Magnetism in multiferroics

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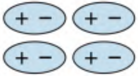
Outline

Multiferroics:

- Definition
- Multiferroic types and mechanisms
- J, DMI, SIA in multiferroic type I (cubic perovskites)
- Spin driven multiferroics (type II) (cubic perovskites)

Ferroic orders

<table>
<tr><th>Space / Time</th><th>Invariant</th><th>Change</th></tr>
<tr><td>Invariant</td><td>Ferroelastic

</td><td>Ferroelectric


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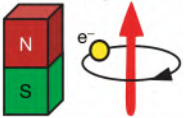
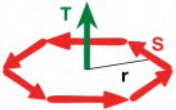
<tr><td>Change</td><td>Ferromagnetic


</td><td>Ferrotoroidic


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Multiferroics

Multiferroics:

more than one ferroic order in the same material

(name coined by Hans Schmidt in 1993 but 1st works by Smolenskii et al. 50's who called them ferroelectromagnets)

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... Well, actually hard to find! (FM metals vs insulating FE)

Multiferroics

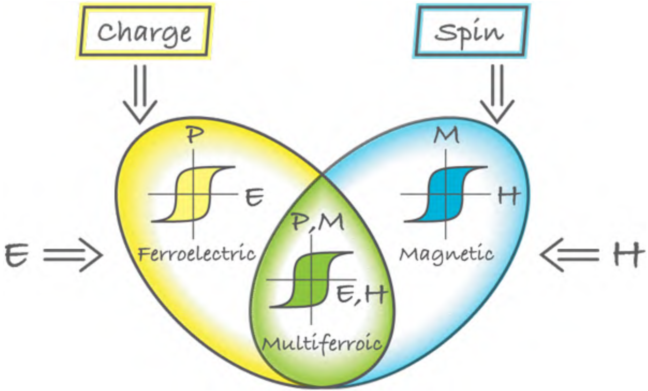
Multiferroics: more than one ferroic order in the same material ...

Lets do a hack!

Multiferroics: Usual definition plus ... Ferroelectricity + whatever magnetic order!

Multiferroics

Multiferroics: more than one ferroic order in the same material!



Multiferroics

Multiferroics: Usual definition plus ... Ferroelectricity + whatever magnetic order!

But ... still not very common?

Hack further: Extension to multi-antiferroics!

Multiferroics

The d^0-ness problem (N. Spaldin 2000)

FE conditions ($BaTiO_3$-type):

- Displacive FE transition (soft polar mode)
- Driven by charge transfer through O-p/Ti-d^0 hybridization
- d^0 is key $\longrightarrow$ in contradiction with magnetic systems that need $d^{n\neq 0}$

Solution: The $BaTiO_3$-type mechanism for FE is actually not the most common:

- Lone pair mechanism (Pb^{2+}, Bi^{3+}, etc)
- Geometric FE: P is not the primary order parameter (improper, triggered, etc)
- Geometric FE: steric effects (as in “polar metals”)
- Spin-driven FE: magnetic order induces FE (P is not the primary OP)

Multiferroics: Type I vs Type II classification

Tentative to classify multiferroics (Khomskii 2009)

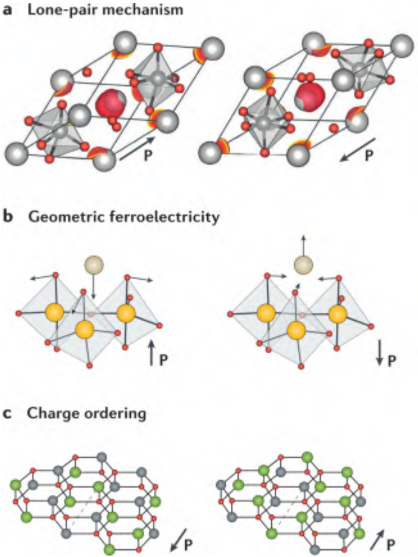
Type I multiferroics:

- Ferroelectric and magnetic orders appear independently ($T_C^{FE} \neq T_C^{FM}, T_N$)
- Polarization can be large
- Weak coupling between FE and magnetic properties

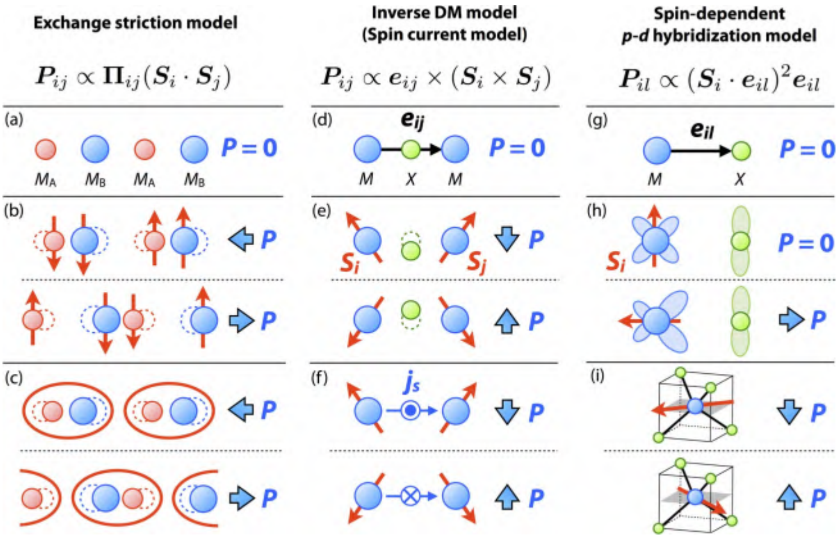
Type II multiferroics:

- Magnetism causes ferroelectricity ($T_C^{FE} = T_C^{FM}, T_N$)
- Polarization is small
- Strong coupling between polarization and magnetic properties

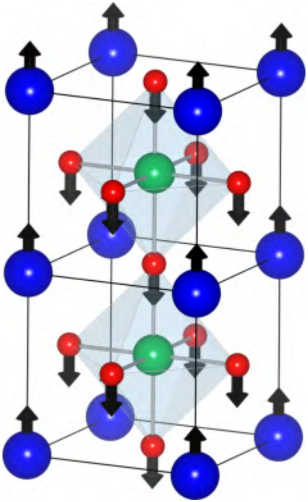
Multiferroic Type I mechanisms



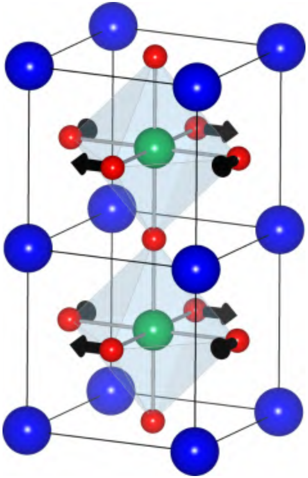
Multiferroic Type II mechanisms



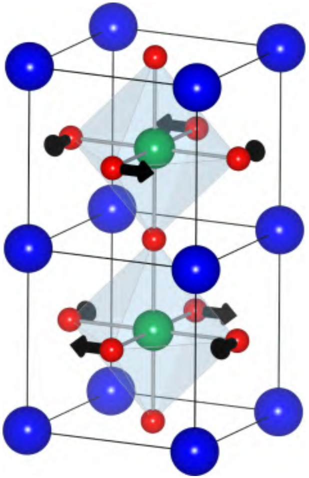
Multiferroic Type I: Focus on cubic perovskites ABO_3



FE distortion



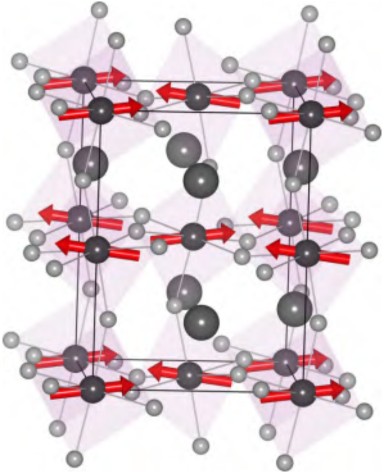
Octahedra rotation
$a^0 a^0 a^+$



Octahedra rotation
$a^0 a^0 a^-$

Multiferroic Type I: Focus on cubic perovskites ABO_3

Complex pattern of distortions: how magnetism behaves?



Magnetic interactions in cubic perovskites

Can be decomposed into 3 parts:

$$S_i \, \Phi_{ij} \, S_j \;=\; J_{ij} S_i . S_j + D_{ij} (S_i \times S_j) + S_i \, A_{ij} \, S_j$$

- Exchange: *J*
- DM: *D*
- The rest: *A* $\dashrightarrow$ SIA

Evaluation of *J*, *D* and *A* vs distortions: DFT analysis in *A*FeO$_3$

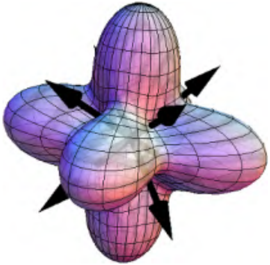
From PRB 86, 094413 (2012), see also PRB 99, 104420 (2019)

Effect of distortions on SIA

Cubic structure: small anisotropy (4th and 6th order)

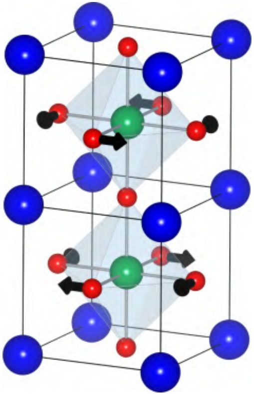
$$E_{SIA} = K_1(S_x^2 S_y^2 + S_y^2 S_z^2 + S_z^2 S_x^2) + K_2(S_x^2 S_y^2 S_z^2)$$

(μeV)	K_1	K_2
$BiFeO_3$	-3.66	0.06

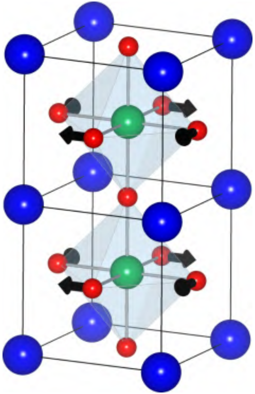


Effect of distortions on SIA

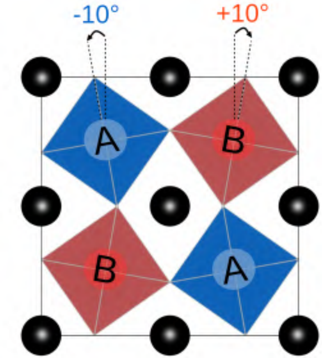
Octahedra rotation: $a^0a^0c^{+/-}$



$a^0a^0a^-$



$a^0a^0a^+$



top view

Effect of distortions on SIA

$a^0 a^0 c^{+/-}$ structures: 2^{nd} and 4^{th} orders

$$E_{SIA}(\theta,\phi) = K_1 \sin^2(\theta) + K_1' \sin^2(\theta)\cos(2\phi) + K_2 \sin^4(\theta) + K_2'' \sin^4(\theta)\cos(4\phi)$$

Effect of distortions on SIA

$a^0a^0c^{+/-}$ structures: 2^{nd} and 4^{th} orders

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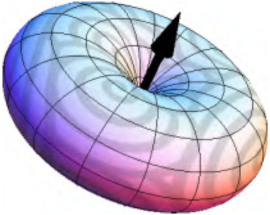
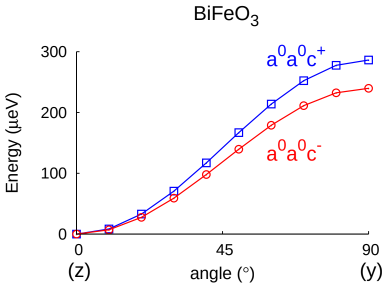
$BiFeO_3$	(μeV)	K_1	K_1'	K_2	K_2''
$0^00^010^+$		264.0	0	3.5	0.7
$0^00^010^-$		235.3	0	4.3	0.8



$K_1 > 0 \Longrightarrow$ easy axis shape

Effect of distortions on SIA

$a^0 a^0 c^{+/-}$ structures: SIA shape and amplitude



Effect of distortions on SIA

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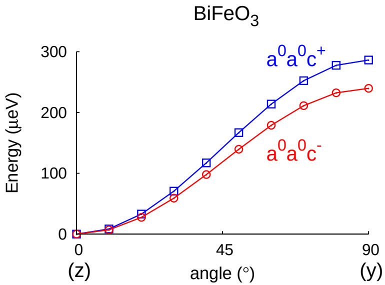

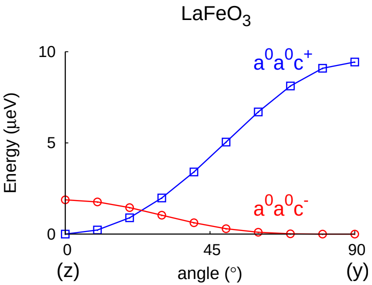

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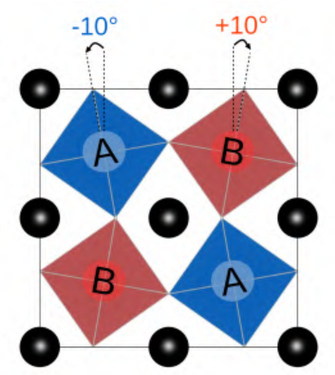

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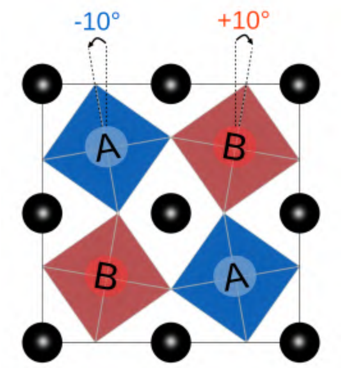
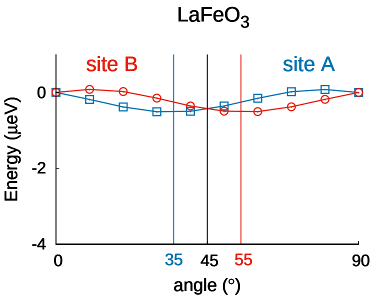
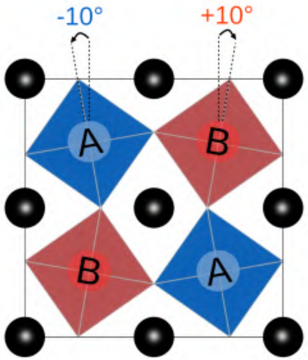
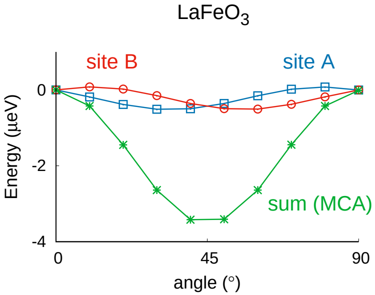




Effect of distortions on SIA

$a^0 a^0 c^{+/-}$ structures: SIA shape and amplitude

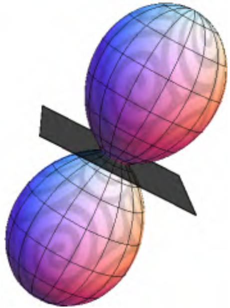




Effect of distortions on SIA

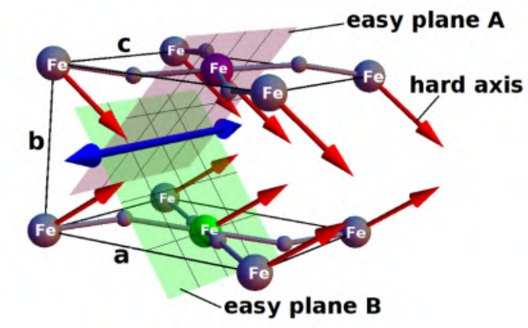
$a^-b^+a^-$ (*Pnma*) and $a^-a^-a^-$ ($R\bar{3}c$) structures: easy-plane

$BiFeO_3$	K_1 (μeV)
Pnma ($7^-8^+7^-$)	-402
$R\bar{3}c$ ($9^-9^-9^-$)	-400



Effect of distortions on SIA

$a^-b^+a^-$ (*Pnma*) structure:



Two different easy planes locally but a global easy axis!

Effect of FE distortions on SIA

		K_1 (μeV)
$9^-9^-9^-$	BFO	-400

Effect of FE distortions on SIA

		K_1 (μeV)
$9^-9^-9^-$	BFO	-400
$9^-9^-9^-$+0.5FE	BFO	-281
$9^-9^-9^-$+1.0FE	BFO	-1.3
$9^-9^-9^-$+1.5FE	BFO	139

Effect of FE distortions on SIA

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$9^-9^-9^-$	BFO	-400
$9^-9^-9^-$+0.5FE	BFO	-281
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$9^-9^-9^-$+1.5FE	BFO	139
1.0 FE	BFO	217
1.5 FE	BFO	349

Effect of FE distortions on SIA

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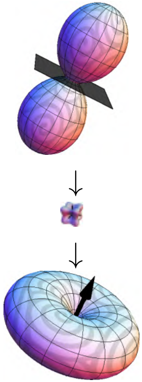


Competition between FE and OR's SIA!

Effects on J

			J_{ac}	J_b	(meV)
$BiFeO_3$	cubic	$(0^0 0^0 0^0)$	7.36	–	
	Pnma	$(7^- 8^+ 7^-)$	6.52	6.68	
	$R\bar{3}c$	$(9^- 9^- 9^-)$	5.96	–	
	$R3c$	$(9^- 9^- 9^- + \text{FE})$	5.36	–	

J decreases with OR distortions because Fe–O–Fe bond angle $< 180^\circ$

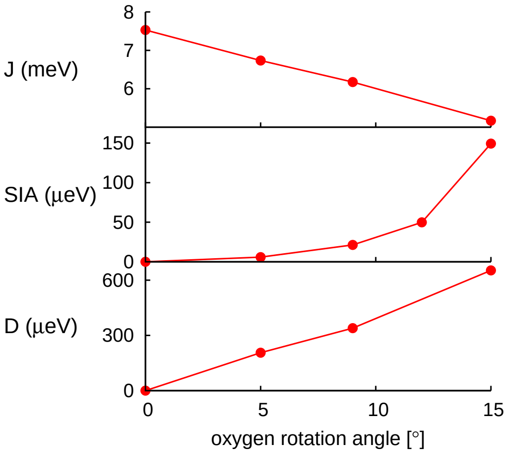
Effects on DM

			D_x	D_y	D_z	(μeV)
$BiFeO_3$	cubic	$(0^0 0^0 0^0)$	0	0	0	
	Pnma	$(7^- 8^+ 7^-)$	454	208	124	
	$R\bar{3}c$	$(9^- 9^- 9^-)$	170	170	170	
	R3c	$(9^- 9^- 9^-$ FE)	146	146	146	

DMI increases with OR distortions because Fe–O–Fe bond angle goes away from 180°

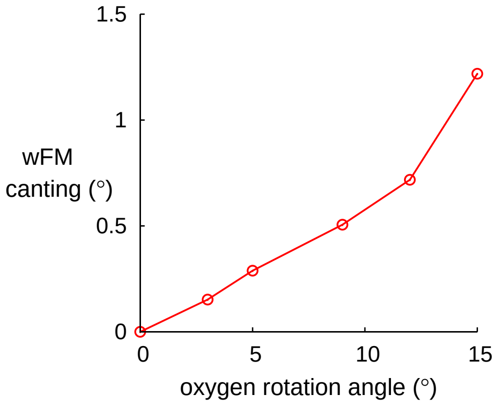
Effect of distortions on wFM

J, DM and SIA vs OR amplitude in $R\bar{3}c$:



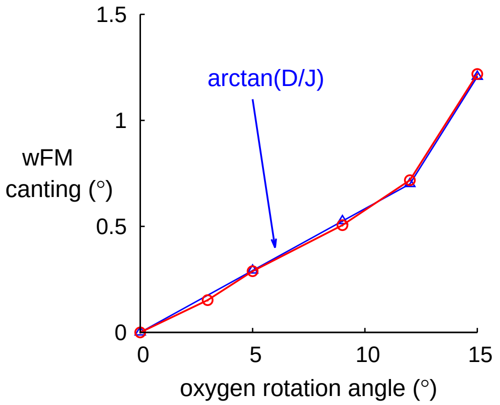
Effect of distortions on wFM

wFM vs AFD amplitude in $R\bar{3}c$:



Effect of distortions on wFM

wFM vs AFD amplitude in $R\bar{3}c$:



$$\text{wFM} = arctan(D/J)$$

Effect of distortions on wFM

Microscopic model: PRL 109, 037207 (2012)

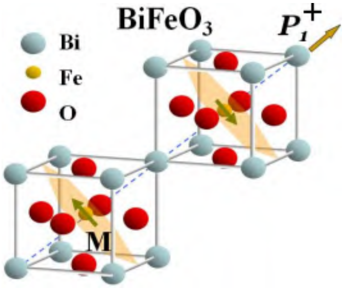
Coupling with the octahedra rotations ω:

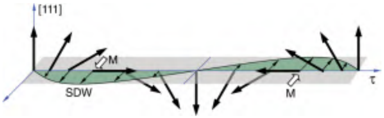
$$D_{wFM} \propto (\omega_i - \omega_j) \cdot (\mathbf{S}_i \times \mathbf{S}_j)$$

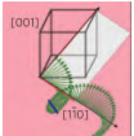
Coupling with the polar distortions **u** ("Spin-Current"):

$$D_{SC} \propto (\mathbf{u}_i - \mathbf{e}_{ij}) \cdot (\mathbf{S}_i \times \mathbf{S}_j)$$

Multiferroic perovskites: $BiFeO_3$







$BiFeO_3$ ($R3c$)

$Fe^{3+} \longmapsto 3d^5$

G-type AFM + ferroelectricity

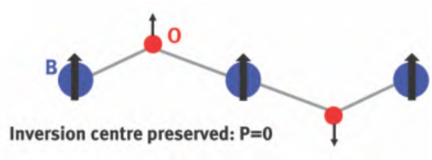
$\longmapsto$ multiferroic at room temperature ($T_{FE} = 1100$ K, $T_N = 640$ K)

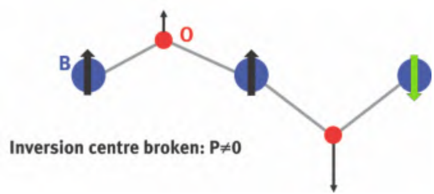
+ Spin cycloid!

from Spin-current driven DMI
PRB 108, 024403 (2023)

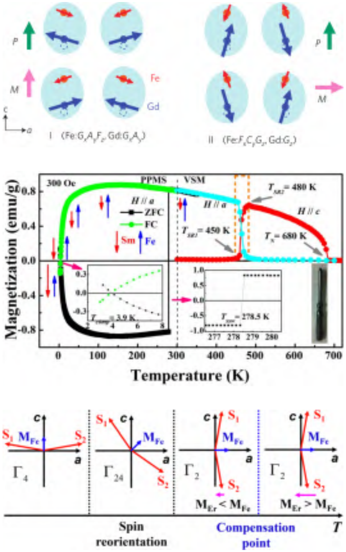
Multiferroic type II perovskites

From exchange striction





Rare Earth perovskites: $R\mathrm{FeO}_3$



R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu

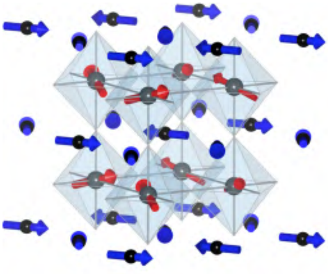
G-type AFM + weak FM of the TM cation

Interaction between R f electron spins and TM d electron spins

Spin reorientation and compensation point of the wFM

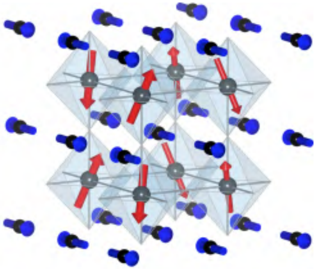
Rare Earth perovskites: $RFeO_3$

Multiferroicity due to the presence of both *R* and Fe magnetic atoms (exchange-striction):



Fe: $\mathbf{G}_x A_y F_z$; Gd: $\mathbf{G}_x A_y$

M // z ; P // z

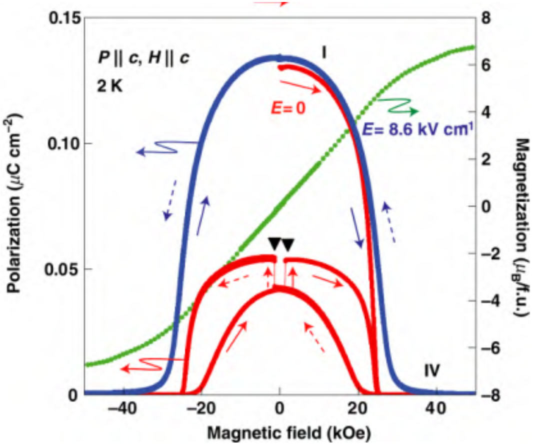


Fe: $F_x C_y \mathbf{G}_z$; Gd: $\mathbf{G}_z$

M // x ; P // x

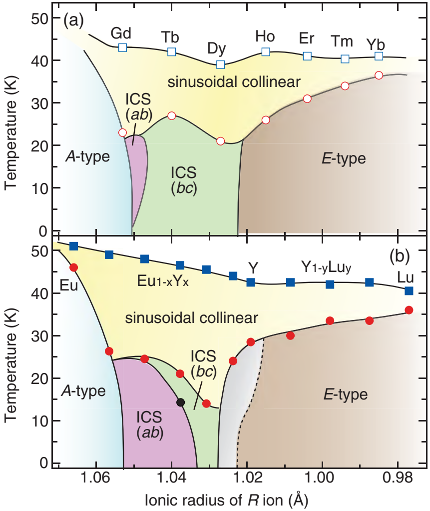
Rare Earth perovskites: $RFeO_3$

Strong magnetoelectric coupling ($GdFeO_3$):



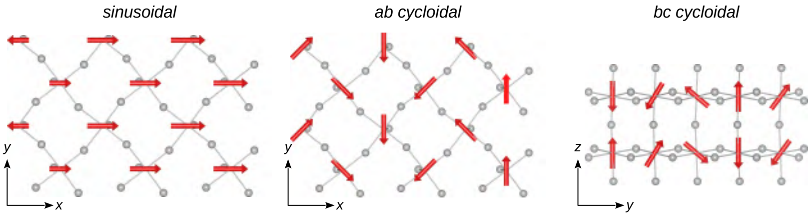
Rare Earth perovskites: $RMnO_3$

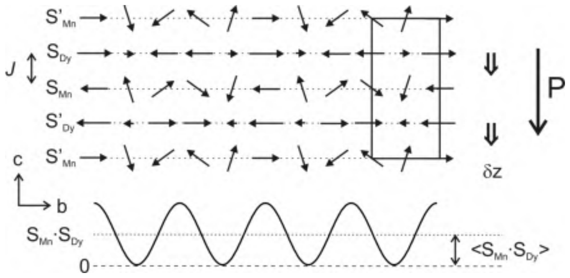
Rich magnetic phase diagram:



Rare Earth perovskites: $RMnO_3$

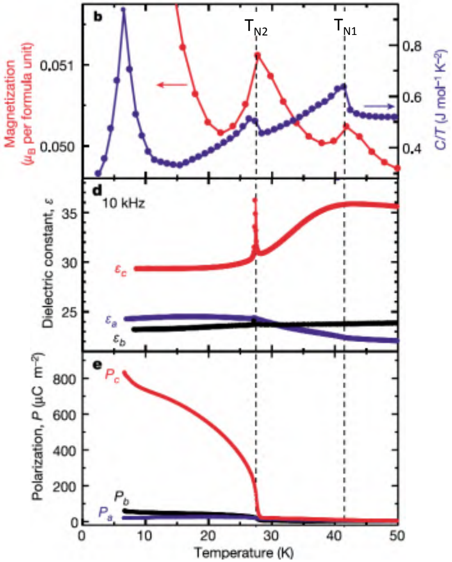
Spiral orders induces ferroelectricity (spin-current & exchange-striction):





Rare Earth perovskites: *R*MnO_3

TbMnO_3:
(spin-current model)



Conclusion

- Multiferroics, in the extended definition, can exhibit numerous possibilities
- Magnetoelectric multiferroics

Going beyond:

- Strain and interface engineering of new multiferroics
- Skyrmions (both magnetic and electric)
- Composites (mixing FE and FM materials)
- 2D materials
- Type III Multiferroics?

Main review references (oldest to most recent)

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Main review references

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- *Multiferroics of spin origin*, Yoshinori Tokura, Shinichiro Seki and Naoto Nagaosa, Rep. Prog. Phys. 77 076501 (2014).
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