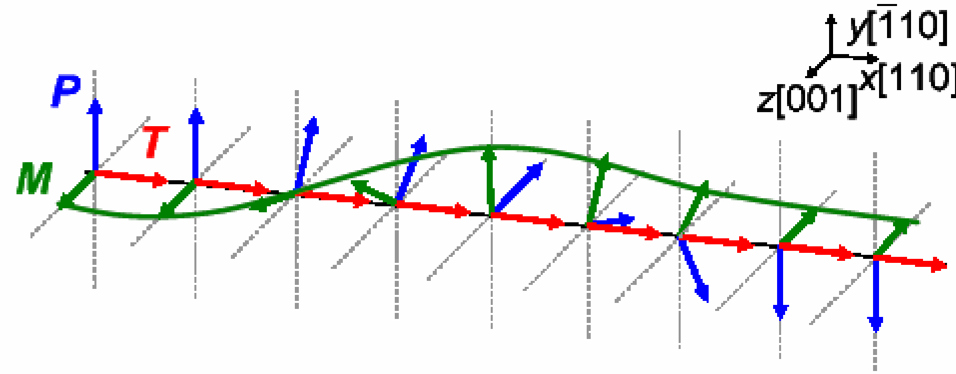
N. Hur et al Nature ***429****, 392 (2004)*

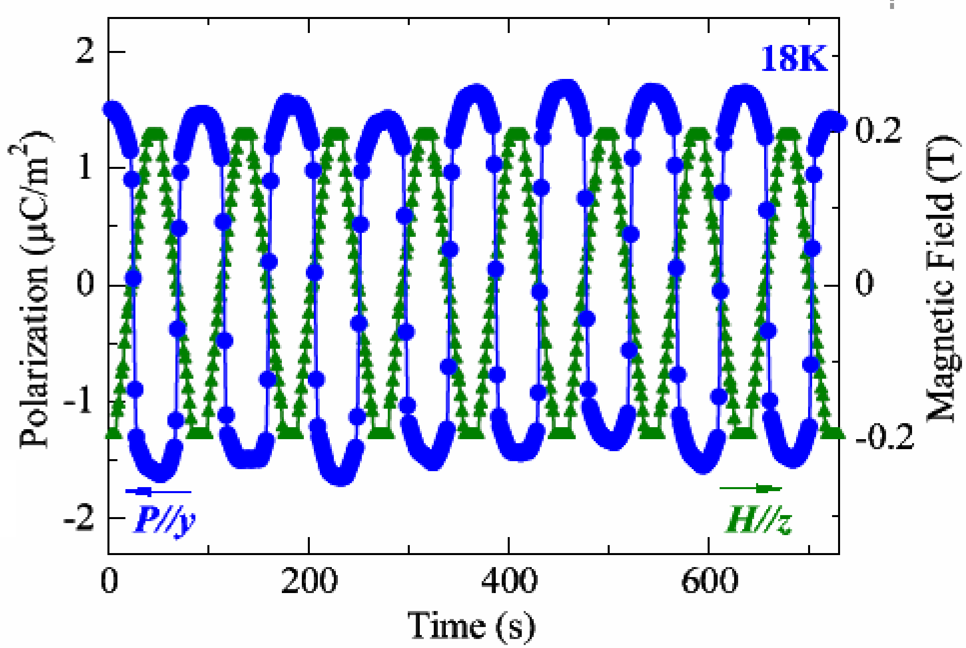
$CoCr_2O_4$

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









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

Outline

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

Linear magnetoelectric effect

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

$$P_i = \alpha_{ij} H_j$$

$$M_i = \alpha_{ji} E_j$$

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

Time-reversal symmetry T (t → - t)
and inversion I (x → - x) are broken

IT symmetry (t → - t, x → - x) is conserved

Cr_2O_3

space group

$R3\bar{c}$

Symmetries of low-T phase

	$\tilde{I}$	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

$$\boxed{\tilde{I} = IT}$$

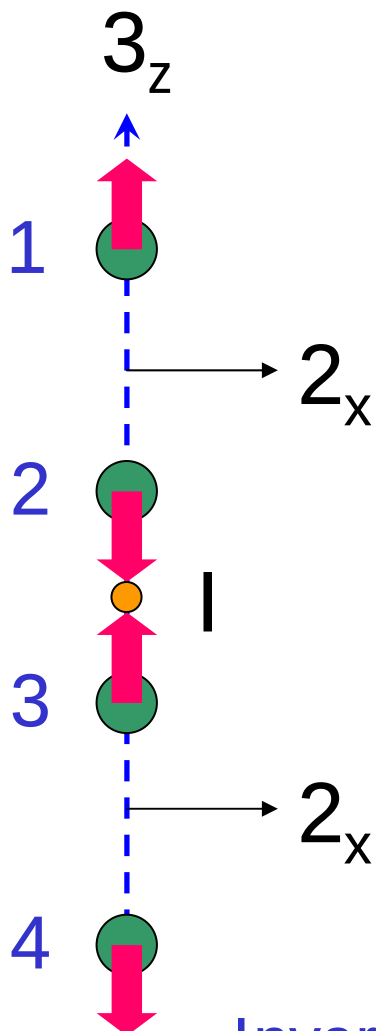
120°-rotation

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

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

Cr_2O_3

$R3\bar{c}$

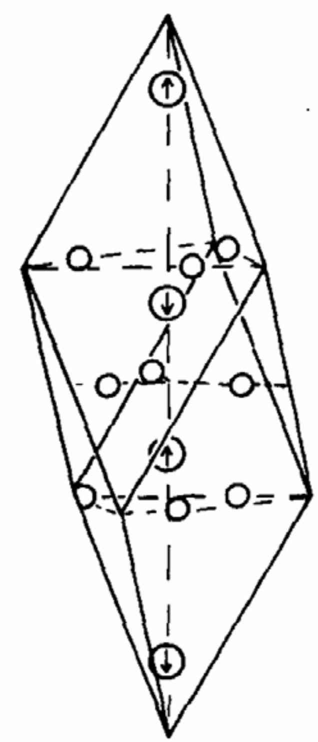


AFM order parameter $T_N = 306K$

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

symmetries of paramagnetic phase

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



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, $CoCr_2O_4$, $MnWO_4$

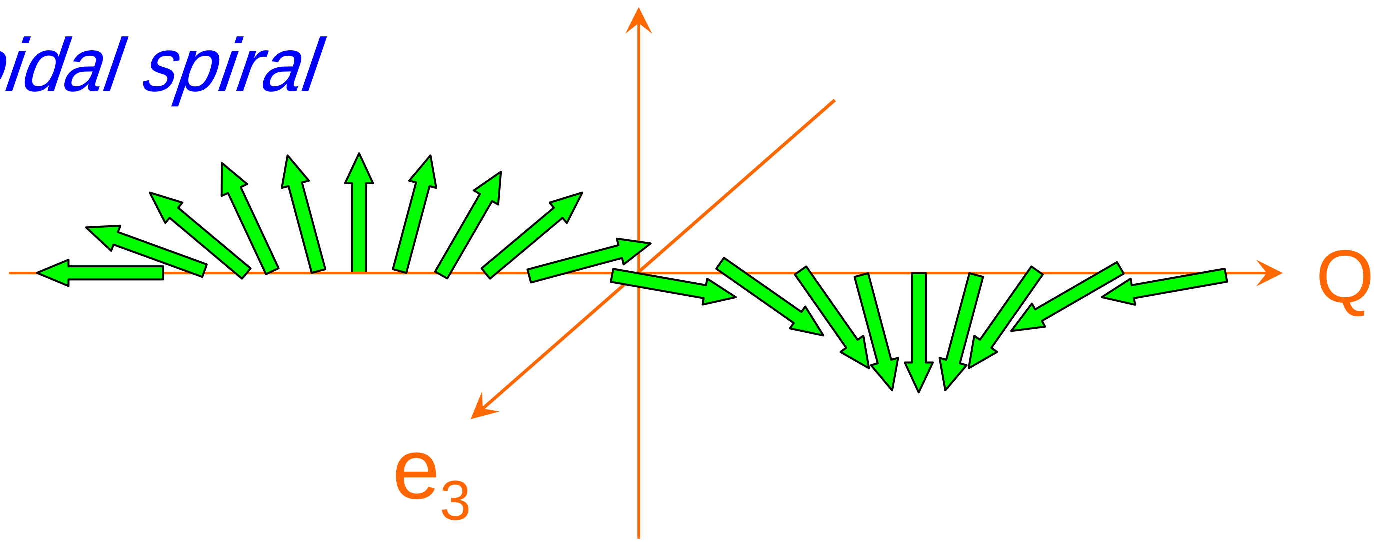
*S.-W. Cheong & M. M. Nature Materials **6**, 13 (2007)*

Novel Multiferroics

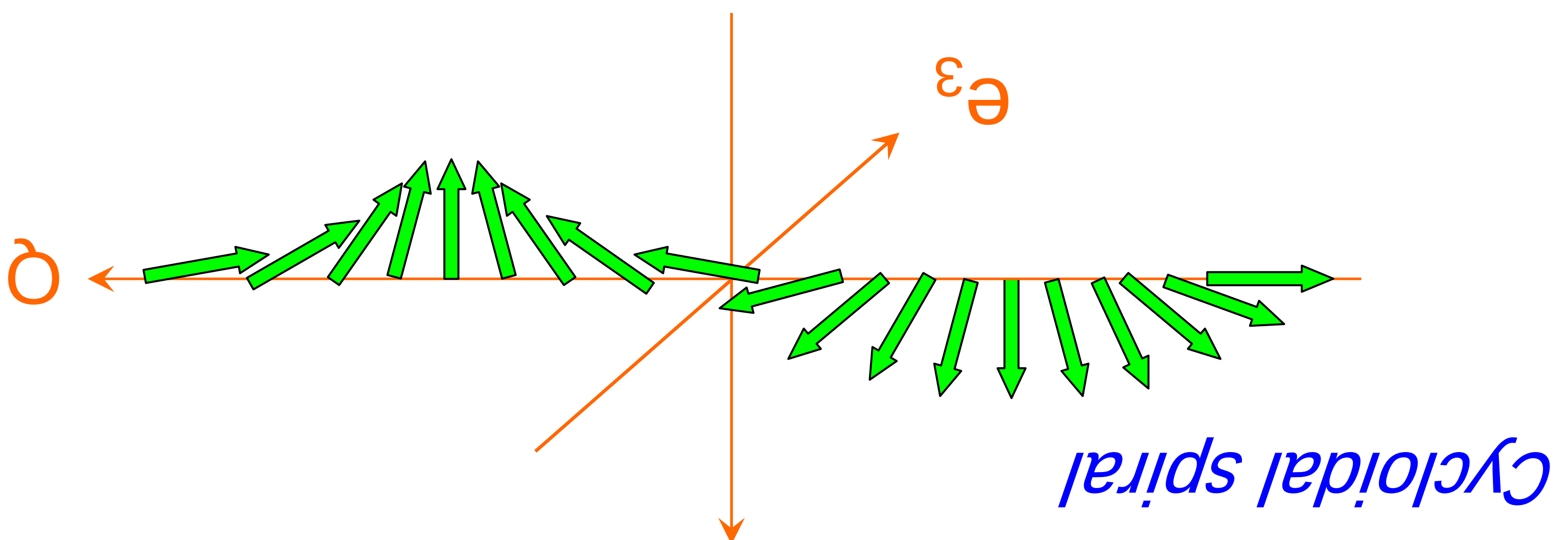
material	T_{FE} (K)	T_M (K)	P(μC m^{-2})
$TbMnO_3$	28	41	600
$TbMn_2O_5$	38	43	400
$Ni_3V_2O_8$	6.3	9.1	100
$MnWO_4$	8	13.5	60
$CoCr_2O_4$	26	93	2
$CuFeO_2$	11	14	300
$LiCu_2O_2$	23	23	5
CuO	230	230	100

Breaking of inversion symmetry by spin ordering

Cycloidal spiral



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

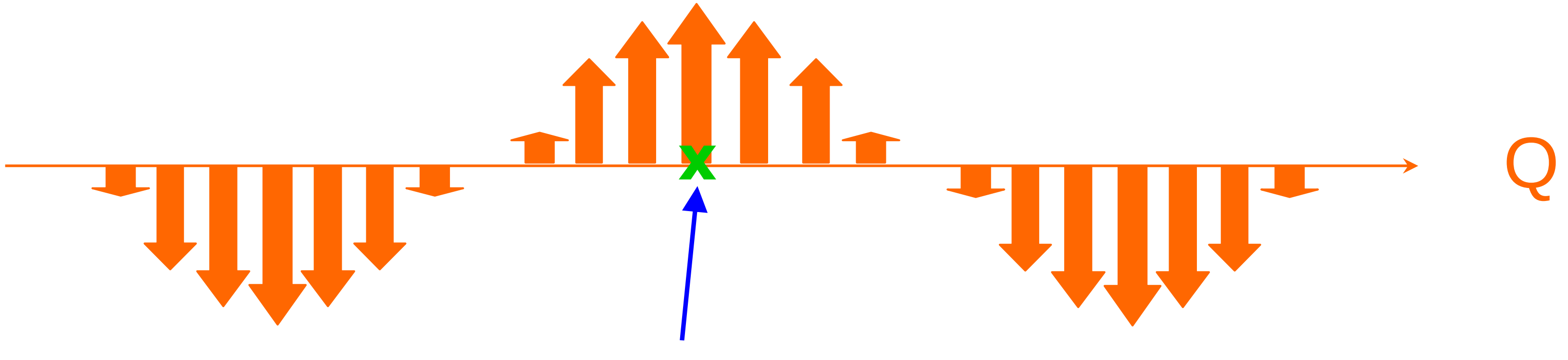
$$\mathbf{P} = \lambda\chi_e\left[(\mathbf{M}\cdot\nabla)\mathbf{M} - \mathbf{M}(\nabla\cdot\mathbf{M})\right]$$

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

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

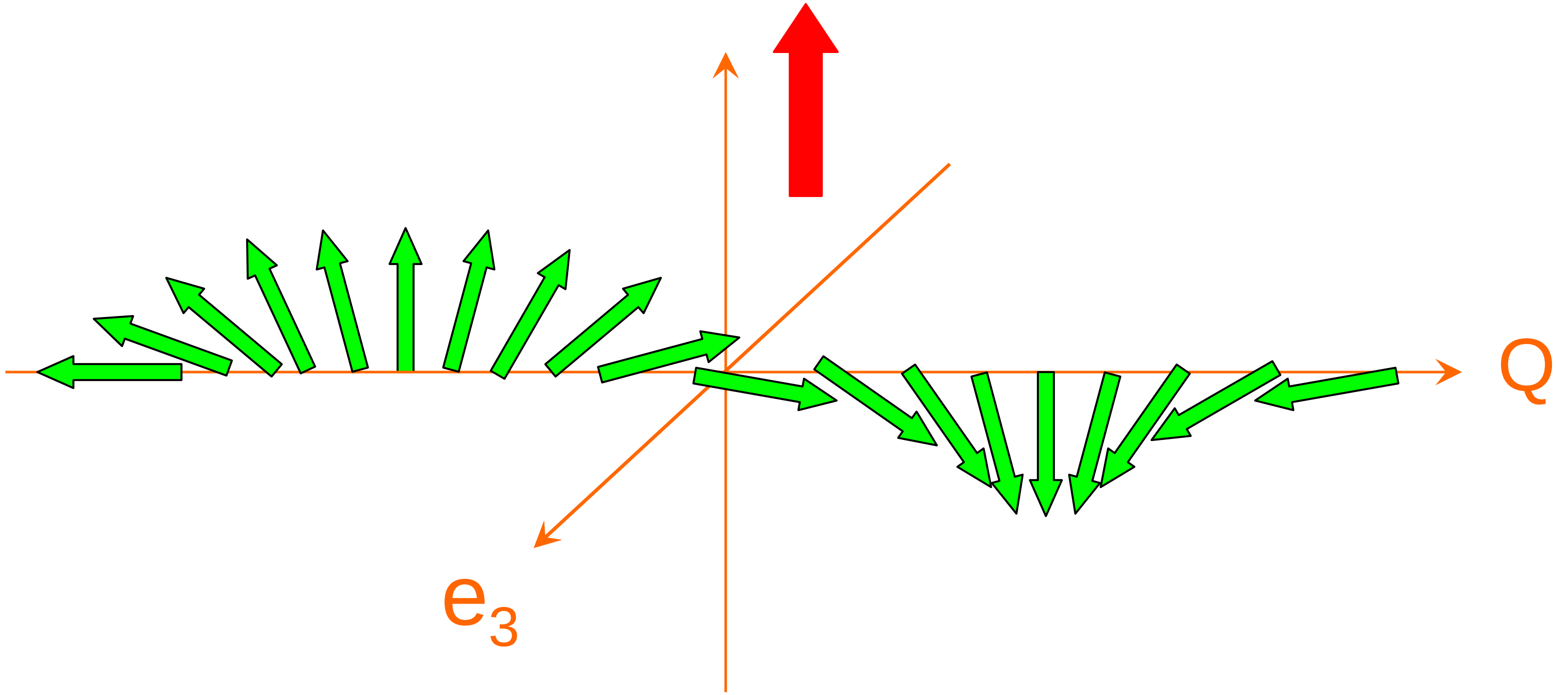
$$\overline{\mathbf{P}} = 0$$



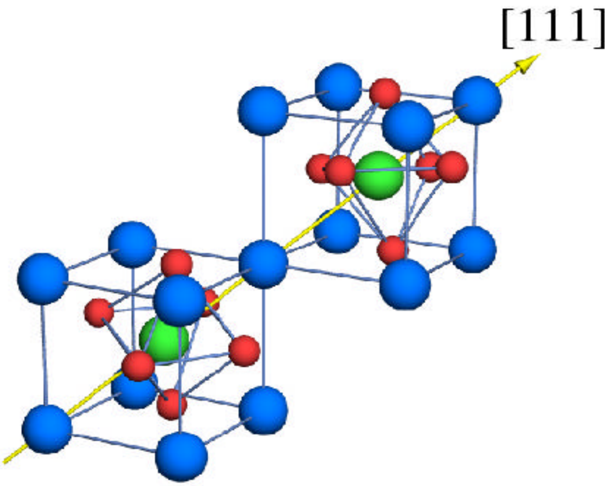
Spiral SDW

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

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



BiFeO$_3$



Ferroelectric $T_{FE} = 1100$ K

Antiferromagnetic $T_N = 640$ K

Free energy

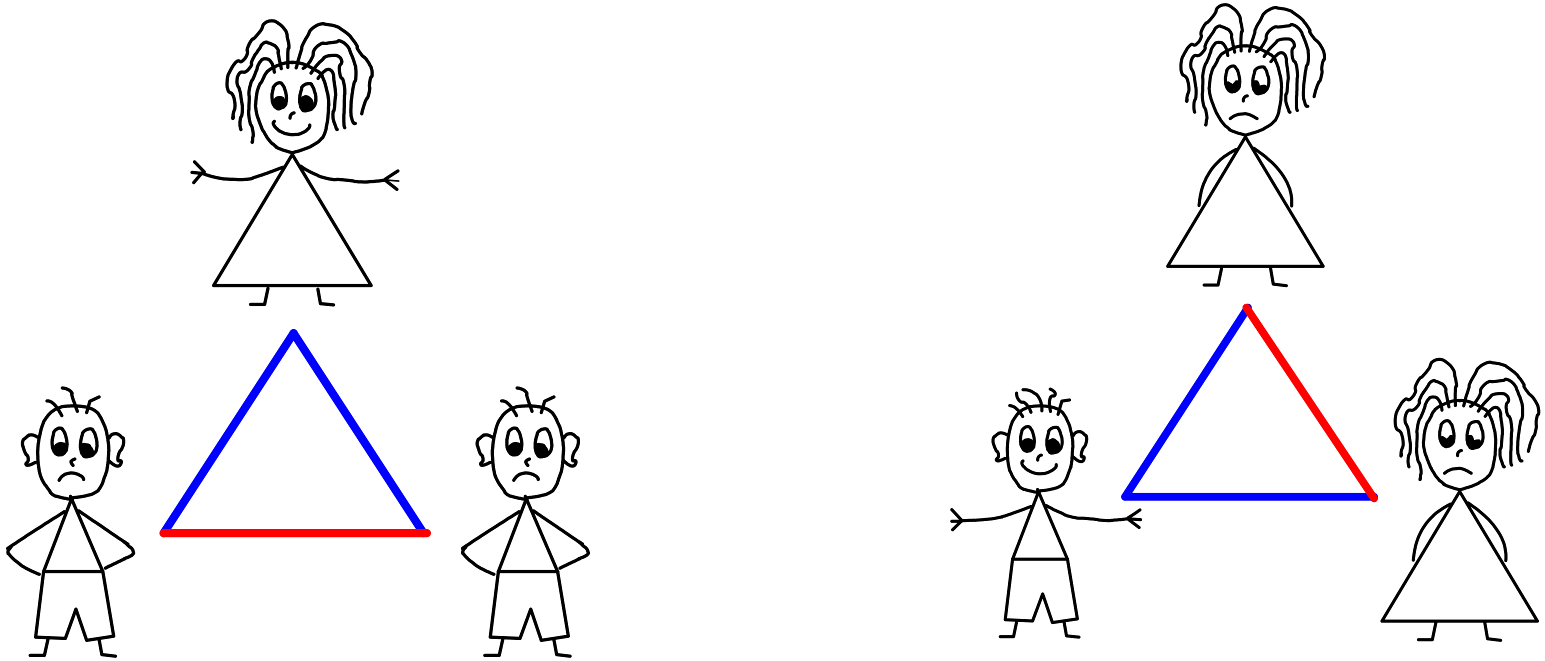
$$\boxed{F = \varphi(L) + (\partial L)^2 - \lambda\, PL\partial L}$$

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

Geometrical Frustration

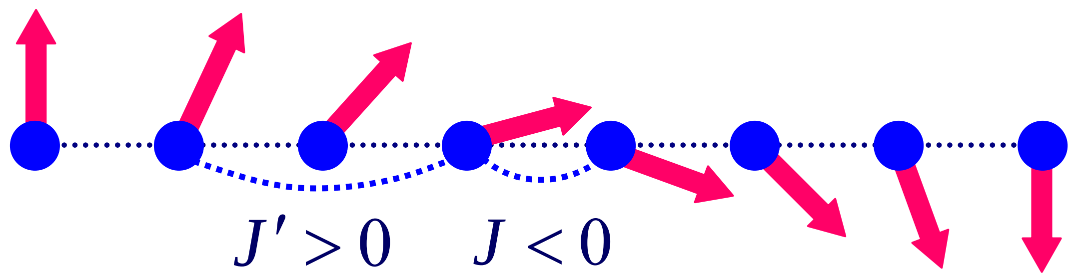


Competing interactions

Frustrated Heisenberg chain

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

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



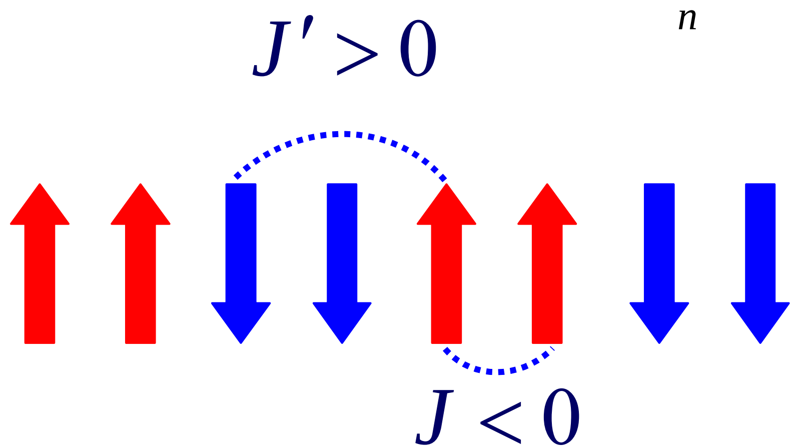
$$\cos Q = \frac{|J|}{4J'}$$

Frustrated Ising chain

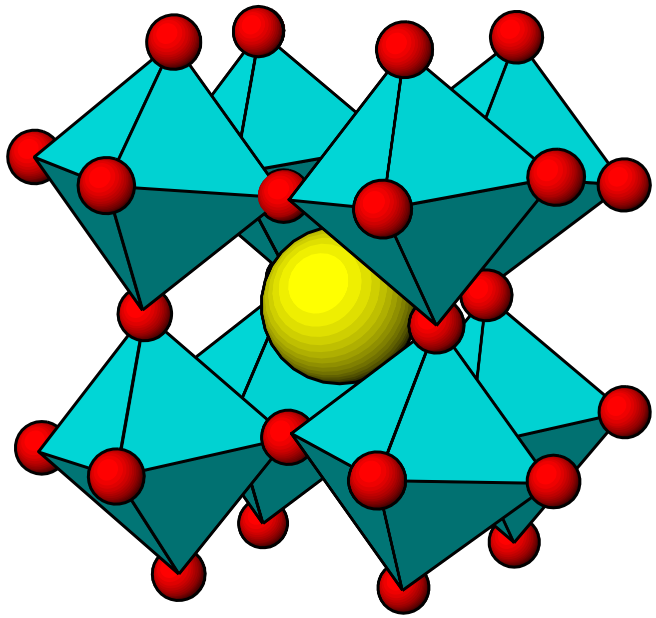
$$E = \sum_n \left[J\,\sigma_n \sigma_{n+1} + J'\,\sigma_n \sigma_{n+2} \right]$$

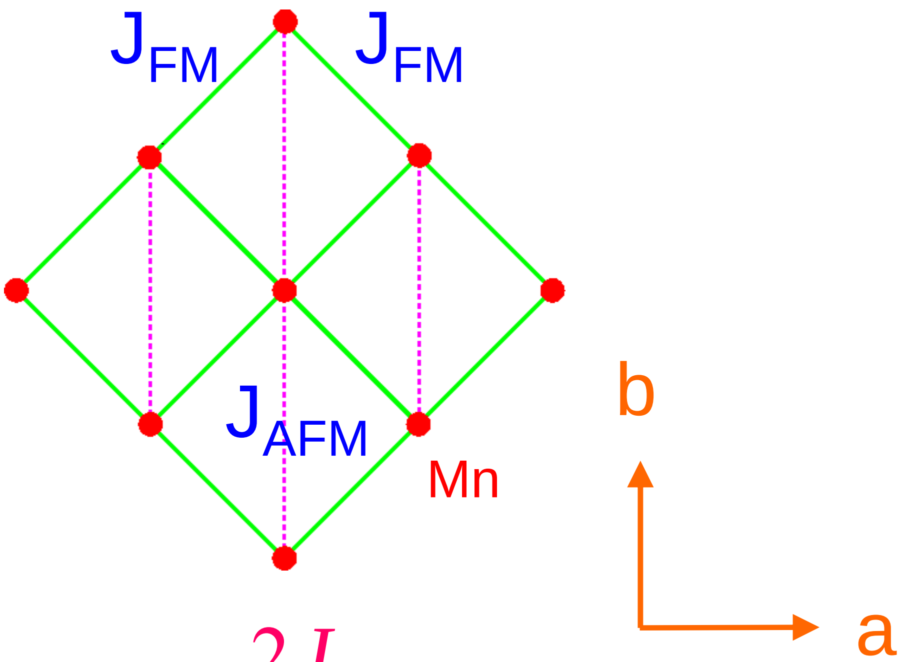
$$\sigma_n = \pm 1$$

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



Magnetic frustration in $RMnO_3$





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

$\kappa < 1$ **Ferromagnetic**

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

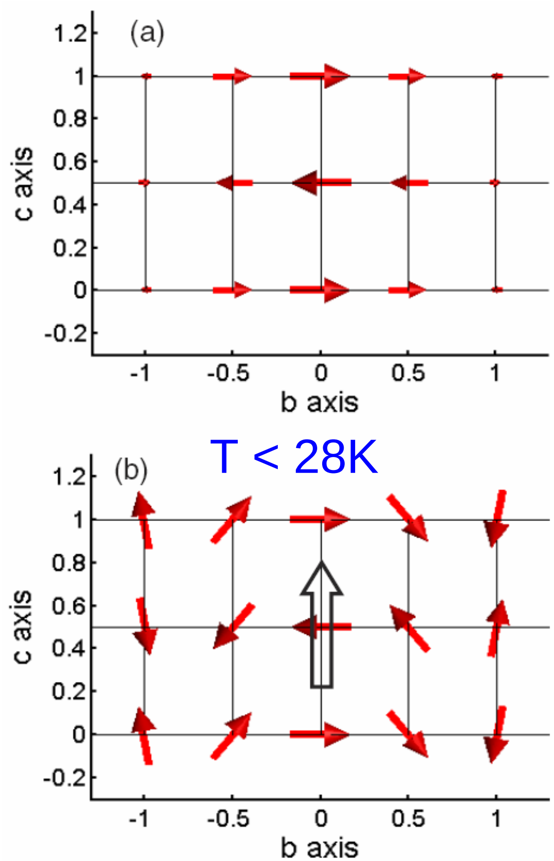
$$\cos\frac{Q_b}{2} = \frac{1}{\kappa}$$

Why T_{FE} is lower than T_M?

$TbMnO_3$

28K < T < 41K

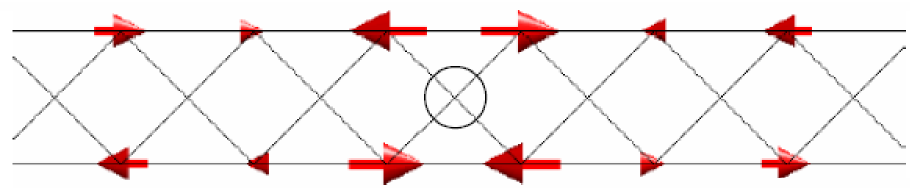
T < 28K



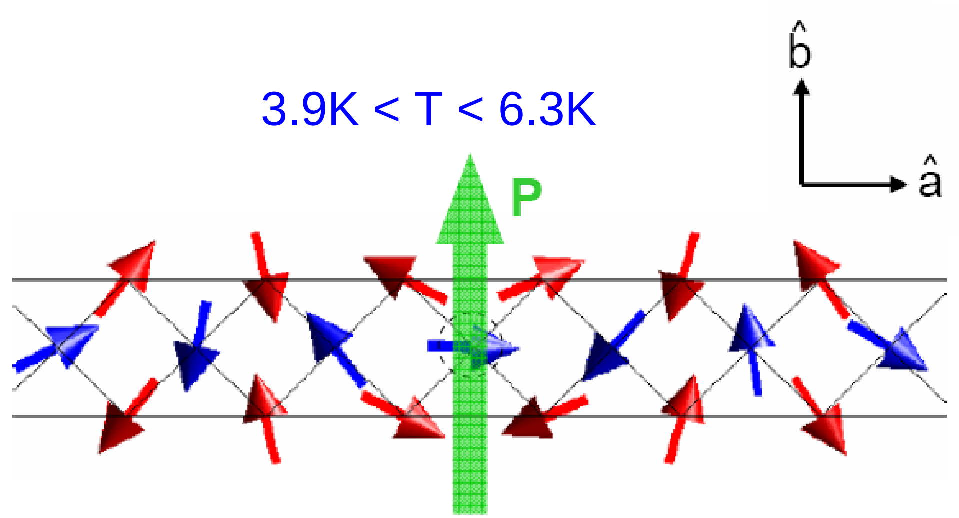
M. Kenzelmann et al PRL ***95****, 087206 (2005)*

$Ni_3V_2O_8$

6.3K < T < 9.1K



3.9K < T < 6.3K



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

Sinusoidal-helicoidal transition

Ginzburg-Landau expansion

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

Anisotropy:

$$\boxed{a_x < a_y = a_x + \Delta < a_z}$$

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

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

P = 0

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

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

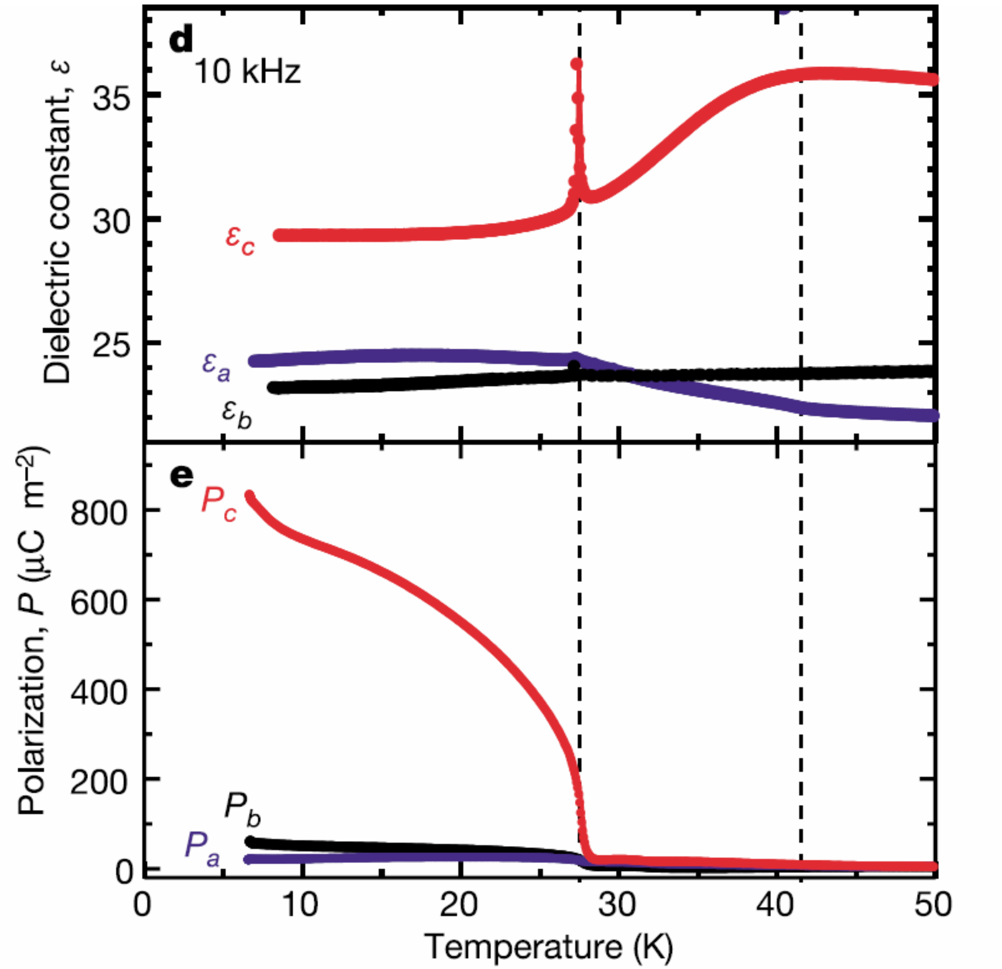
$$\boxed{T_{SP} = T_{SDW} - \frac{3}{2}\frac{\Delta}{\alpha}}$$

P || y

Dielectric constant anomaly at the transition to spiral state

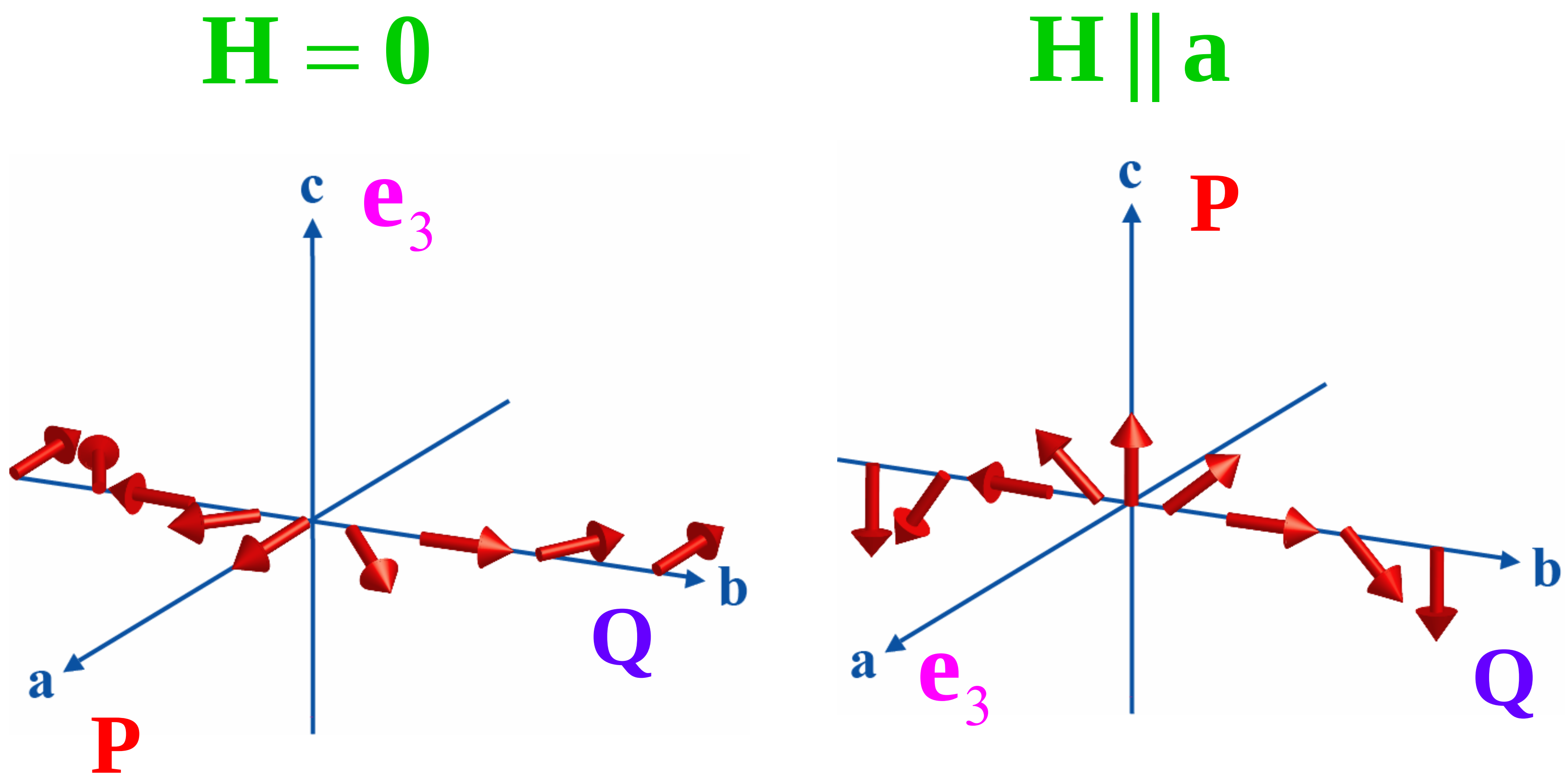
$$\varepsilon_{yy} = \begin{cases} \dfrac{A}{T - T_{SP}}, & T > T_{SP} \\ \dfrac{1}{2}\dfrac{A}{T_{SP} - T}, & T < T_{SP} \end{cases}$$

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



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

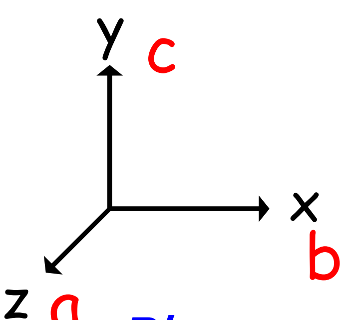
Polarization Flop in $Eu_{1-x}Y_xMnO_3$



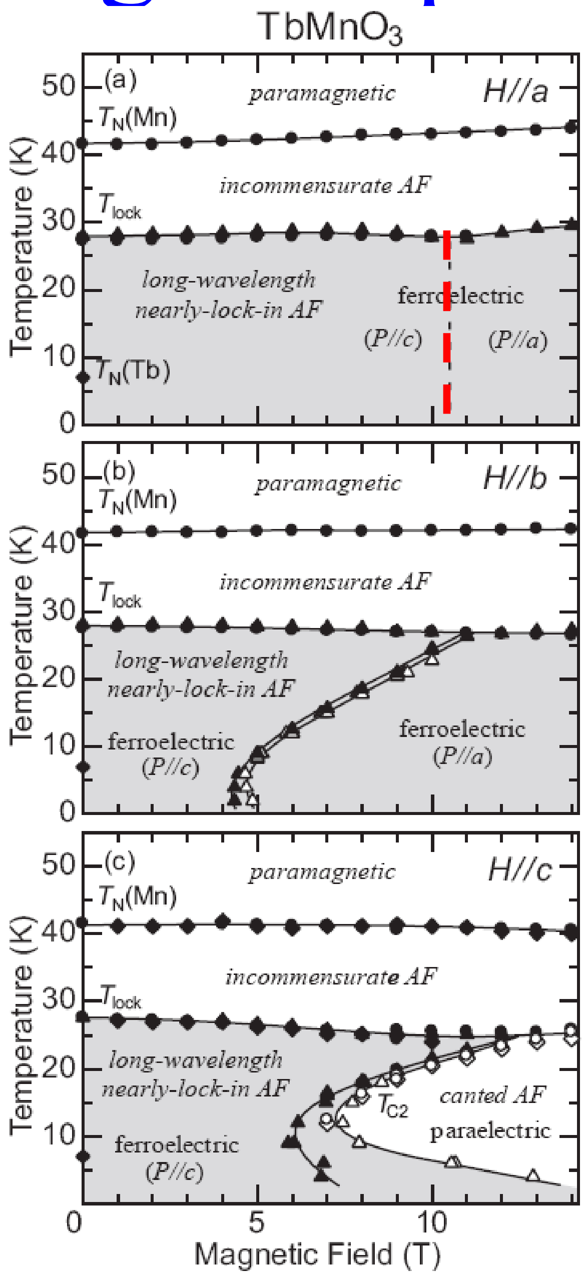
$$\mathbf{P} \propto \mathbf{e}_3 \times \mathbf{Q}$$

Spin flops **Polarization flops**

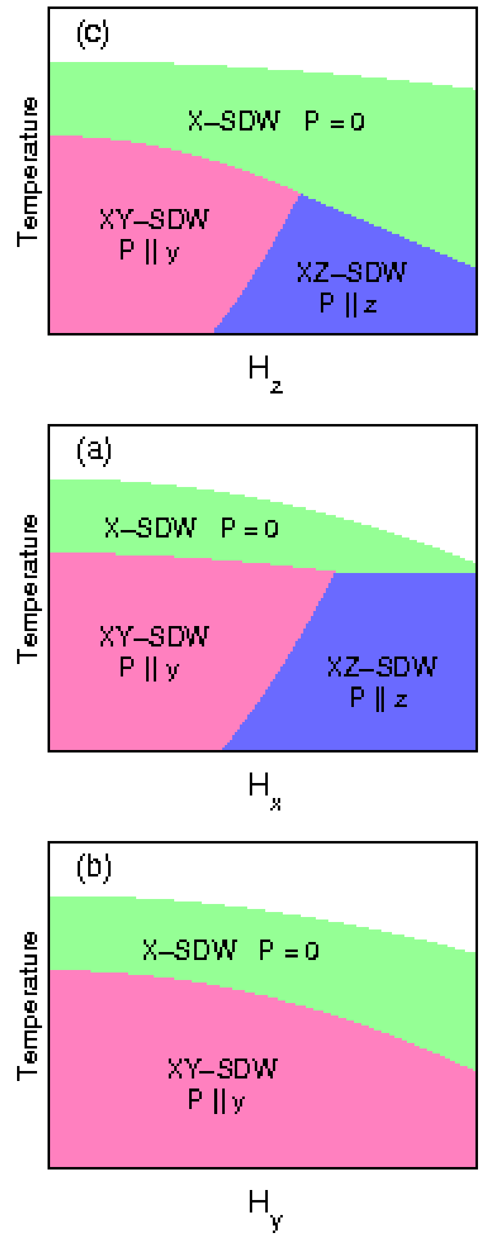
Magnetic phase diagrams



Pbnm



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

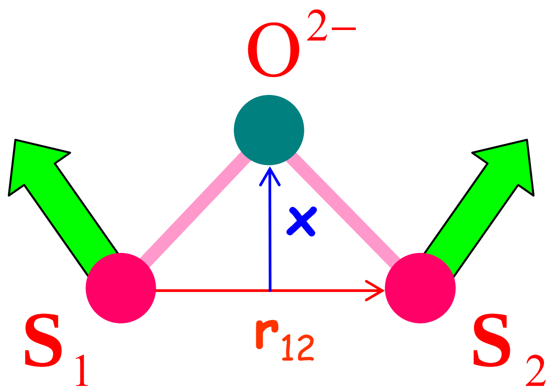


*M.M. PRL **96**, 067601 (2006)*

Outline

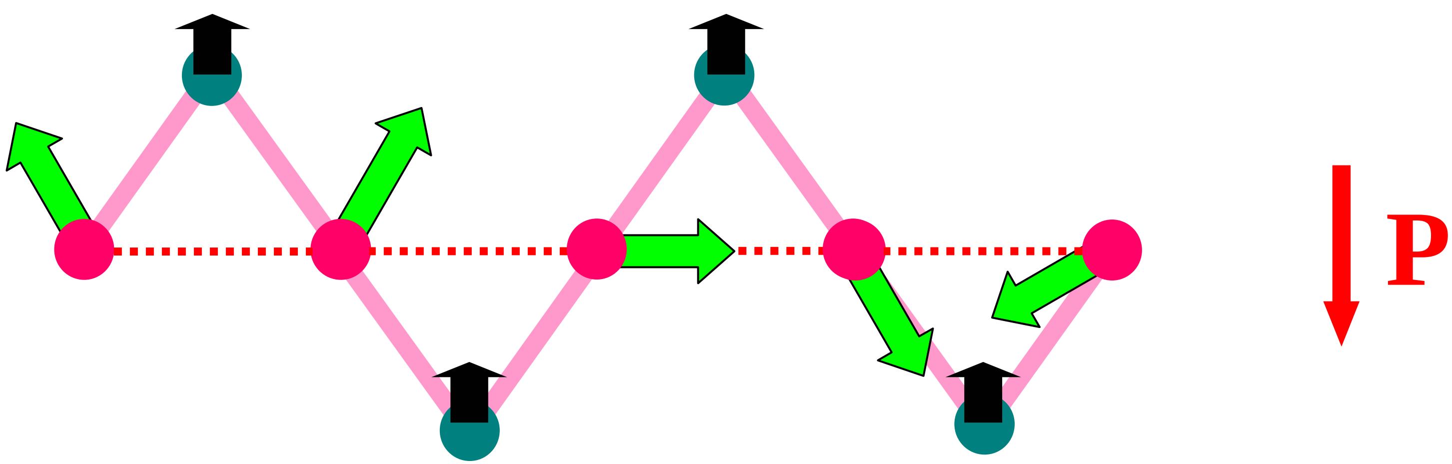
- Linear magnetoelectric effect, multiferroics
- Phenomenological description
- Microscopic mechanisms of magnetoelectric coupling
- Outlook

Effects of Dzyaloshinskii-Moriya interaction



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

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

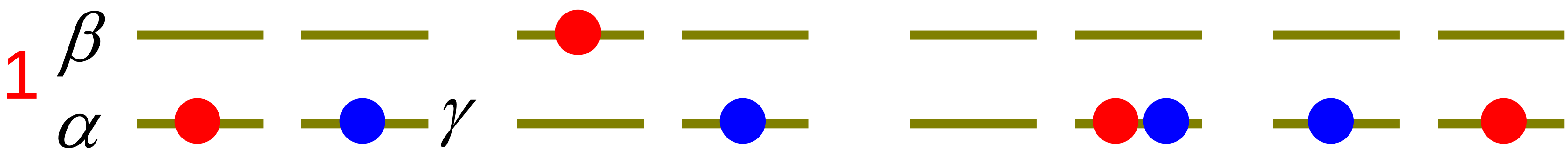


H. Katsura et al PRL ***95*** *057205 (2005),*
Sergienko & Dagotto PRB ***73*** *094434 (2006)*

Dzyaloshinskii-Moriya interaction

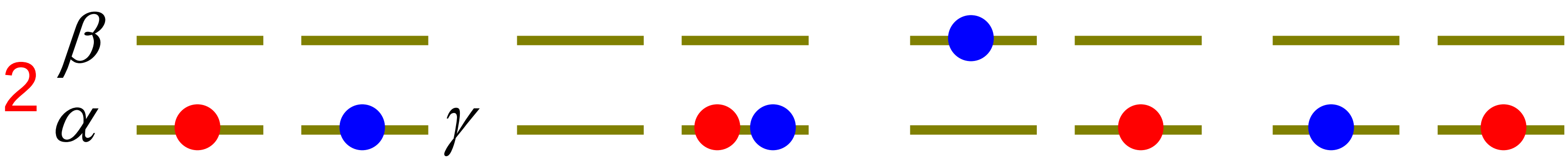
$$H_{SO} = \lambda(\mathbf{l}\cdot\mathbf{s})$$

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



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

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



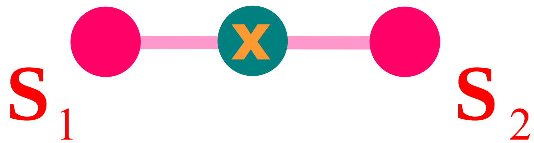
real wave functions

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

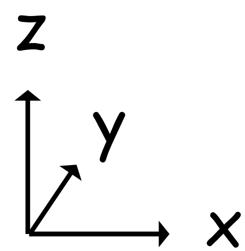
$$\delta H_{ex} \propto [S_{12}, \mathbf{s}_1] = \left[2\mathbf{s}_1\cdot\mathbf{s}_2 + \frac{1}{2}, \mathbf{s}_1\right] \propto \mathbf{s}_1\times\mathbf{s}_2$$

Moriya rules

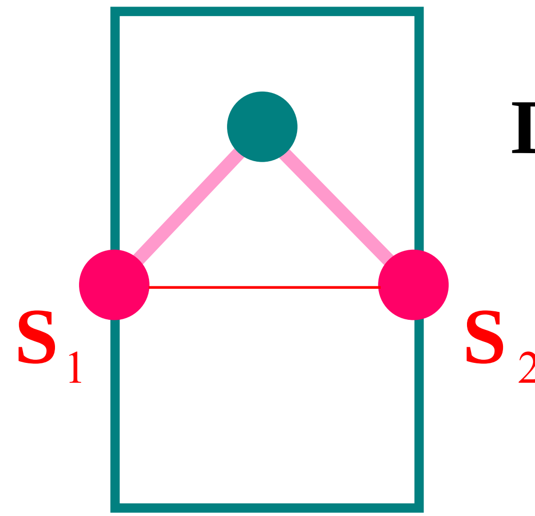
Inbersion center



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

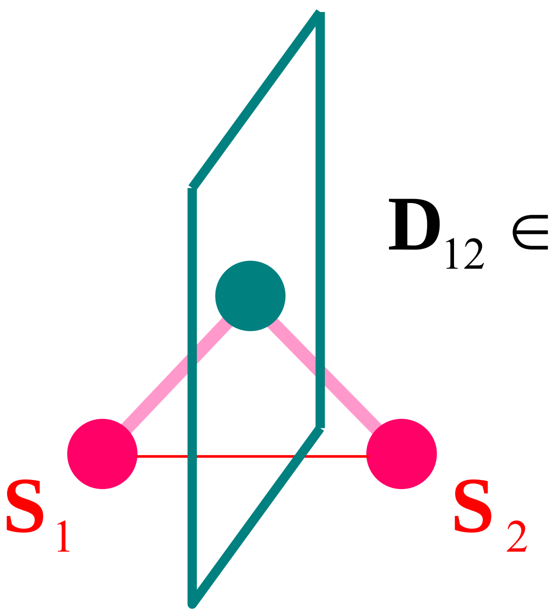


mirror xz plane

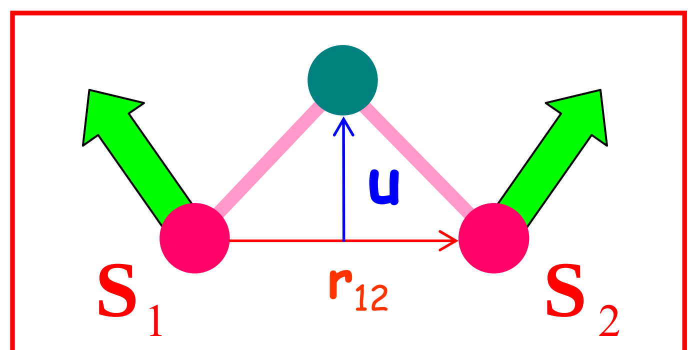


$$\mathbf{D}_{12} \perp xz$$

mirror yz plane



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



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

Ferroelectricity induced by magnetostriction

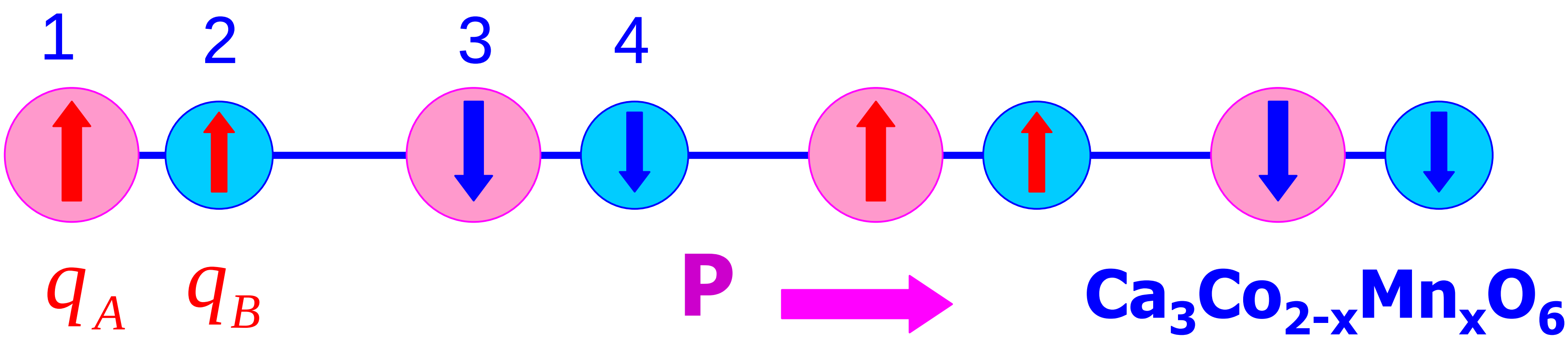
$$\Phi_{\text{int}} = -\lambda P\left(L_1{}^2 - L_2{}^2\right)$$

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

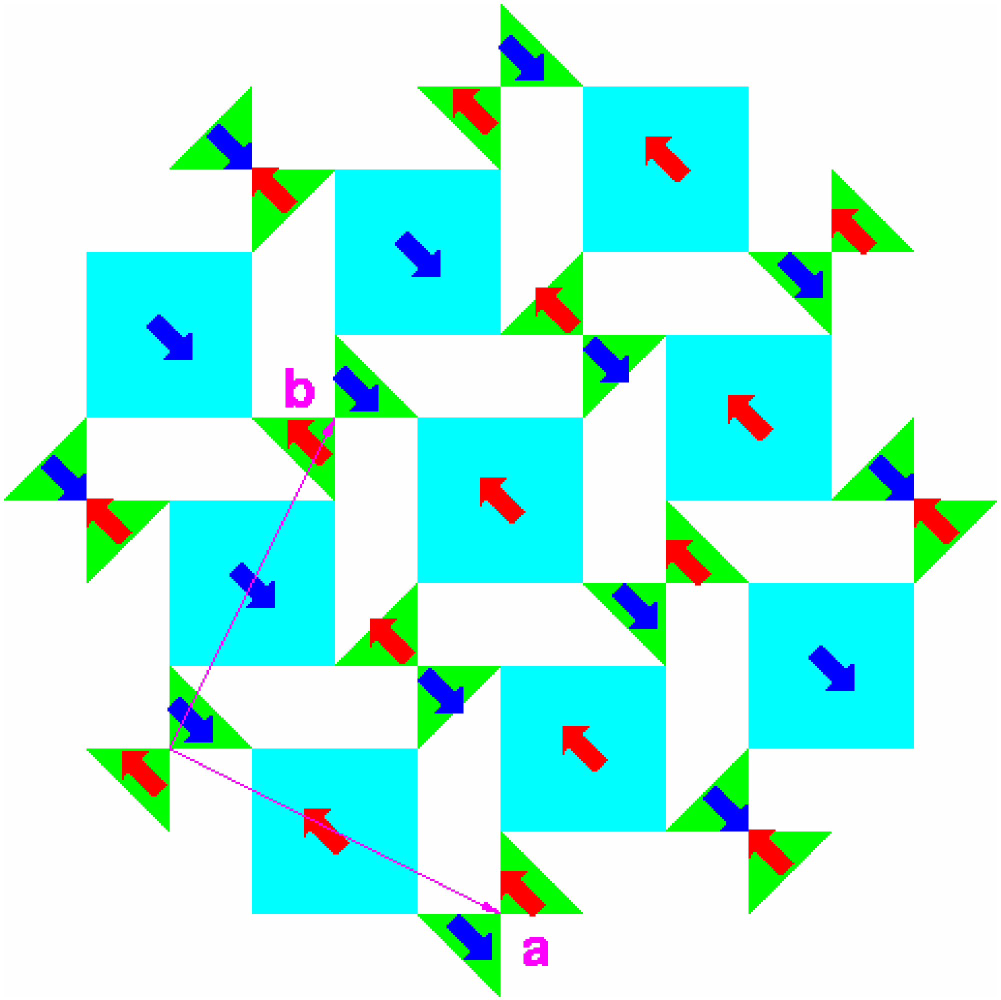
$$\mathbf{L}_1 = \mathbf{S}_1 + \mathbf{S}_2 - \mathbf{S}_3 - \mathbf{S}_4$$

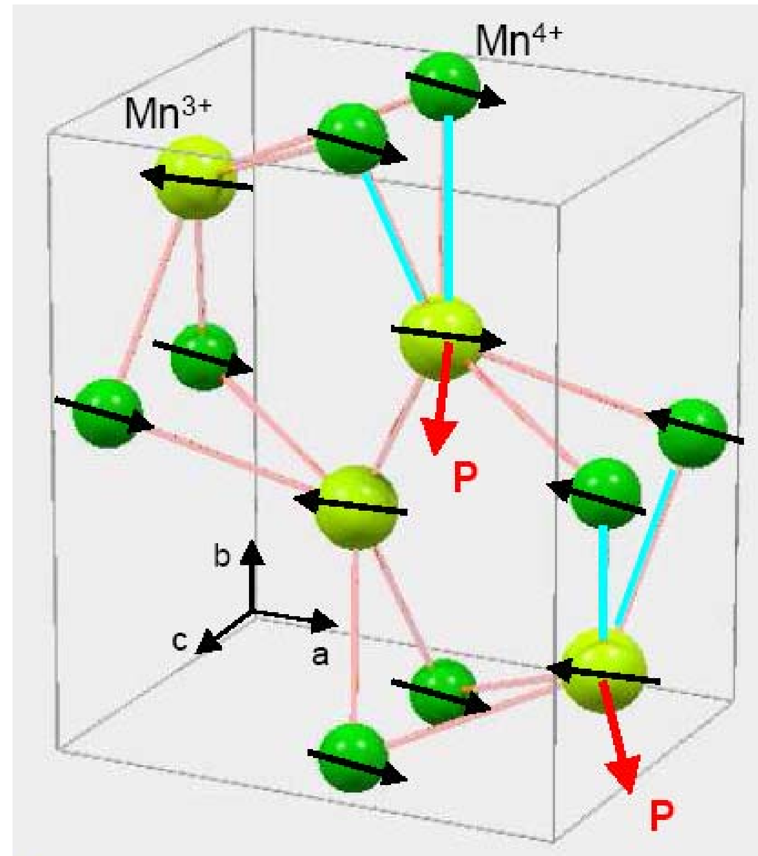
$$\mathbf{L}_2 = \mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3 + \mathbf{S}_4$$

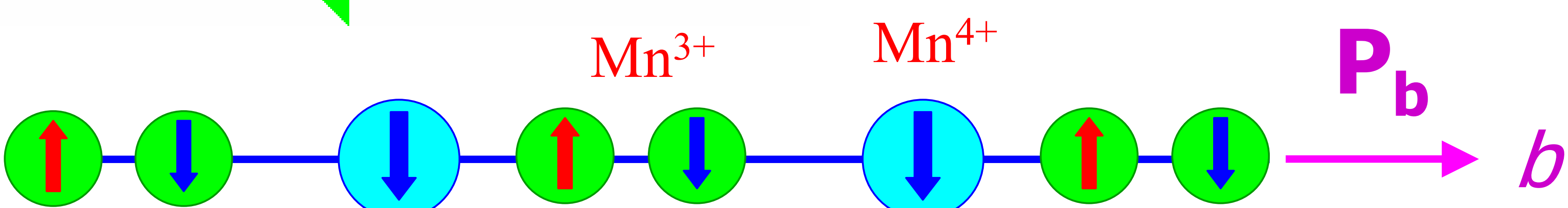
$$P \propto L_1{}^2 - L_2{}^2$$



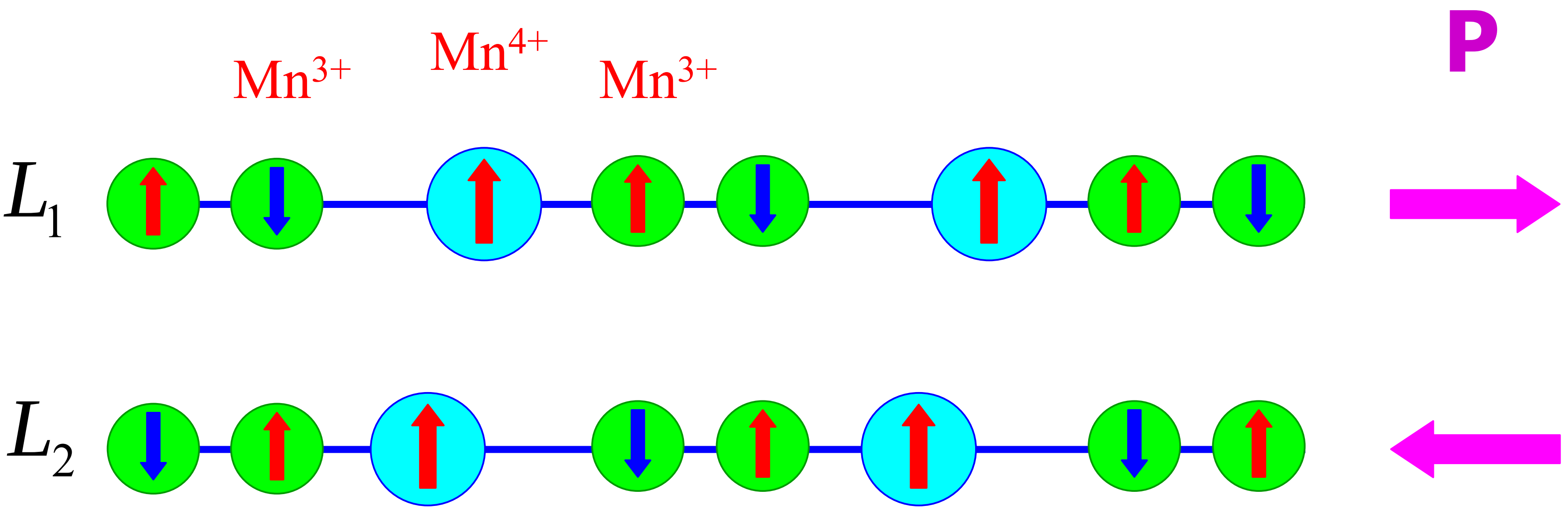
RMn_2O_5





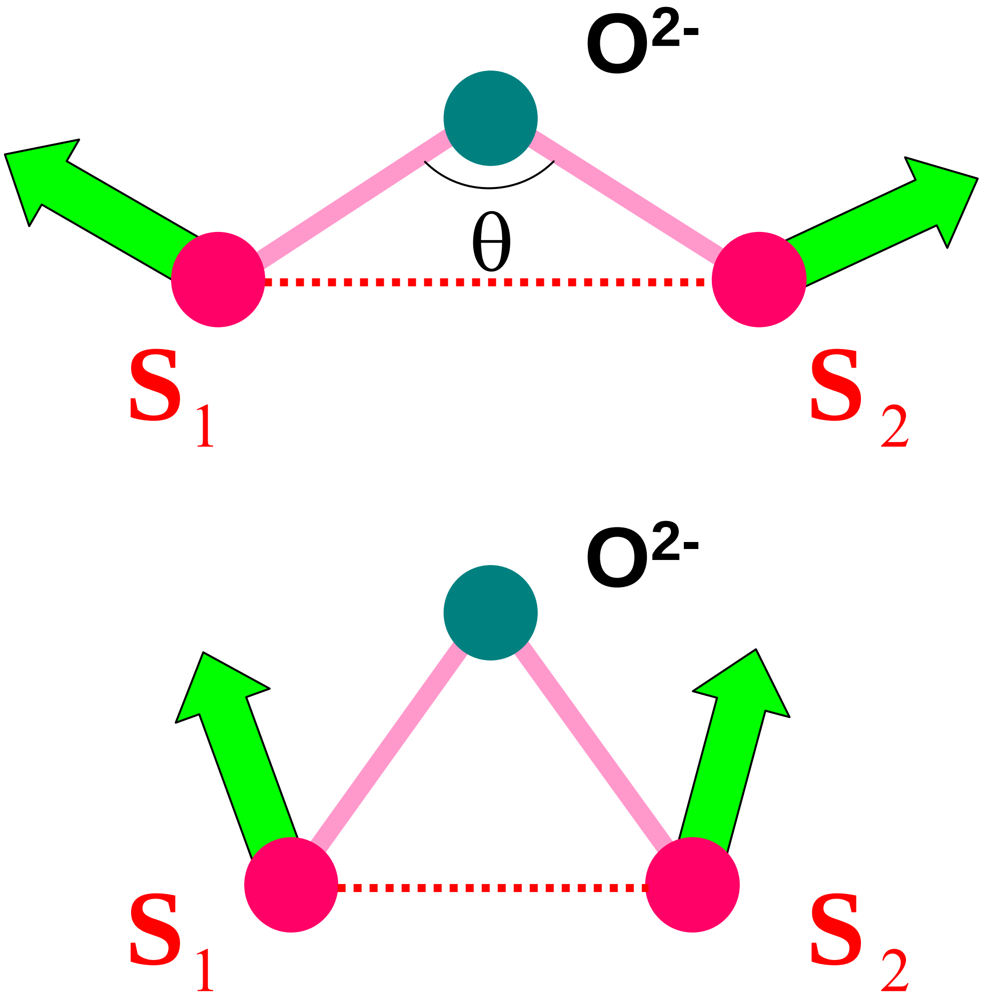


Two-dimensional representation and induced polarization



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

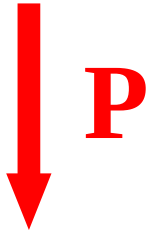
Exchange striction



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

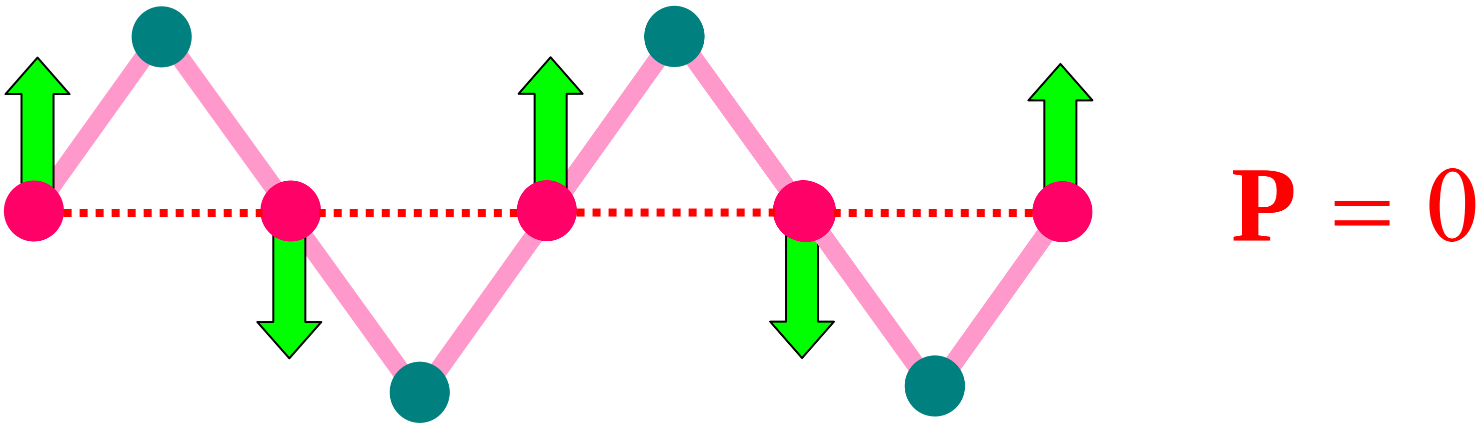
$\theta = 180^o \quad J > 0$

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

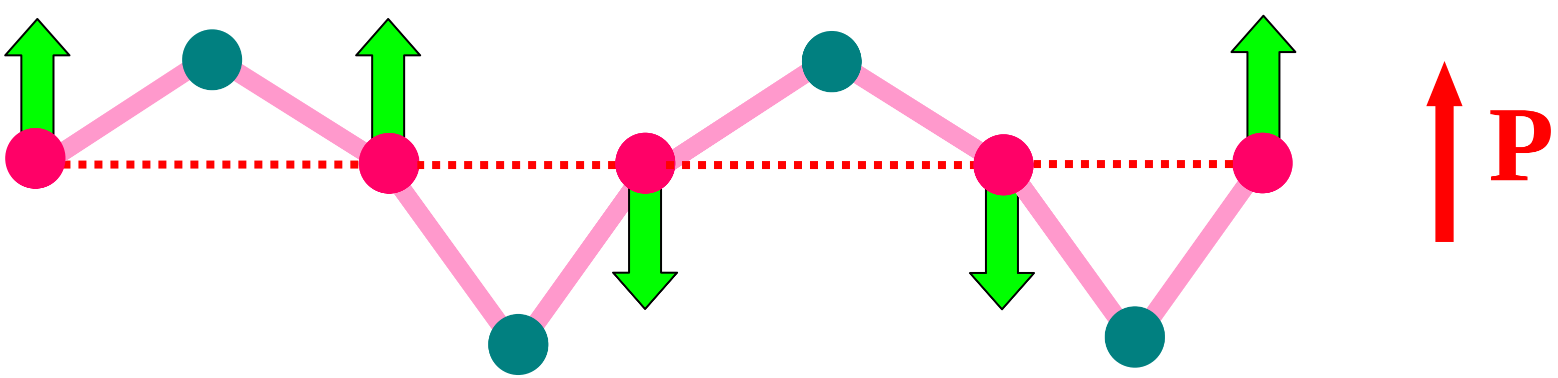


Role of frustration

Néel ordering: Inversion symmetry not broken



↑↑↓↓ ordering: Inversion symmetry is broken



To induce P spin ordering must break inversion symmetry

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

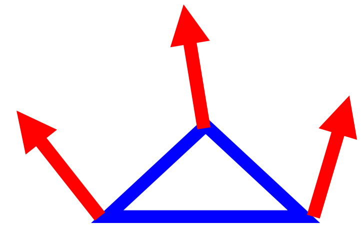
$$H = \sum_{i \neq j, \sigma} t e^{-\frac{2\pi i}{\Phi_0} \int_{\mathbf{x}_i}^{\mathbf{x}_j} d\mathbf{x} \cdot \mathbf{A}} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U}{2} \sum_i (n_i - 1)^2$$

$$- e \sum_i \varphi_i n_i + \mu_B \sum_{i\alpha\beta} c_{i\alpha}^{\dagger} \mathbf{H} \cdot \sigma_{\alpha\beta} c_{i_\beta},$$

Effective spin Hamiltonian (2nd order)

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

Effective spin Hamiltonian
(3[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)

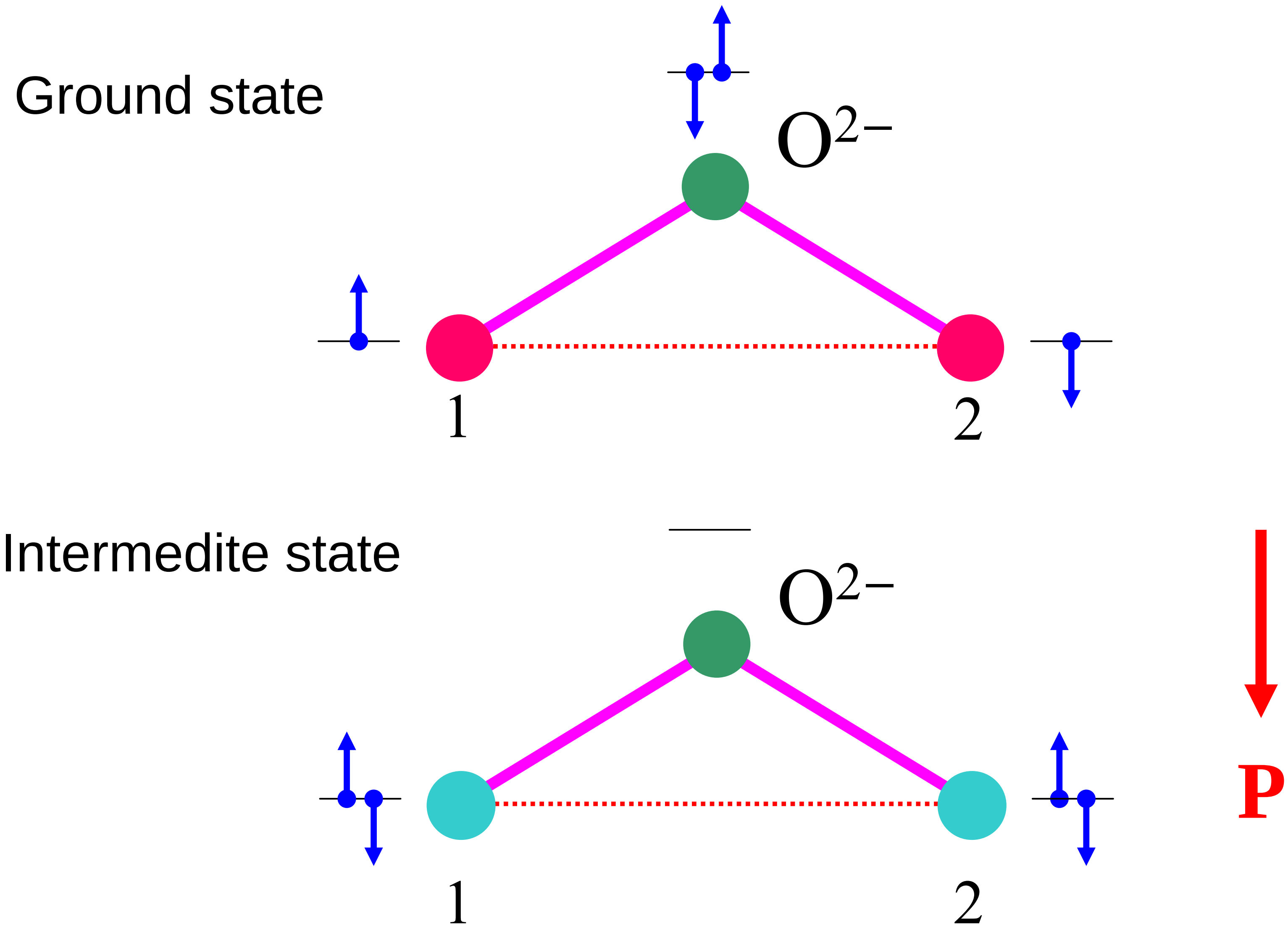
Interaction with electric field

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

Spin-induced charge

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

Polarization of electronic orbitals



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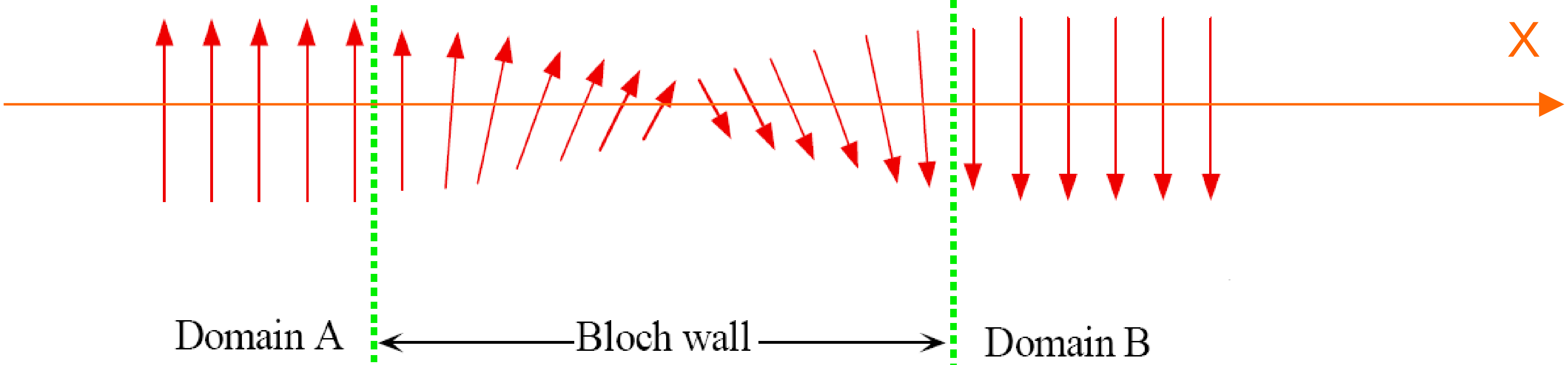
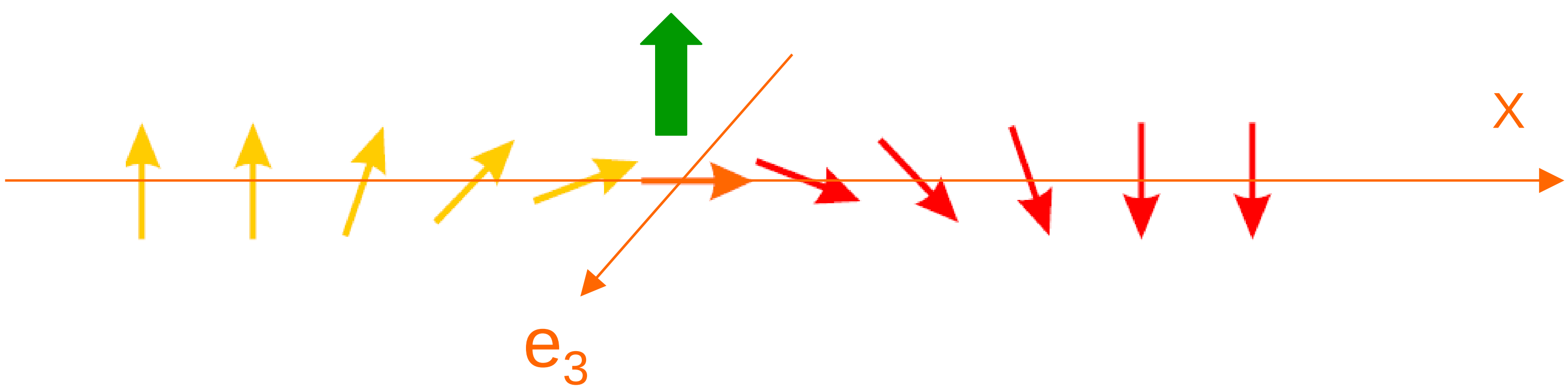
Polarization of domain walls

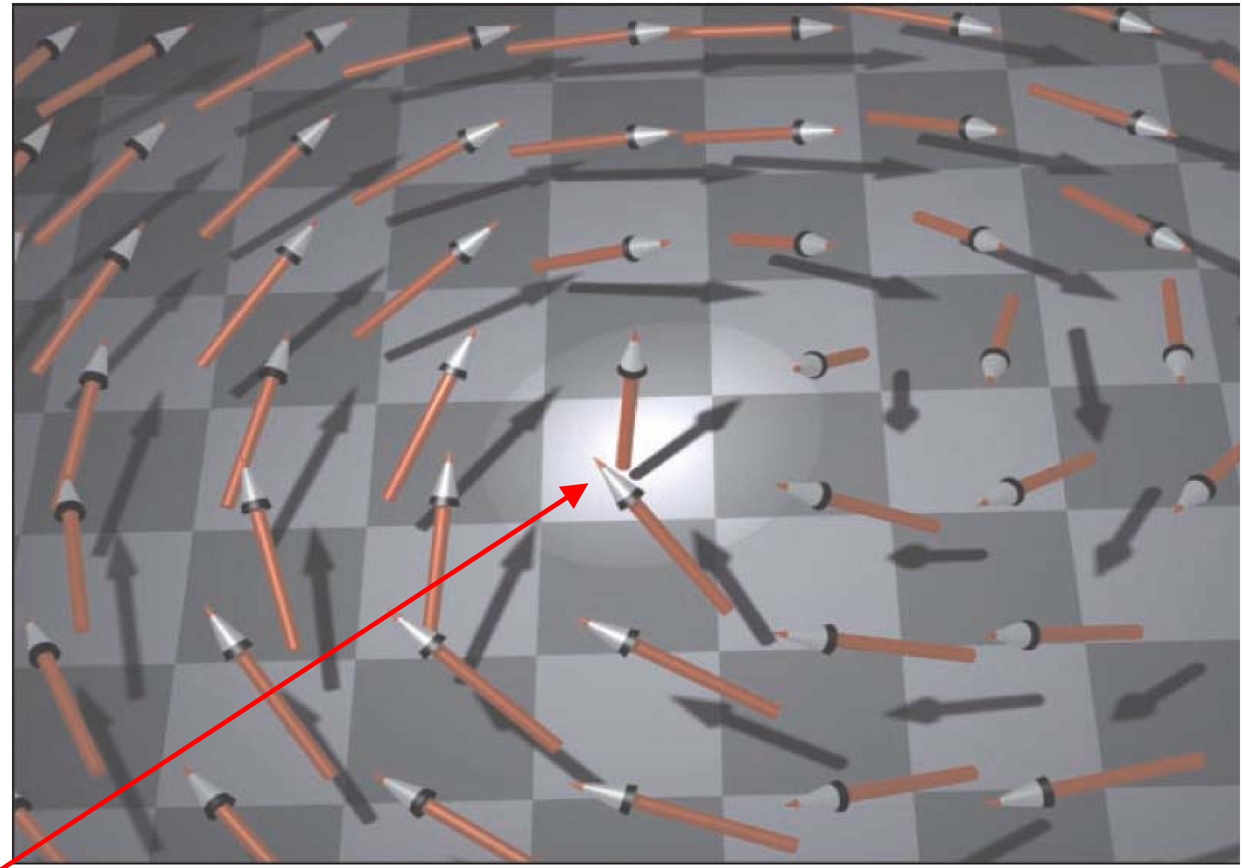
Bloch wall $\mathbf{P} = 0$ $\mathbf{e}_3 \parallel \hat{\mathbf{x}}$



Néel wall $\mathbf{P} \parallel [\mathbf{e}_3 \times \hat{\mathbf{x}}]$ $\mathbf{e}_3 \perp \hat{\mathbf{x}}$



Electric charge of magnetic vortex



Charge in the vortex core

Electrostatics of magnetic defects

Easy plane spins: $$\mathbf{M} = M\left[\mathbf{e}_1 \cos\varphi + \mathbf{e}_2 \sin\varphi\right]$$

Polarization: $$P_b = -\gamma\chi_e M^2 \varepsilon_{ab}\partial_b\varphi$$

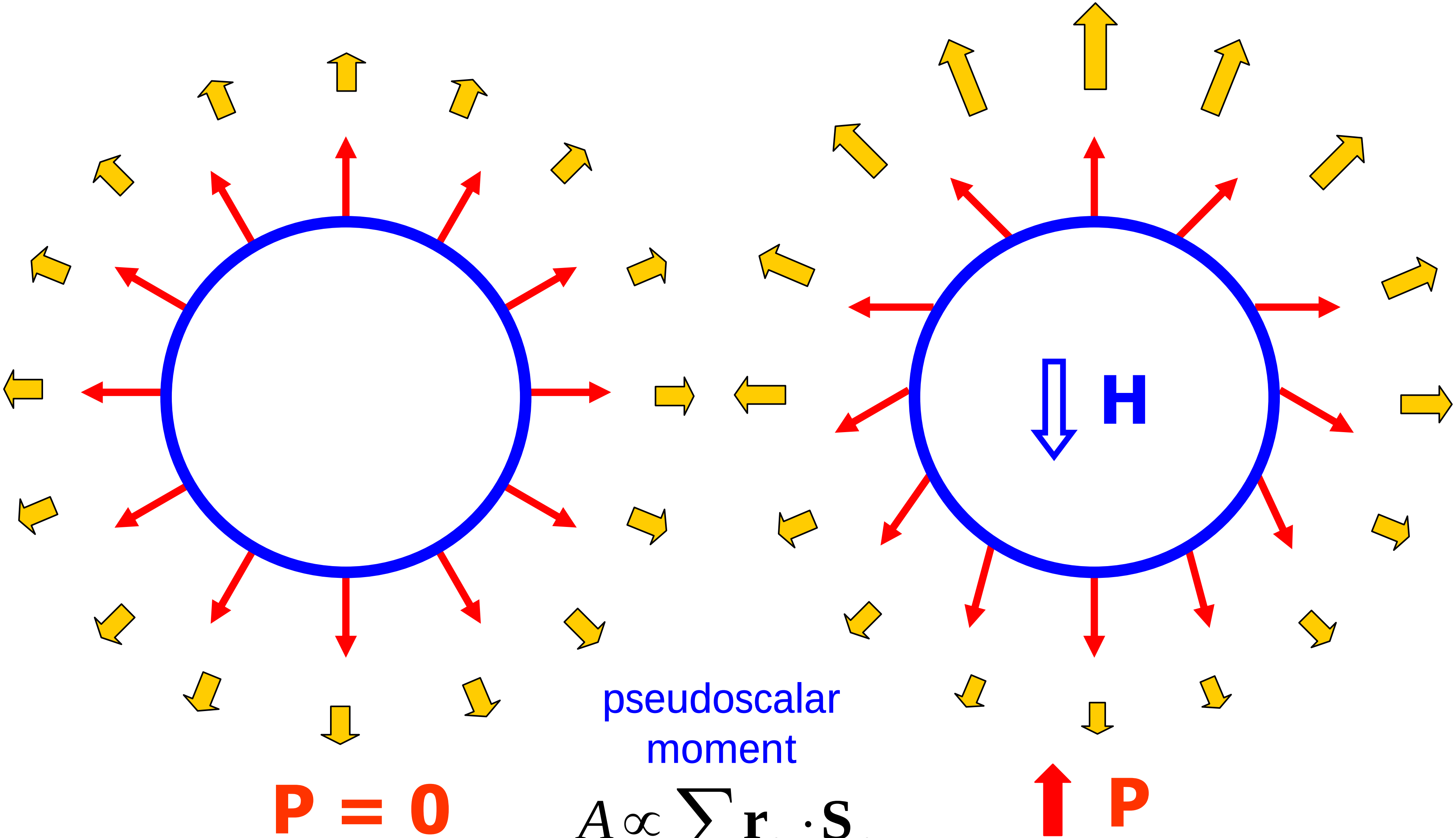
Total polarization of domain wall:

$$\int dx P_y = \gamma\chi_e M^2\left[\varphi(+\infty) - \varphi(-\infty)\right]$$

Charge density: $$\rho = -\mathrm{div}\mathbf{P} = 2\pi\gamma\chi_e M^2 \Gamma \delta^{(2)}(\mathbf{x}_\perp)$$

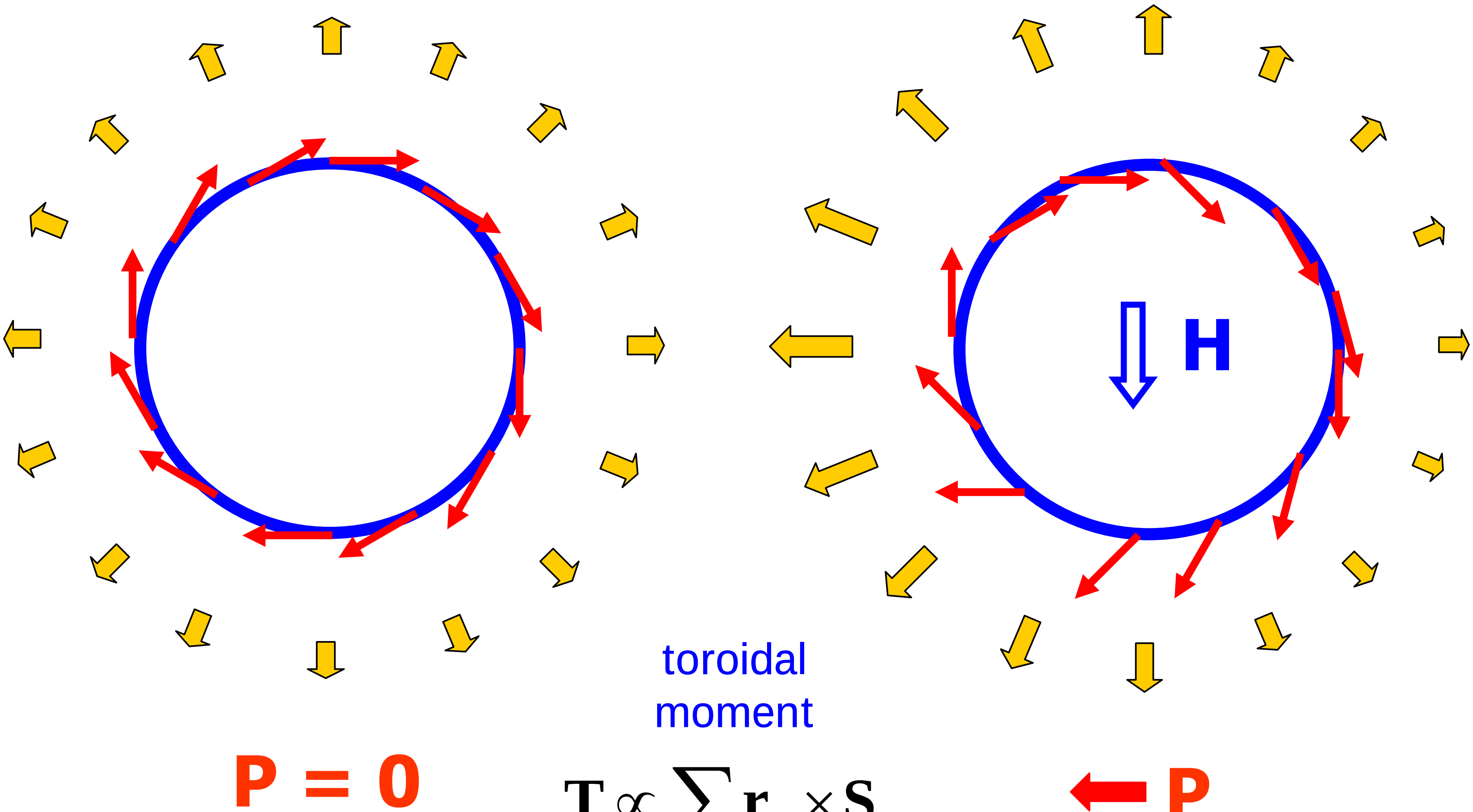
Vortex charge: $$Q \propto \Gamma = \frac{1}{2\pi}\oint_C d\mathbf{x}\cdot\nabla\varphi$$ **winding number**

Magnetic vortex in magnetic field



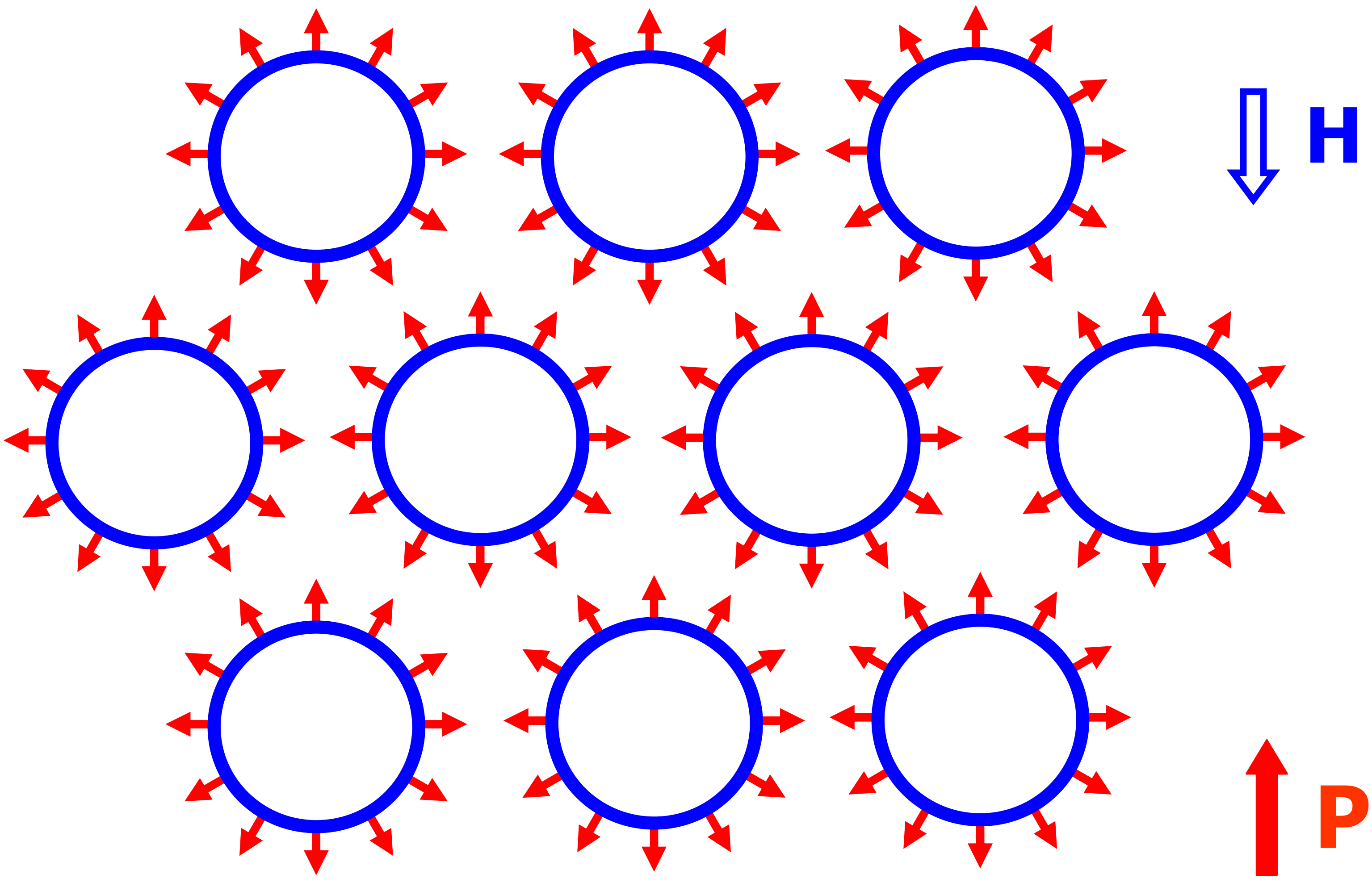
$$A \propto \sum_{\alpha} \mathbf{r}_{\alpha} \cdot \mathbf{S}_{\alpha}$$

Magnetic vortex in magnetic field

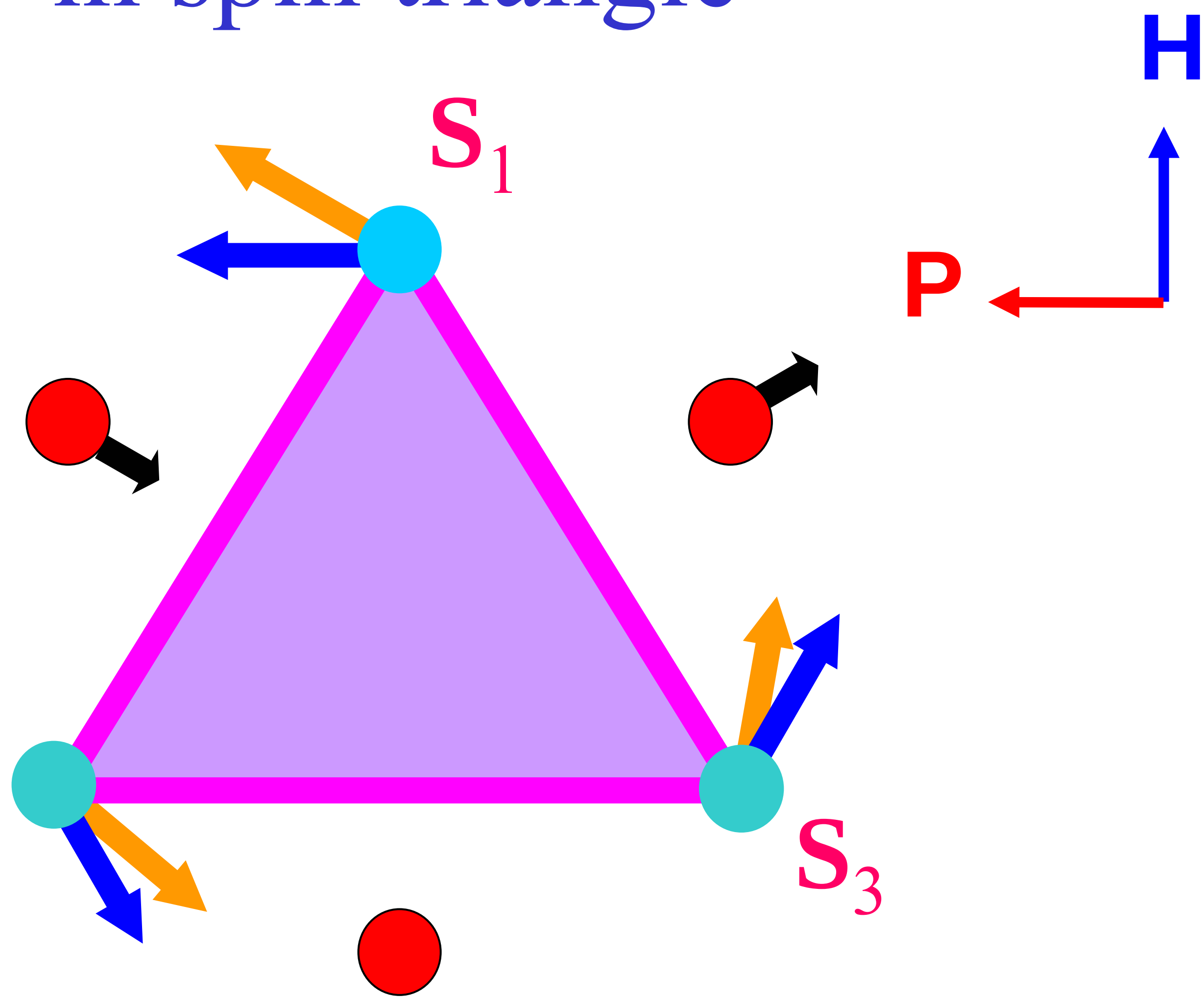


$$\mathbf{T} \propto \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{S}_{\alpha}$$

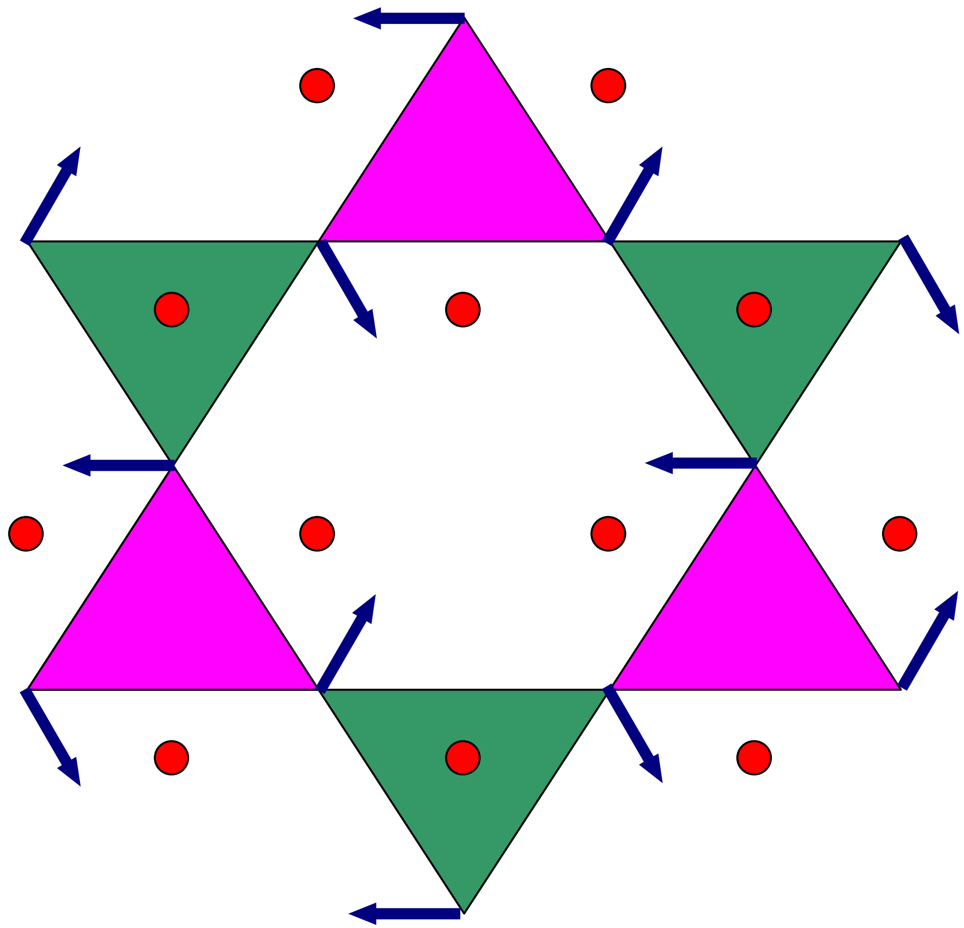
Array of magnetic vortices is magnetoelectric



Magnetoelectric effect in spin triangle



KITPITE



layered
Kagomé lattice

$$\alpha = \alpha_0 \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

C. Delaney, M. M. and N. A. Spaldin,
to be published

Conclusions

- Magnetic frustration gives rise to unusual spin orders that break inversion symmetry and give rise to multiferroic behavior and linear magnetoelectric effect