Multiferroics

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References

Multiferroics: a magnetic twist for ferroelectricity S.-W. Cheong and M. Mostovoy Nature Mat. 6, 13 (2007)

Multiferroics of spin origin Y. Tokura, S. Seki and N. Nagaosa Rep. Prog. Phys. 77, 076501 (2014)

Non-collinear magnetism in multiferroic perovskites E. Bousquet and A. Cano J. Phys.: Condens. Matter 28, 123001 (2016)

The evolution of multiferroics M. Fiebig, Th. Lottermoser, D. Meier, and M. Trassin Nature Reviews Materials 1, 16046 (2016)

... and the original papers therein!

Outline

1. Definitions & motivation

2. Type I

3. Type II

4. Dynamics

Ferroic

Generic name given to (anti-)ferromagnets, ferroelectrics and ferroelastics.

Ferromagnetism: spontaneous magnetization $\mathbf{M} eq 0$	1	1	1	1
Antiferromagnetism: spontaneous magnetization $\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2 \neq 0$	1	↓	1	↓
<i>Ferroelectricity</i> : spontaneous electric polarization $\mathbf{P} \neq 0$		ł		₽
<i>Ferroelasticity</i> : spontaneous strain $u_{ij} \neq 0$	I			I

Multiferroics

Materials that exhibit more than one ferroic property... ...and preferably a strong coupling!

Ferromagnetism: spontaneous magnetization $\mathbf{M} eq 0$	1	↑	1	1
Antiferromagnetism: spontaneous magnetization $\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2 \neq 0$	↑	↓	↑	↓
<i>Ferroelectricity</i> : spontaneous electric polarization $\mathbf{P} \neq 0$		ł		ł
<i>Ferroelasticity</i> : spontaneous strain $u_{ij} \neq 0$				I

Maxwell's equations (electromagnetism)

$$\nabla \cdot \mathbf{D} = \rho_f, \quad \nabla \cdot \mathbf{B} = 0,$$
$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B}, \quad \nabla \times \mathbf{H} = \mathbf{J}_f + \partial_t \mathbf{D}$$

Constitutive equations (matter)

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$$
 $\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}$

Standard dielectrics & paramagnets

$$\frac{1}{\varepsilon_0 \chi_e} P = E \qquad \qquad \frac{1}{\chi_m} M = H$$



Ferroelectrics & ferromagnets → multiferroics

$$\left(\frac{1}{\varepsilon_0\chi_e} + \beta_e P^2 + \dots\right)P = E$$
$$\left(\frac{1}{\chi_m} + \beta_m M^2 + \dots\right)M = H$$



Magnetoelectric multiferroics

$$\left(\frac{1}{\varepsilon_0 \chi_e} + \beta_e P^2 + \dots\right) P + \alpha_{\rm ME} M = E$$
$$\left(\frac{1}{\chi_m} + \beta_m M^2 + \dots\right) M + \alpha_{\rm ME} P = H$$

$$F_{\rm ME} = \alpha_{\rm ME} P M + \dots$$



Multiferroic RAM



electric-field writing of magnetic information: faster and more energy-efficient



Types of multiferroics





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Type-I multiferroics (alias ferroelectromagnets before 1993)

	1		<u> </u>	1	1	1 30 Fe-B-(1C)	L FE	WEM	~ 600	~ 11	m
Compound	Type of	Type of	Θ _r , K	Θ _M , K	Magnetoelectric mea-	31. Fe.B.O. Br	FE	WFM	≈ 495	≈ 17	$m(\tilde{E})$
	order	order		IAI .	surements	32. FesBrO13I	FE	WFM	≈ 349	\$ 30	
	- <u>(</u>	1	<u>{</u>	1	1	33. Co ₃ B ₇ O ₁₃ Cl	FE	WFM	623	11,5, 15	$X^{ME}, m(\tilde{E})$
1. Pb (Fe _{2/8} W _{1/3}) O ₃	FE	AFM	178	363	Measurement of in-	34. Co3B-O13Br	FE	WFM	458	20	
		1			ternal magnetic field	35. Co ₃ B ₇ O ₁₃ I	FE	WFM	≈ 197	38	$m(\widetilde{E}), \ \varepsilon(\Theta_M)$
		1			at the FE transition	36. Cu ₃ B ₇ O ₁₃ Cl	FE	AFM	365	20	X ^{ME}
2. Pb (Fe _{1/2} Nb _{1/2} , O_3	FE	AFM	387	143	$M_{c}(\tilde{E})$	37. Cu ₃ E ₇ O ₁₈ Br	FE	WFM	226	24	ε (Θ _M)
5. Bireo ₂	FE	APM	1123	≈ 650	$\mathcal{C}(\Theta_{\mathbf{M}})$, induction of <i>P</i> in spin-flop	38. Ni ₃ B ₇ O ₁₈ Cl	FE	AFM WFM	610	25 9113	XME
4. $Eu_{1/2}Ba_{1/2}TiO_{s}$ 5. Pb (Mn _{2/s} W _{1/s}) O ₃	FE AFE?	FM AFM	165156 473144	4,2156 203144	ε (Θ _M)	39. Ni ₃ B ₇ O ₁₃ Br	FE	WFM	398	30, 40	$m(\widetilde{E})$
6. Pb $(Mn_{1/2}He_{1/2}) O_3$ 7. Pb $(Mn_{1/2}W_{1/2}) O_3$ 8. Pb $(Fe_4, Te_4) O_3$	AFE?	FIM AFM	393 423	103 100		40. Ni ₃ B ₇ O ₁₃ I	FE	WFM	64	64	X ^{ME} , ε(H), P(H).
9. Pb (Fe _{1/2} Re _{1/2}) O_3	AFE?	FIM	433	> 293	{	41. BaNiF ₄	FE	AFM	1593	70122	Anomaly in the
10. PB $(Co_{1/2}Re_{1/2}) O_3$ 11. Pb $(Ni_{1/2}Re_{1/2}) O_3$	AFE?	AFM	403 343								pyroelectric signal at $T \approx \Theta_{14}^{160}$
12. Pb $(CO_{1/2}W_{1/2})O_3$	AFE	I IM	305			19 BaMnF	DE	WEM		05	- M
13. BiMnO _a	AFE	FM	773	103. 110		43. BaCoF	FE	AFM	1153	69,6	8 (OM)
14. Cd $(Fe_{1/2}Nb_{1/2}) O_8$	AFE?	AFM	753	48		44. BaFeF ₄	PE	AFM	853	54,2112	To do at a form
13. D12D14Fe2118018	FE	FM:	OEI-11/1	7927 159	VME2 158	40. Li (i c1/2 1 a1/2) 0 21	FE		000	000	electric current by
16. BigTigF5027	FE	WFM	1103, 1073	363, 403	Induction of an					}	a magnetic field
		1	,		electric signal by	46. Cr ₂ BeO ₄	FE	AFM	2832	2832	ĺ
	}	}		}	a magnetic field	47. $PbMn_2O_4$	FE?	WFM	250129	63129	$m(\widetilde{E})$
7. $YMnO_3$	FE	AFM	913, 933	≈ 80		48. $Co_{1,75}Mn_{1,25}O_{4}$	FE	FIM	170136	170136	XME
10. 1 <i>D</i> 3/10 ₃	FE	WFM	900, 990	3.8		50. β -Tb ₂ (MoO ₄) ₃	FE	AFM	≈ 235	2161	
19. НоМпО ₃	FE		873	76		51. β-NaFeO ₂	FE	WFM	723162	723162	j
20. ErMn(),	FE	AFM	833	79		04. FC	FE	Агм	4117	≈ 095	
24. $TmMnO_3$	FE.	AFM	> 573	86		Notes: The data	marked w	ith a q	uestion m	ark req	uire more
3. ScMnO.	FE	AFM AFM		91 120		precise determin	nation. N	otation	n: Fe fe	rroelec	tric. AFE-
24. $Cr_3 B_7 O_1 Cl$	FE	AFM	≈ 260	25		antiferroelectric	PE-nu	roeleo	tric. FM-	-ferror	nagnet.
26. Cr ₂ D ₅ C ₁₃ Br	FE FE	AFM	4	50 95		AFM-antiferro	magnet V	VFM	antiforro	nagnet	with weak
27. Mn ₃ H ₇ O ₁₃ Cl	FE	AFM	680	$\approx 6^{21}$		for nome another to	TIM_ F	nnime.	and VME	statio	ME gugoonti-
28. $Mn_{3}B_{7}O_{13}Br$	FE	AFM	566	$\approx 6^{21}$	- ()	halita M	, r 11v11e		guet, A	-static	tudo of the
29. 3(1131) 2(,131	, FE	WFM	412	20115	(<i>m</i> (<i>L</i>)	builty, $M_{\rm c}$ —spon	taneous n	agnen	zation, E		tude of the
						alternating elect	ric neid,	$\varepsilon - di \epsilon$	electric pe	ermittiv	ity.





F-type



A-type





C-type

G-type

 $BiFeO_3$ ($T_c = 1083$ K, $T_N = 643$ K)



Spontaneous polarization $P \rightarrow$ spiral modulation of the primordial antiferromagnetic order

$$H_L = -KL_z^2 + A(\nabla \mathbf{L})^2 + \underbrace{gP[\mathbf{L}(\nabla \cdot \mathbf{L}) - (\mathbf{L} \cdot \nabla)\mathbf{L}]_z}_{z}$$

ME coupling

Kadomtseva et al., JETP Lett. 79, 571 (04)

 $BiFeO_3 (T_c = 1083 \text{ K}, T_N = 643 \text{ K})$

$$H_L = -KL_z^2 + A(\nabla \mathbf{L})^2 + \underbrace{gP[\mathbf{L}(\nabla \cdot \mathbf{L}) - (\mathbf{L} \cdot \nabla)\mathbf{L}]_z}_{\text{ME coupling}}$$

 $\mathbf{L} = L_0 \big(\cos \phi \sin(\mathbf{q} \cdot \mathbf{r}), \sin \phi \sin(\mathbf{q} \cdot \mathbf{r}), \cos(\mathbf{q} \cdot \mathbf{r}) \big)$ $\mathbf{q} = (q_x, q_y, 0) \qquad \phi = \arctan(q_y/q_x)$



...but otherwise ferroelectricity and antiferromagnetism emerge in BiFeO₃ as independent phenomena

 $BiFeO_3 (T_c = 1083 \text{ K}, T_N = 643 \text{ K})$



Generalization to other ABO₃ perovskites?

 $Bi^{3+} \rightarrow 6s^2$ lone pair (not involved in the *sp* hybridization) $\rightarrow A$ -site ferroelectricity

But in general ferroelectricity is *B*-site with empty $3d^0$ shells (e.g. BaTiO₃)...

... while 3d electrons are necessary for the magnetic ordering of transition-metal elements

No-Go Theorem

Hill, J. Phys. Chem. B 104, 6694 (00)

Type-I multiferroics (alias ferroelectromagnets before 1993)

	Type of	Type of		1		30). Fe ₃ B ₇ () ₁₃ Cl	FE	WFM	≈ 609	≈ 11	m(E)
Compound	electric	magnetic	Θ _E , K	ө _М , К	Magnetoelectric mea- surements	3	l. Fe ₃ B ₇ O ₁₈ Br L. Fe ₂ B ₇ O ₁₈ Br	FE FE	WFM WFM	≈ 495 ≈ 349	≈ 17 ≈ 30	$m(\tilde{E})$
			/ 1	1		33	. Co ₃ B ₇ O ₁₃ Cl	FE	WFM	623	11,5, 15	$X^{ME}, m(\tilde{E})$
1. Pb (Fe _{2/3} W _{1/3}) O ₃	FE	AFM	178	363	Measurement of in-	34	. Co ₃ B ₇ O ₁₃ Br	FE	WFM	458	22 20	_
]			ternal magnetic field	32	6. Co ₃ B ₇ O ₁₃ I	FE	WFM	≈ 197	38	$m(\tilde{E}), \varepsilon(\Theta_M)$
					at the FE transition	30	5. Cu ₃ B ₇ O ₁₃ Cl	FE	AFM	365	20	X ^{ME}
2. Pb (Fe _{1/2} Nb _{1/2)} O_3 1 3 BiFeO	FE	AFM	387	143	$M_{c}(\tilde{E})$	37	. Cu ₃ E ₇ O ₁₈ Br	FE	WFM	226	24	ε (Θ _M)
Di Direca	FE		1125	≈ 000	$\mathcal{E}(\Theta_{\mathbf{M}})$, induction of P in spin-flop	38	. Ní3B7013Cl	FE	AFM WFM	610	25 9113	XME
4. $Eu_{1/2}Ba_{1/2}TiO_3$ 5. Pb (Mn _{2/3} W _{1/8}) O ₃	FE AFE?	FM AFM	165156 473144	4,2156 203144	E (Ox)	39). Ni ₃ B ₇ O ₁₃ Br	FE	WFM	398	30, 40	$m(\widetilde{E})$
6. Pb $(Mn_{1/2}Re_{1/2})$ O ₃ 7. Pb $(Mn_{1/2}W_{1/2})$ O ₃	AFE? AFE?	FIM AFM	393 423	103 100		40	. Ni ₃ B ₇ O ₁₃ l	FE	WFM	64	64	X ^{ME} , & (H), P (H).
8. Pb ($Fe_{1/2}Ta_{1/2}$) O ₃ 9. Pb ($Fe_{1/2}Re_{1/2}$) O ₃	FE AFE?	AFM	233 433	$ 180^{157} > 293$	{	41	. BaNiF ₄	FE	AFM	1593	70122	m (E) Anomaly in the
10. PB $(Co_{1/2}Re_{1/2}) O_3$ 11. Pb $(Ni_{1/2}Re_{1/2}) O_3$	AFE?	AFM	403 343									pyroelectric signal at $T \approx \Theta_{14}^{160}$
12. Pb $(CO_{1/2}W_{1/2}) O_{3}$	AFE	WEM	305	0]]	42	. BaMnF.	PF	WFM		25	е (Э)
13. BiMnO ₃	AFE	FM	773	103, 110		43	BaCoF ₄	FE	AFM	1153	69,6	e (OM)
14. Cd (Fe _{1/2} Nb _{1/2}) O ₈ 15. Bi ₂ Bi ₂ Fe ₂ Ti ₂ O ₂₂	AFE?	AFM FM?	753 0 1171	48		44	. BareF ₄ Li (Fe,/, Ta,/,) O.F	PE	AFM AFM	853	$\begin{bmatrix} 54, 2^{122} \\ 883 \end{bmatrix}$	Induction of an
	FE		OEI -1025188	723? 159	XME? 168							electric current by
16. Bi ₉ Ti ₃ F ₅ O ₂₇	FE	WFM	1103, 1073	363, 403	Induction of an						}	a magnetic field
					electric signal by	46	. Cr ₂ BeO ₄	FE FF?	AFM	2832	2832	(B)
7 VMpO	EF	ATM	042 022	- 80		47	$C_{0} = M_{T} = O$	EE	WCM EIM	470125	400126	m (E)
18. YBMnÜ ₃	FE	AFM AFM	913, 933 983, 993	≈ 80 87,3		49	$Cu_{1,75}Mu_{1,25}O_4$. Cu (HCOO) ₂ ·4H ₂ O	AFE	WFM	≈ 235	170136	Xm2
19. HoMnO.	FE	WFM AFM	873	3.8 76		50 51	. β-Tb ₂ (MoO ₄) ₃ β-NaFe()	FE	AFM	723162	2161	
	EE	WFM	010	5		52	FeS	FE	AFM	411?	≈ 593	
20. ErMnO ₃ 21. TmMnO.	FE	AFM AFM	833 > 573	79 86					•••		,	•
22. LuMnO ₃	FE	AFM	2 010	.91		Λ	otes: The data ma	irked w	ith a q	uestion m	ark req	uire more
23. $SCMnO_3$ 24. $Cr_{*}B_{*}O_{*}Gl$	FE	AFM	≈ 260	120 25		p	recise determinat	10n. N	otation	n: Fe—fe	rroelec	ITIC, AFE-
25 B . 13Br	FE	AFM	4	50		a	ntiferroelectric,	рЕру	roelec	tric, FM-	-ferror	nagnet,
26. $Cr_3D_7O_{18}l$ 27. $Mn_*H_*O_{18}cl$	FE	AFM	680	$95 \approx 621$		A	FM-antiferroma	gnet, V	VFM—	antiferro	magnet	with weak
28. $Mn_7B_7O_{13}Br$	FE	AFM AFM	566	$\approx 6^{21}$		f	erromagnetism, F	'IM-fe	rrima	gnet, X ^{ME}	-static	ME suscepti-
29. Mn ₃ B ₇ O ₁₃ I	FE	WFM	412	26113	$m(\dot{E})$	b	ility, M _c -spontar	neous m	agneti	zation, <i>É</i>	—ampli	tude of the
			-		~	а	lternating electric	field.	ε—di€	electric pe	e r mittiv	ity.

Type-I multiferroics: hexagonal manganites

h- $RMnO_3$ ($T_c \ge 1200$ K, $T_N \le 120$ K)





Type-I multiferroics: hexagonal manganites

h- $RMnO_3$ ($T_c \ge 1200$ K, $T_N \le 120$ K)



Ferroelectricity is the by-product of the unit-cell trimerization (not a primary order parameter)



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Types of multiferroics





Type-II multiferroics: TbMnO₃

Simultaneous ferroelectric & magnetic transition



Kimura et al., Nature **426**, 55 (03)

Type-II multiferroics: TbMnO₃

Can magnetic order be the direct consequence of ferroelectricity?
No
(*P* preserves time-reversal symmetry)

Can ferroelectricity be the direct consequence of magnetic order?

Can ferroelectricity be the direct consequence of magnetic order?



Can ferroelectricity be the direct consequence of magnetic order?

Néel wall



Néel walls are not invariant under inversion symmetry \rightarrow local polar axis Idem for Bloch walls in e.g. D_{2h} systems

Bar'yakhtar et al. JETP Lett. 37, 673 (83)

Can ferroelectricity be the direct consequence of magnetic order? YES!

How?

$$F_{ME} = -g\mathbf{P} \cdot \left[(\mathbf{M} \cdot \nabla)\mathbf{M} - \mathbf{M}(\nabla \cdot \mathbf{M}) \right]$$

Inhomogeneous magnetoelectric effect (universal)



The direction of the (local) polarization is linked to the chirality of the wall

Bloch walls: It does not work in this simple form

Bar'yakhtar et al. JETP Lett. 37, 673 (83)

Can ferroelectricity be the direct consequence of magnetic order? YES!

Can the magnetically-induced polarization be global?

$$F_{ME} = -g\mathbf{P} \cdot \left[(\mathbf{M} \cdot \nabla)\mathbf{M} - \mathbf{M}(\nabla \cdot \mathbf{M}) \right]$$

Néel wall

$$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \land \checkmark \rightarrow \searrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow$$

Long-range cycloidal order

$$\uparrow \nearrow \rightarrow \curlyvee \downarrow \checkmark \leftarrow \land \uparrow \nearrow \rightarrow \curlyvee \downarrow \checkmark \leftarrow \land \uparrow \nearrow \rightarrow \curlyvee \downarrow$$

 $\mathbf{M} = M_0[\sin(\mathbf{q} \cdot \mathbf{r})\hat{\mathbf{e}}_1 + \cos(\mathbf{q} \cdot \mathbf{r})\hat{\mathbf{e}}_2]$

Ferroelectricity in spiral magnets

$$F_{ME} \rightarrow \mathbf{P} \propto (\hat{\mathbf{e}}_1 \times \hat{\mathbf{e}}_2) \times \mathbf{q}$$

Mostovoy, PRL 96, 067601 (06)

Can ferroelectricity be the direct consequence of magnetic order? YES!

Can the magnetically-induced polarization be global? YES!

Does TbMnO₃ display cycloidal order? YES!





The spontaneous electric polarization in TbMnO₃ has a magnetic origin previous example: Cr₂BeO₄, Newnham et al., J. Appl. Phys. **49**, 6088 (78)

Can ferroelectricity be the direct consequence of magnetic order? YES!

Can the magnetically-induced polarization be global? YES!

Does TbMnO₃ display cycloidal order? YES!

- Why does TbMnO₃ display cycloidal order?

- What is the microscopic version of $F_{ME} = -g\mathbf{P} \cdot [(\mathbf{M} \cdot \nabla)\mathbf{M} - \mathbf{M}(\nabla \cdot \mathbf{M})]$?

Type-II multiferroics Why does TbMnO₃ display cycloidal order?



Type-II multiferroics Why does TbMnO₃ display cycloidal order?

FM nearest- vs. AFM next-nearest-neighbor exchange interactions in the *ab* plane

$$H = -J_1^{\text{FM}} \sum_{i} \mathbf{S}_i \cdot (\mathbf{S}_{i-x} + \mathbf{S}_{i+x} + \mathbf{S}_{i-y} + \mathbf{S}_{i+y})$$
$$+ J_2^{\text{AFM}} \sum_{i} \mathbf{S}_i \cdot (\mathbf{S}_{i-x-y} + \mathbf{S}_{i+x+y} + \mathbf{S}_{i+x-y} + \mathbf{S}_{i-x+y})$$

FM state

$$E_{\rm FM} = -4S^2 J_1 (1 - J_2 / J_1)$$

Cycloidal state

$$E_{\text{cycloidal}} = 2S^2 \left[-J_1 \cos \frac{Q}{\sqrt{2}} + J_2 (1 + \cos \sqrt{2}Q) \right] = \frac{-2S^2 J_1^2}{\sqrt{2}} - \frac{2S^2 J_1^2}{2J_2}$$

 $J_2 > 2J_1 \quad \rightarrow \quad$ The cycloidal wins

 $\mathbf{Q} = \frac{Q}{\sqrt{2}} (1, 1, 0)$ $\mathbf{S}_i = S \cos(\mathbf{Q} \cdot \mathbf{r}_i) \hat{\mathbf{x}} + S \sin(\mathbf{Q} \cdot \mathbf{r}_i) \hat{\mathbf{y}}$



Type-II multiferroics What is the microscopic version of $F_{ME} = -g\mathbf{P} \cdot [(\mathbf{M} \cdot \nabla)\mathbf{M} - \mathbf{M}(\nabla \cdot \mathbf{M})]$?

If **P** is mostly due to:



Is spin-spiral magnetism the only type of magnetism that induces ferroelectricity?

HoMnO₃

E-type AFM order



inversion $(\mathbf{r} \rightarrow -\mathbf{r})$

two different magnetic domains

 E_1



*E*₂

Is spin-spiral magnetism the only type of magnetism that induces ferroelectricity?

HoMnO₃

E-type AFM order

$${f E}_1 = {f S}_1 + {f S}_2 - {f S}_3 - {f S}_4 \ {f E}_2 = {f S}_1 - {f S}_2 - {f S}_3 + {f S}_4$$

	$(2_a \frac{1}{2}\frac{1}{2}0)$	$(2_c 00\frac{1}{2}), (I 000)$	(1 010), (1' 000)
E_1 E_2	$-1 \ 0 \ 0 \ 1$	0 1 1 0	-1 0 0 -1
$\overline{P_a}$	1	-1	1

$$F_{ME} = -gP_a(E_1^2 - E_2^2)$$

= $-4gP_a(\mathbf{S}_1 \cdot \mathbf{S}_2 - \mathbf{S}_1 \cdot \mathbf{S}_4 - \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_4)$
= $-P_a \sum_{\langle i,j \rangle} J'_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$
Exchange striction



2



Sergienko, Sen & Dagotto, PRL 97, 227204 (2006)

$$H = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$$

in a dielectric (= polarizable lattice):

$$J_{ij} = J_{ij}(\mathbf{P}_{ij}) = J_{ij}^{(0)} + \mathbf{J}'_{ij} \cdot \mathbf{P}_{ij} + \dots$$
$$\mathbf{D}_{ij} = \mathbf{D}_{ij}(\mathbf{P}_{ij}) = \mathbf{D}_{ij}^{(0)} + \underline{\mathbf{D}_{ij}} \cdot \mathbf{P}_{ij} + \dots$$

Mechanisms for multiferroicity

Symmetric exchange striction (\mathbf{J}'_{ij}) : works for collinear orders but requires special symmetry

Antisymmetric exchange striction (\mathbf{D}'_{ij}) : works for any symmetry but needs non-collinearity

+ single-site mechanisms

$$H_{\rm sia} = -\sum_i K(\mathbf{S}_i \cdot \hat{\mathbf{n}}_i)^2$$

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Spin-waves



Cazayous et al. PRL 101, 037601 (2008)

Spin-waves



In RMnO₃

 $H_{ME} = g\mathbf{P} \cdot \left[\mathbf{M}(\nabla \cdot \mathbf{M}) - (\mathbf{M} \cdot \nabla)\mathbf{M}\right] \quad \rightarrow \qquad g\delta\mathbf{P}(t) \cdot \left[\delta\mathbf{M}(t)(\nabla \cdot \mathbf{M}) + \mathbf{M}(\nabla \cdot \delta\mathbf{M}(t)) - (\delta\mathbf{M}(t) \cdot \nabla)\mathbf{M} - (\mathbf{M} \cdot \nabla)\delta\mathbf{M}(t)\right]$

Pimenov et al. Nature Phys. 2, 97 (06) Katsura et al., PRL 98, 027203 (07); Cano & Kats, PRB 78, 012104 (08)

Spin-waves





Dynamical ME effect

$$H = \underbrace{\sum_{i,j} [J_{ij}(\mathbf{P}) \ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij}(\mathbf{P}) \cdot (\mathbf{S}_i \times \mathbf{S}_j)]}_{\text{spin} + \text{striction}} + \frac{1}{2\chi_e} P^2 - \mathbf{E} \cdot \mathbf{P} - \mathbf{H} \cdot \mathbf{M}$$

Equations of motion \rightarrow constitutive equations

$$\begin{pmatrix} \mathbf{P} \\ \mathbf{M} \end{pmatrix}_{\omega} = \begin{pmatrix} \hat{\chi}_e(\omega) & \hat{\alpha}_{ME}(\omega) \\ \\ \hat{\alpha}_{ME}^T(\omega) & \hat{\chi}_m(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{E} \\ \\ \mathbf{H} \end{pmatrix}_{\omega}$$

The dynamical magnetoelectric coupling $\hat{\alpha}_{ME}(\omega)$ can emerge even if:

- there is no static counterpart
- there is no multiferroicity

The propagation of light is affected by phonon, magnon, and electromagnon excitations



Dynamical ME effect & directional dichroism



The propagation of light depends on $\mathbf{P} imes \mathbf{M}$ via the dynamical ME effect