Multiferroics:
from magnetoelectric memories to photonic devices

István Kézsmárki

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Prof. A. Loidl, University of Augsburg, Germany

Dr. T. Rõõm, Dr. U. Nagel, NICPB, Estonia

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Winter school/Workshop:
New Frontiers in 2D materials: Approaches & Applications
Villard-de-Lans, France, January 15-20, 2017
LE SOIN AU NATUREL
SHAMPOOING CORPS & CHEVEUX AMANDE DOUCE
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GEL BAIN DOUCHE PÉPINS DE RAISINS
EXFOLIATING SOAP

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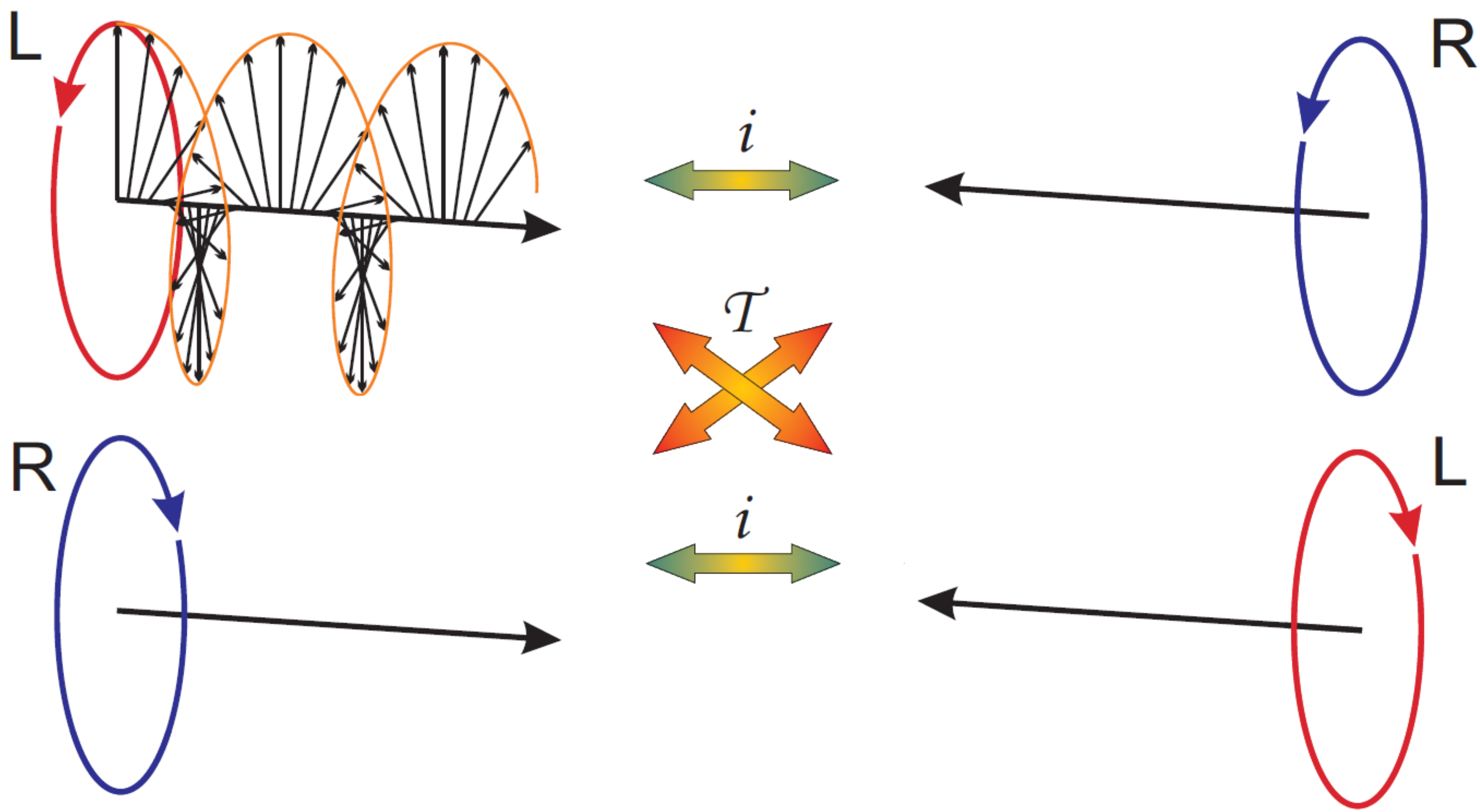
Quadrochroism

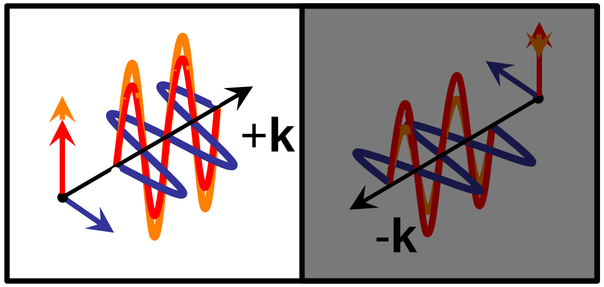


Outline

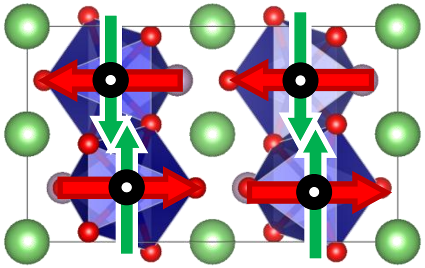
Static & optical magnetoelectric effects in multiferroics

$$\begin{bmatrix} D \\ B \end{bmatrix} = \begin{bmatrix} \hat{\varepsilon} & \hat{\chi}^{em} \\ \hat{\chi}^{me} & \hat{\mu} \end{bmatrix} \begin{bmatrix} E \\ H \end{bmatrix}$$

Quadrochroism & one-way trasparency via the optical magnetoelectric effect

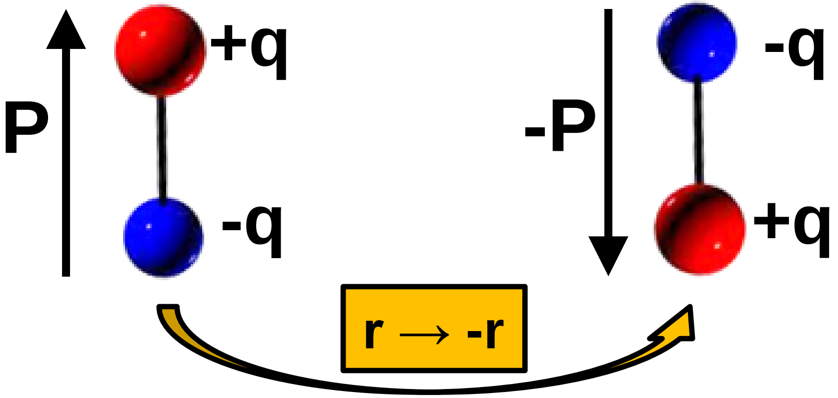


Target compounds: $Ba_2CoGe_2O_7$, $LiCoPO_4$, GaV_4S_8

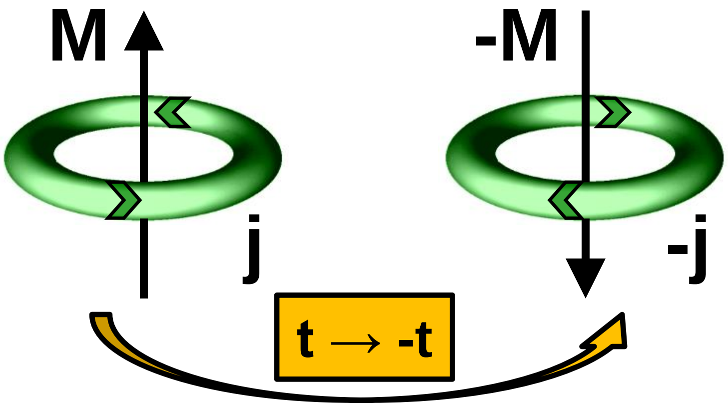


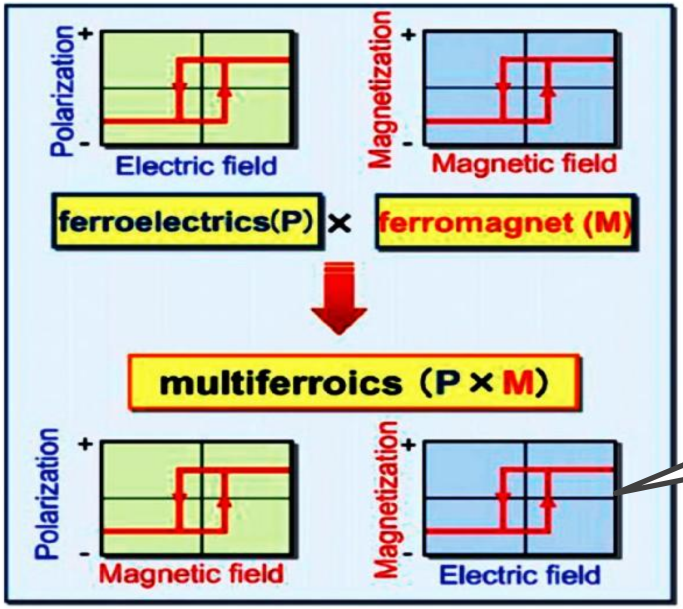
Multiferroics & magnetoelectric effect

Ferroelectricity



Ferromagnetism





Holy Grail of the field:
Magnetoelectric
memory devices

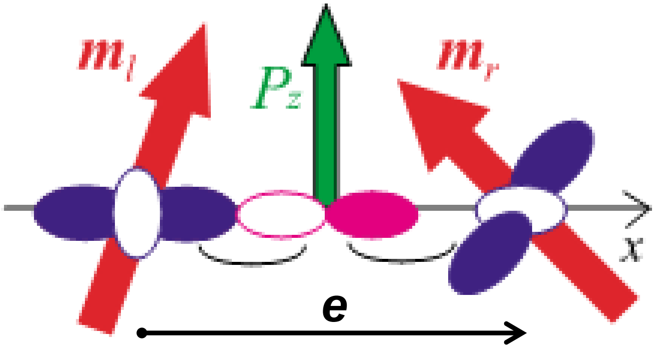
„Materials should exist, which can be polarized by a magnetic field and magnetized via an electric field.”

P. Curie, Journal de Physique **3**, 393 (1894)

Multiferroics & magnetoelectric effect

Basic mechanisms

- Two magnetic ions (e.g. transition metal ions) at ***r*** and ***r***+***e***
- Intermediate ligand atom
- Polarization preservs time reversal ⇨ second order in ***m***
- Polarization breaks spatial inversion ⇨ first order in ***e***

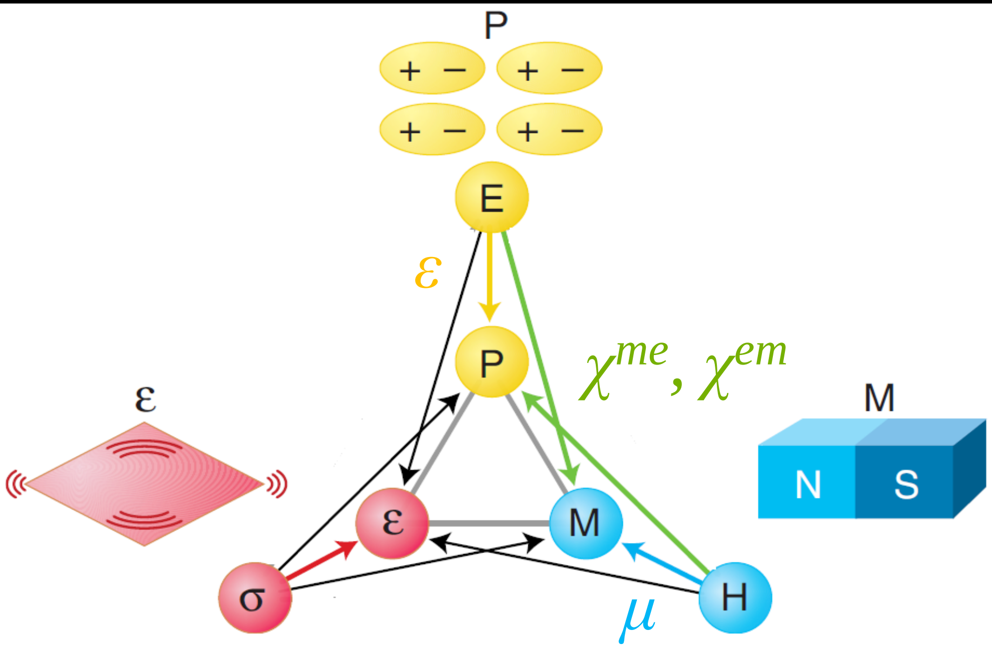


$$\mathbf{P}_{\mathbf{r}+\frac{\mathbf{e}}{2}} = P^{MS}(\mathbf{m}_{\mathbf{r}}\mathbf{m}_{\mathbf{r}+e})\mathbf{e} + P^{SC'}\mathbf{e}\times(\mathbf{m}_{\mathbf{r}}\times\mathbf{m}_{\mathbf{r}+e}) + P^{OR}[(\mathbf{e}\mathbf{m}_{\mathbf{r}})\mathbf{m}_{\mathbf{r}} - (\mathbf{e}\mathbf{m}_{\mathbf{r}+e})\mathbf{m}_{\mathbf{r}+e}]$$

C. Jia et al., Phys. Rev. B **76**, 144424 (2007)
S. Dong et al., Adv. Phys. **64**, 519 (2015)
P.S. Wang et al., Comp. Mat. Sci. **112**, 448 (2016)

- Magnetostriction (MS) mechanism in collinear spin structures,
  $HoMnO_3$, Ca_3CoMnO_6, ...
- Spin-current (SC) or inverse DM mechanism in cycloidal spin structures,
  $CoCr_2O_4$, $TbMnO_3$, $BiFeO_3$, $Ni_3V_2O_8$, ...
- Spin dependent orbital hybridization (OR) mechanism,
  $Ba_2CoGe_2O_7$, $Sr_2CoSi_2O_7$, $CuFeO_2$, ...
- Room-temperature multiferroics existing but few

Multiferroics & magnetoelectric effect



Spaldin and Fiebig, Science (2005)

Generalized constituve relations

$$\begin{bmatrix} D \\ B \end{bmatrix} = \begin{bmatrix} \hat{\varepsilon} & \hat{\chi}^{em} \\ \hat{\chi}^{me} & \hat{\mu} \end{bmatrix} \begin{bmatrix} E \\ H \end{bmatrix}$$

$$\chi_{ij}^{me}(\omega) = \frac{2}{\hbar N V} \sum_n \frac{\overbrace{\omega_{no} \Re\{\langle 0|M_i|n\rangle\langle n|P_j|0\rangle\}}^{\chi'_{ij}(\omega)} + \overbrace{i\omega \Im\{\langle 0|M_i|n\rangle\langle n|P_j|0\rangle\}}^{\chi''_{ij}(\omega)}}{\omega_{no}^2 - \omega^2 - 2i\omega\delta}$$

$\chi'_{ij}(\omega)$
- inversion (I) odd
- time reversal (T) odd
- static magnetoelectric effect
- directional anisotropy

$\chi''_{ij}(\omega)$
- inversion (I) odd
- time reversal (T) even
- vanishes in the static limit
- natural optical activity

L.D. Barron, *Molecular light scattering and optical activity* (Cambridge, 2004)

Outline

Static & optical magnetoelectric effects in multiferroics

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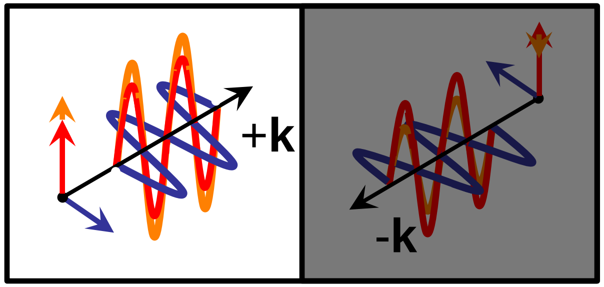
Quadrochroism & one-way trasparency via the optical magnetoelectric effect



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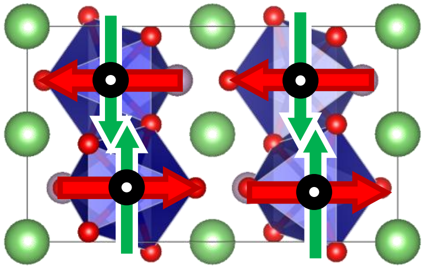
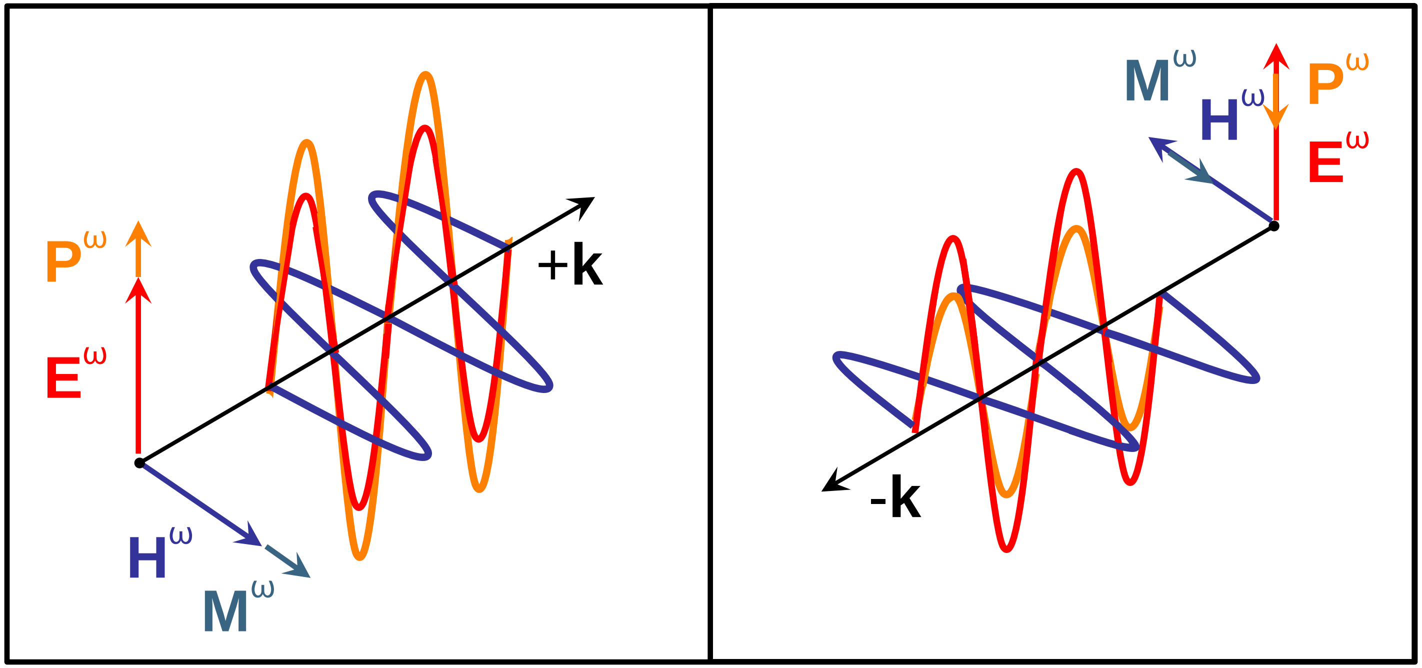


Optical magnetoelectric effect: Four-coloured optics

$$\chi'_{ji}(\omega)$$
$$\varepsilon = 1$$
$$\mu = 1$$



$$N^{\pm}(\omega) \approx \sqrt{\epsilon_{ii}(\omega)\mu_{jj}(\omega)} \pm \underbrace{\tfrac{1}{2}[\chi_{ji}^{\mathrm{me}}(\omega) + \chi_{ij}^{\mathrm{em}}(\omega)]}_{\chi'_{ji}(\omega)}$$

- different refractive indices for ±**k** propagation and two polarizations, termed as quadrochroism
- directional (±**k**) optical anisotropy is generally weak, $\Delta N/N \sim 10^{-2}$-10^{-6} Rikken, Nature (1997)
- BUT can be strong in multiferroics!

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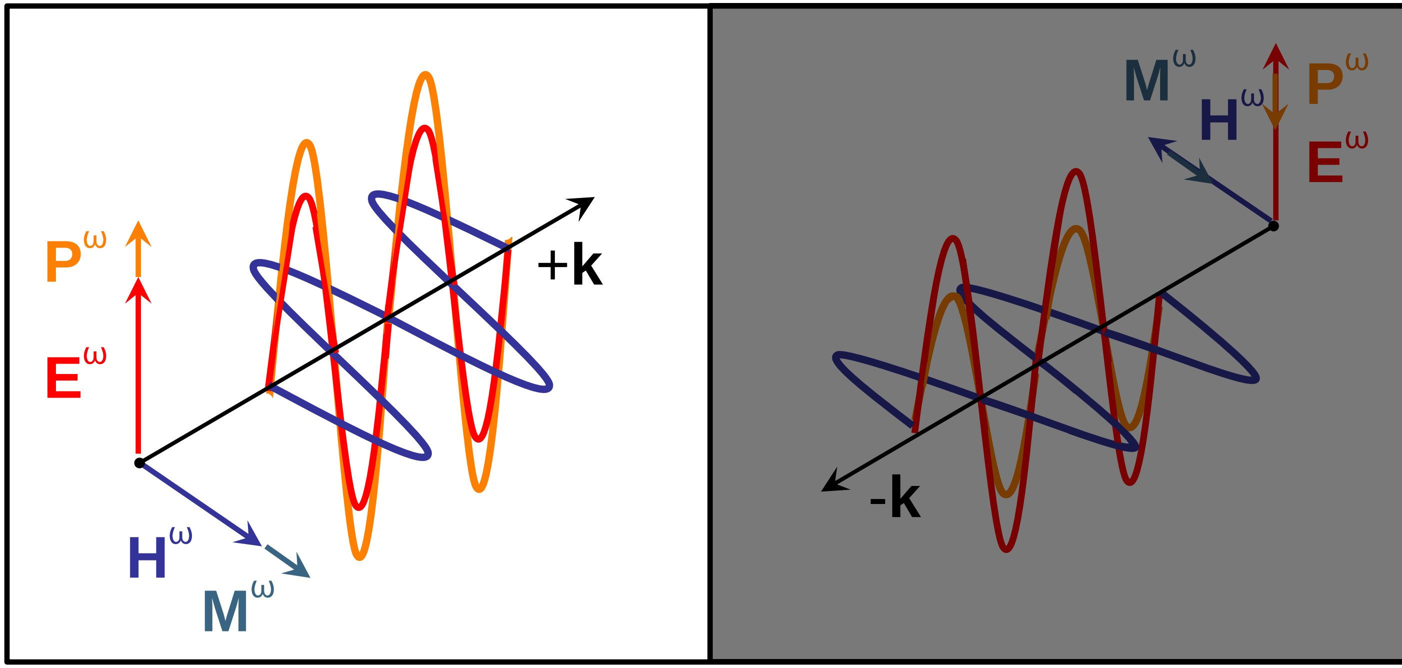

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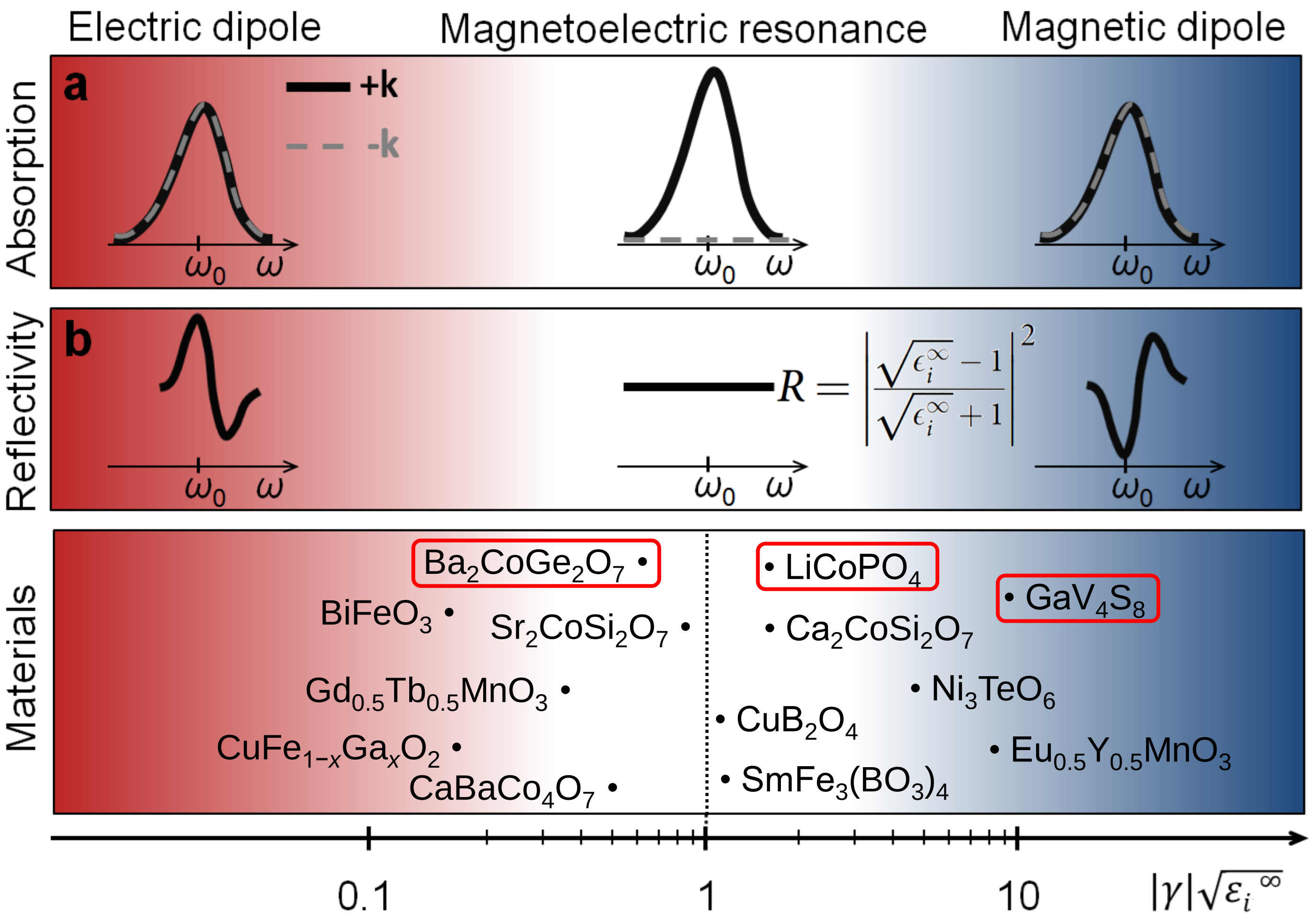
Optical magnetoelectric effect: One-way transparency

Condition for one-way transparency: $\left|\frac{\langle n|\, \mathrm{M_j}\, |0\rangle}{\langle n|\mathrm{P_i}|0\rangle}\right| \triangleq |\gamma| = \frac{1}{\sqrt{\epsilon_i^\infty}}$ [CGS]

Kézsmárki, NatCommun (2014)



$Ba_2CoGe_2O_7$
Kézsmárki, PRL (2011)
Bordács, NatPhys (2012)

$Eu_{0.5}Y_{0.5}MnO_3$
Takahashi, NatPhys (2012)

$Gd_{0.5}Tb_{0.5}MnO_3$
Takahashi, PRL (2013)

$Sr_2CoSi_2O_7$ & $Ca_2CoSi_2O_7$
Szaller, PRB (2014)
Kézsmárki, NatCommun (2014)

$CuFe_{1-x}Ga_xO_2$
Kibayashi, NatCommun (2014)

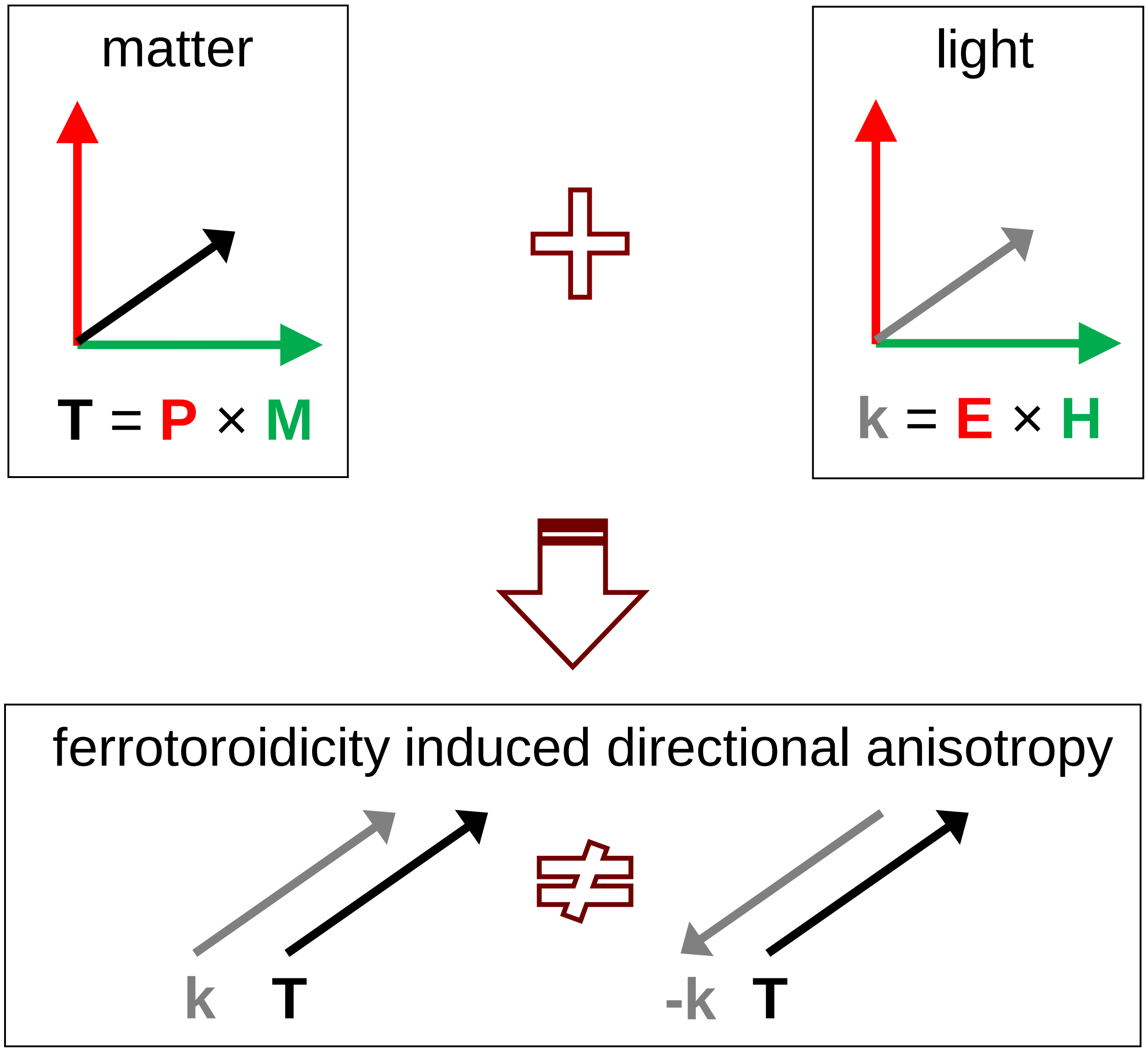
$SmFe_3(BO_3)_4$
Pimenov, PRB (2015)

CuB_2O_4
Arima, PRL (2015)

$CaBaCo_4O_7$
Bordács, PRB (2015)

$BiFeO_3$
Kézsmárki, PRL (2015)

Optical magnetoelectric effect: One-way transparency



Kézsmárki, PRL (2011)

Optical magnetoelectric effect: One-way transparency

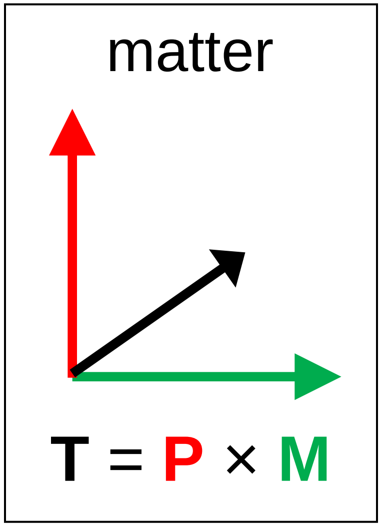
PHOTON MOMENTUM EFFECTS IN THE MAGNETO-OPTICS OF EXCITONS

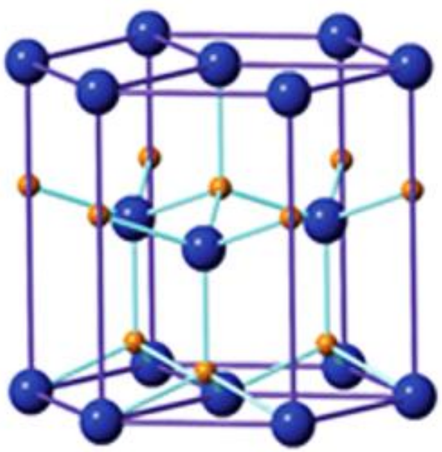
J. J. Hopfield and D. G. Thomas
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received February 26, 1960)

The optical selection rules and energy levels for exciton and band-to-band transitions as ordinarily calculated ignore the small but finite wave vector of visible light. No effects due to the finite wave vector have previously been noticed except the occasional observation of weak forbidden lines.[1] We describe here two pronounced magneto-optic effects (on excitons) due to the finite wave vector of light. The first effect is the drastic alteration of the magneto-optic absorption spectrum when the magnetic field is reversed.....

Hopfield, PRL (1960)

Optical magnetoelectric effect: One-way transparency





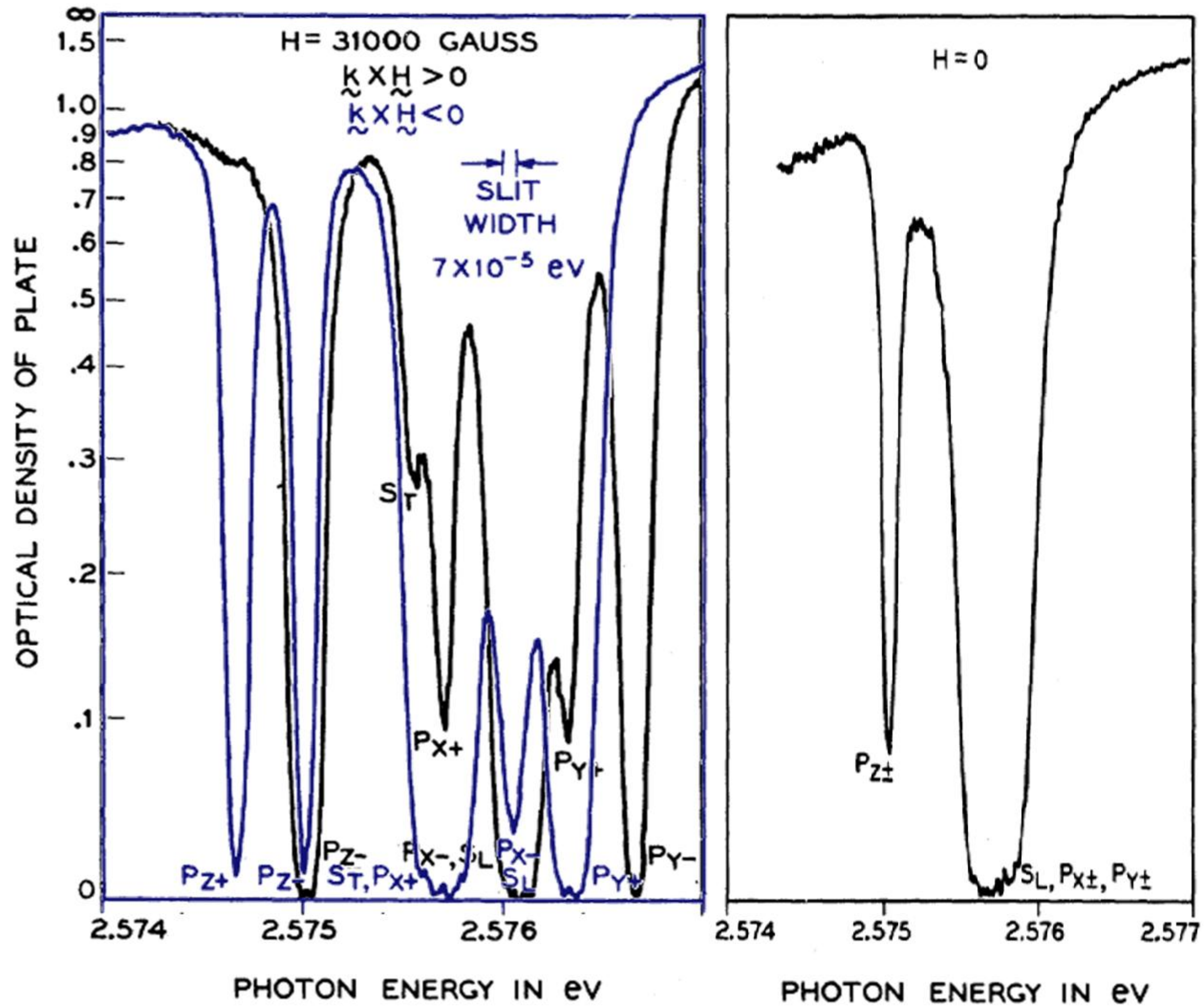
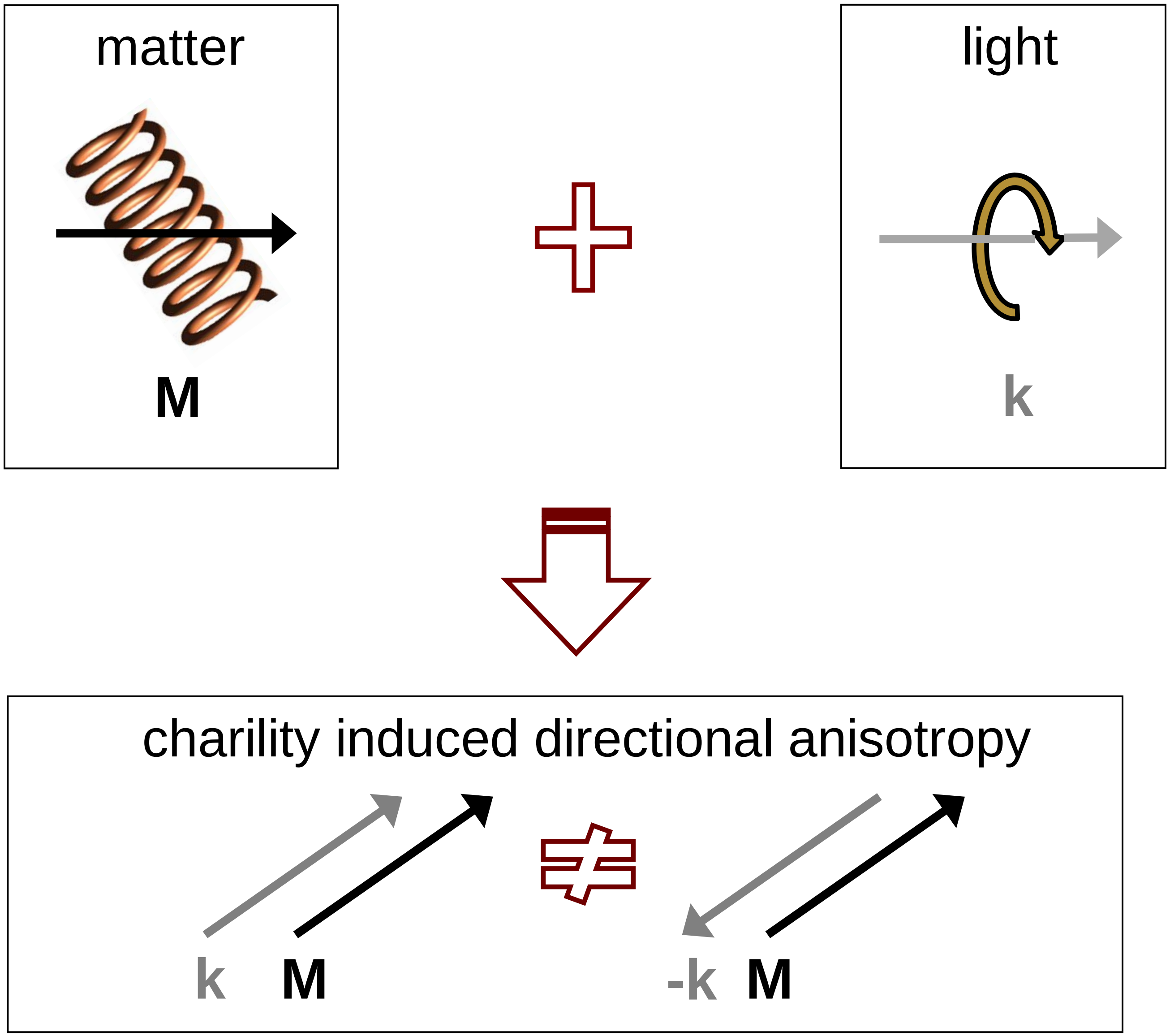


FIG. 1. Microphotometer trace of Zeeman effects in CdS of $n = 2$ exciton state at 1.6°K. The geometry is $\vec{c} \perp \vec{H}$, $\vec{k} \perp \vec{H}$, and $\vec{k} \perp \vec{c}$.

Optical magnetoelectric effect: One-way transparency



Optical magnetoelectric effect: One-way transparency

~~i : r → -r~~

~~T : t → -t~~

Crystal system	International notation	DA ∥ to PA	DA ⊥ to PA	Materials
Triclinic	1 (F)	T, MC, t	T, MC, t	$Ba_2Ni_7F_{18}$[37]
	$\bar{1}'$ (AF)	T, t	–	
Monoclinic	m (F)	–	T, t	$BiFeO_3$ $B_{[1\bar{1}0]}$[38,b]
	m' (F)	T, t	–	$Ni_3B_7O_{13}I$[40,c]
	2 (F)	MC, P, t	–	$BaNiF_4$[42,d]
	2′ (F)	–	T, MC, t	$LiCoPO_4$[43,e]
	$2/m'$ (AF)	t	–	TbOOH;[46] $Ba_2Ni_3F_{10}$[37]
	$2'/m$ (AF)	–	t	$TbPO_4$[47,f]
Rhombic	$2mm$ (AF)	P, t	–	
	$2'm'm$ (F)	–	T, t	$Ba_2CoGe_2O_7$ $B_{[110]}$[27,h]
	$2m'm'$ (F)	–	–	
	222 (AF)	–	–	
	22′2′ (F)	MC, t	–	$Ba_2CoGe_2O_7$ $B_{[100]}$[35,i]
Tetragonal	$4/m'$ (AF)	t	–	
	$4'/m'$ (AF)	–	–	
	$\bar{4}2m$ (AF)	–	–	
	$\bar{4}'2'm$ (AF)	t	–	
	$\bar{4}'2m'$ (AF)	–	–	
	$\bar{4}2'm'$ (F)	–	–	
	$4mm$ (AF)	P, t	–	
	$4'mm'$ (AF)	–	–	
	$4m'm'$ (F)	–	–	
	42(422) (AF)	–	–	
	4′2(4′2′2) (AF)	–	–	
	42′(42′2′) (F)	MC, t	–	Nd_5Si_4[57]
	$4'/m'm'm$ (AF)	–	–	
	$4/m'mm$ (AF)	t	–	
	$4/m'm'm'$ (AF)	–	–	

Crystal system	International notation	DA ∥ to PA	DA ⊥ to PA	Materials
Rhombohedral	3 (F)	MC, P, t	X	Cu_2OSeO_3 $B_{[111]}$[19,a]
	$\bar{3}'$ (AF)	t	X	Cr_2O_3[59]
	$3m$ (AF)	P, t	X	
	$3m'$ (F)	–	X	BiTeI $B_{[001]}$[41]
	32 (AF)	–	X	
	32′ (F)	MC, t	X	
	$\bar{3}'m$ (AF)	t	X	$Gd_2Ti_2O_7$[60]
	$\bar{3}'m'$ (AF)	–	X	$Nb_2Mn_4O_9$[61,g]
	$\bar{6}$ (F)	–	X	
	$\bar{6}'$ (AF)	t	–	
	6 (F)	MC, P, t	–	
	6′ (AF)	–	X	$ScMnO_3$, $LuMnO_3$[62]
	$6'/m$ (AF)	–	X	
				P[63]
	$6'mm'$ (AF)	–	X	$HoMnO_3$[62,64,k]
	$6m'm'$ (F)	–	–	
	62(622) (AF)	–	–	
	6′2(6′22′) (AF)	–	X	
	62′(62′2′) (F)	MC, t	–	
	$6'/mm'm$ (AF)	–	X	
	$6/m'mm$ (AF)	t	–	
	$6/m'm'm'$ (AF)	–	–	
		∥ to 3-axis		
Cubic	23 (AF)	X		
	$m'\bar{3}$ (AF)	X		
	$\bar{4}3m$ (AF)	X		
	$\bar{4}'3m'$ (AF)	–		
	43(432) (AF)	–		
	4′3(4′32) (AF)	X		
	$m'\bar{3}m$ (AF)	X		
	$m'\bar{3}m'$ (AF)	–		

Plenty of non-centrosymmetric magnets potentially exhibiting DA!

Szaller, PRB (2013)
Szaller, PRB (2014)

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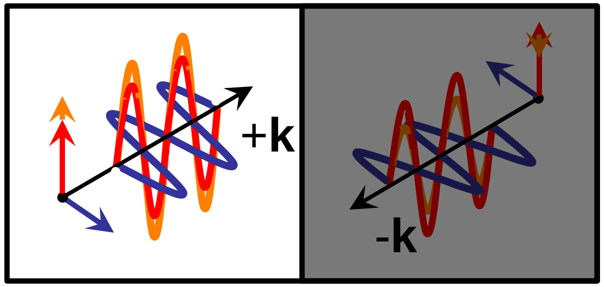

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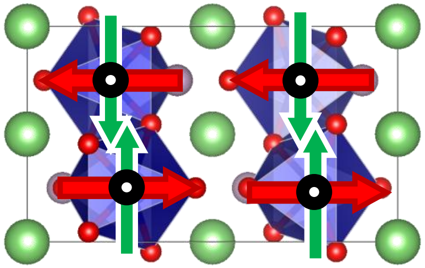
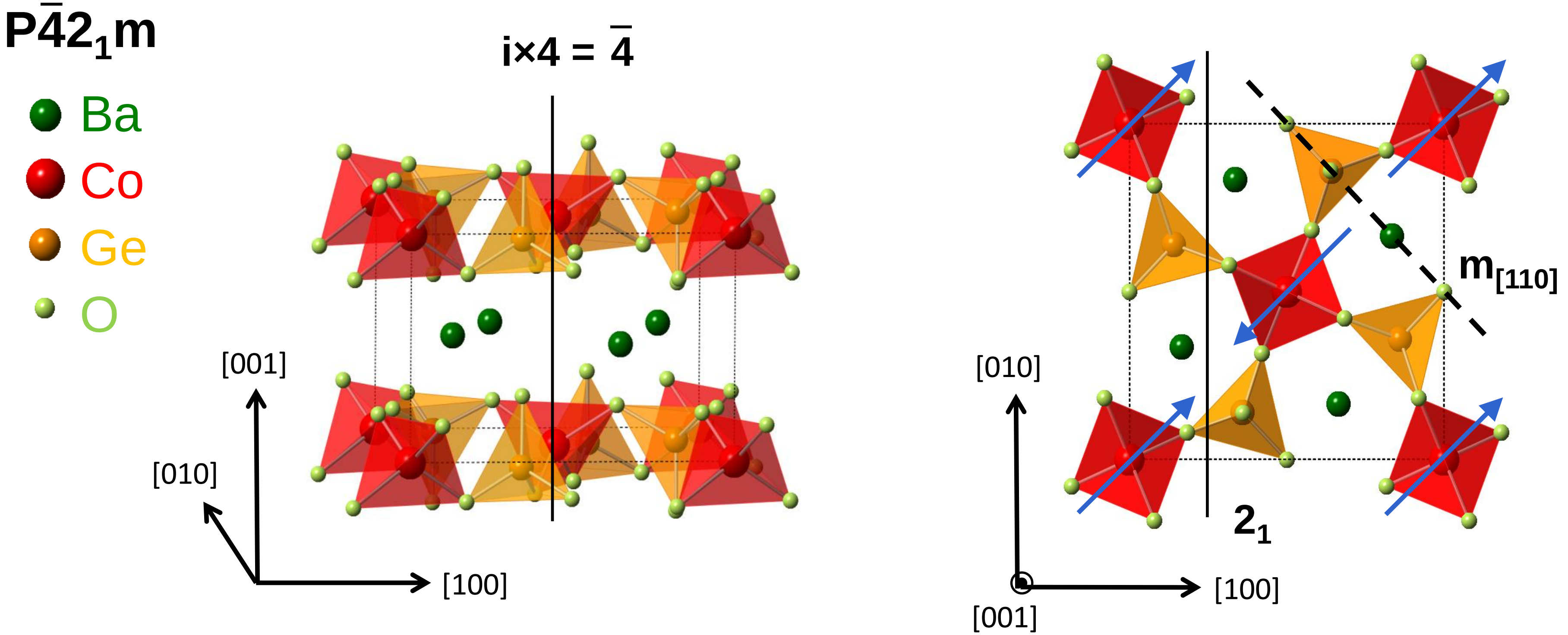
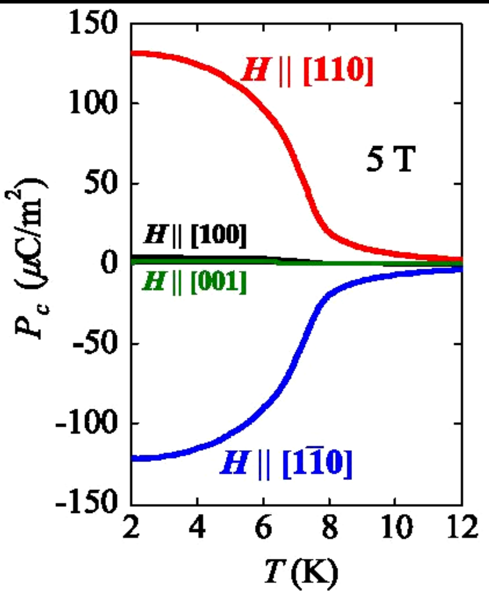


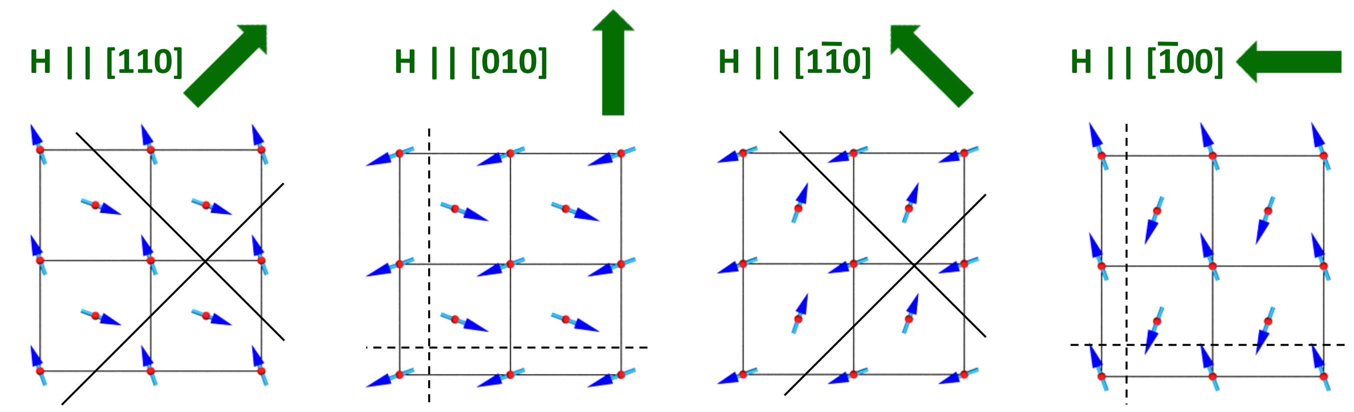
Multiferroic $Ba_2CoGe_2O_7$



- Tetragonal noncentrosymmetric crystal structure Hutanu, PRB (2011)
- Magetic Co^{2+} ions with S=3/2 in tetrahedral oxygen cages
- Easy-plane Néel antiferromagnet Hutanu, PRB (2012)

Multiferroic $Ba_2CoGe_2O_7$

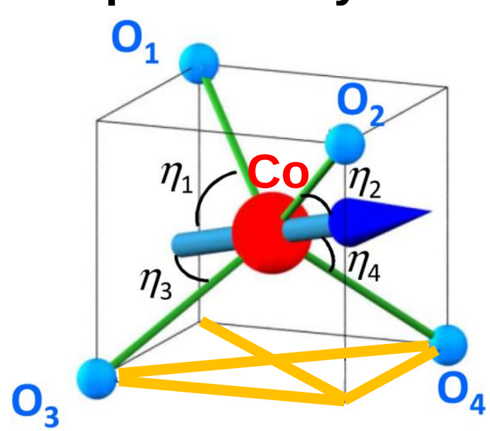




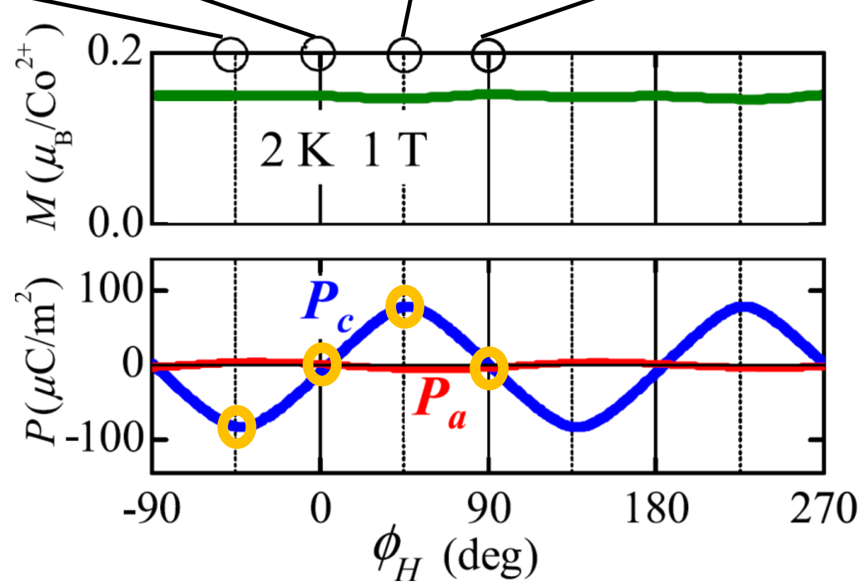
$m_{[110]}, m'_{[1\bar{1}0]}, 2'_{[001]}$ — $2'_{[100]}, 2_{[010]}, 2'_{[001]}$ — $m'_{[110]}, m_{[1\bar{1}0]}, 2'_{[001]}$ — $2_{[100]}, 2'_{[010]}, 2'_{[001]}$

P ⊗ — P=0, left-handed — P ⊙ — P=0, right-handed

Spin-dependent hybridization:



$$P \propto \sum_{i=1}^{4} (S \cdot e_i)^2 e_i \propto \sum_{i=1}^{4} (S \cos \eta_i)^2 e_i$$

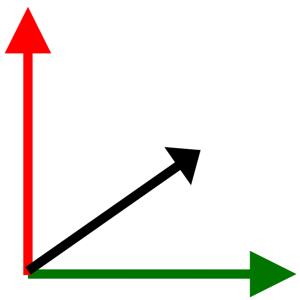


Arima, JPSJ (2007)

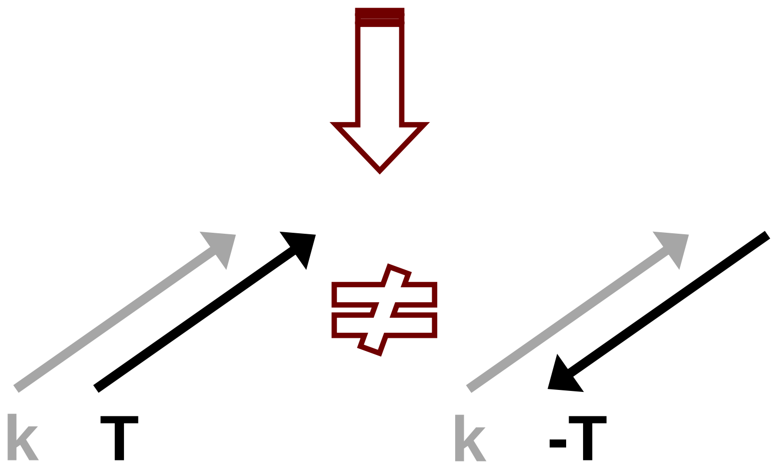
Murakawa, PRL (2010)

Multiferroic $Ba_2CoGe_2O_7$

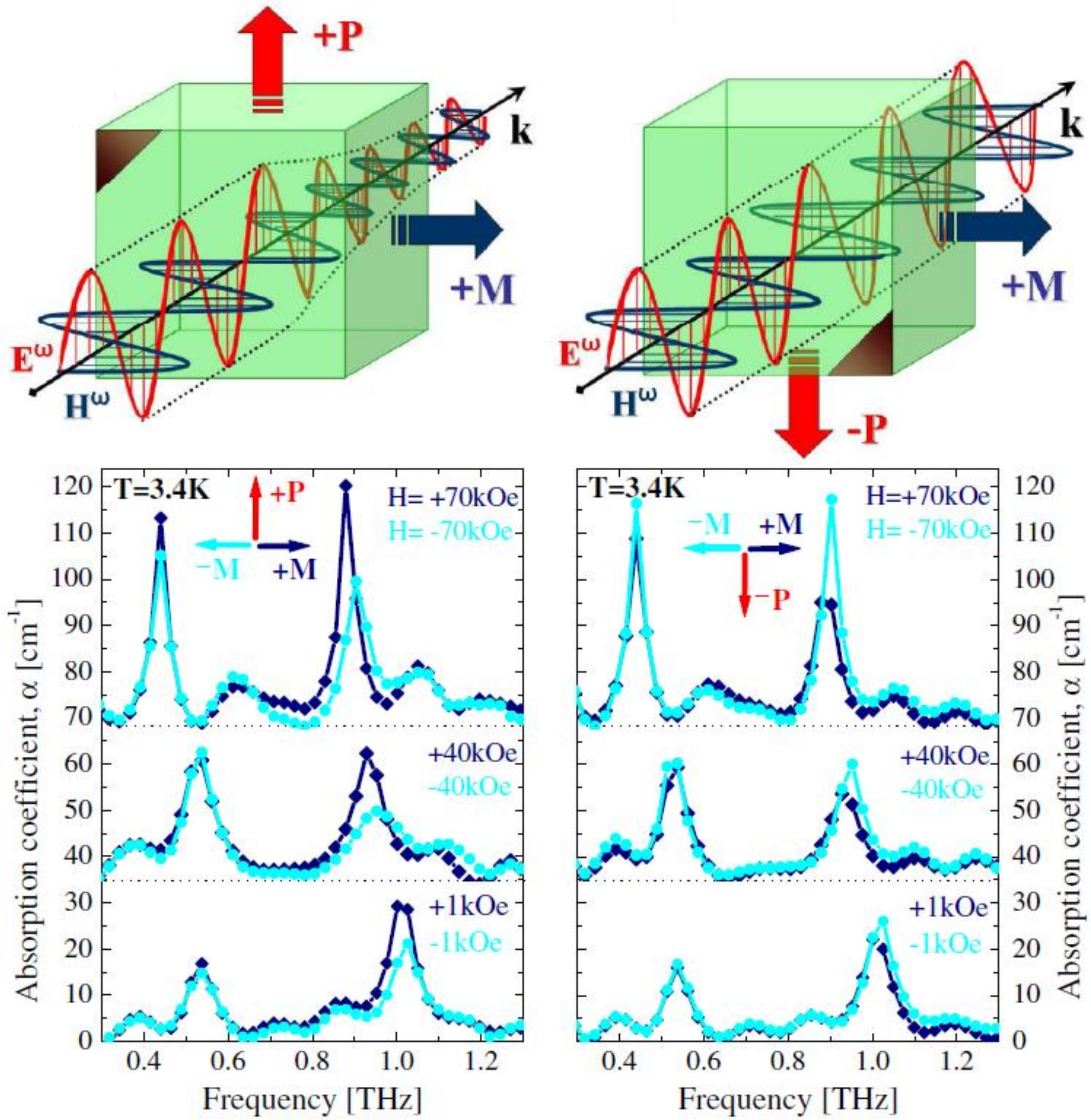
mm’2’



$T = P \times M$



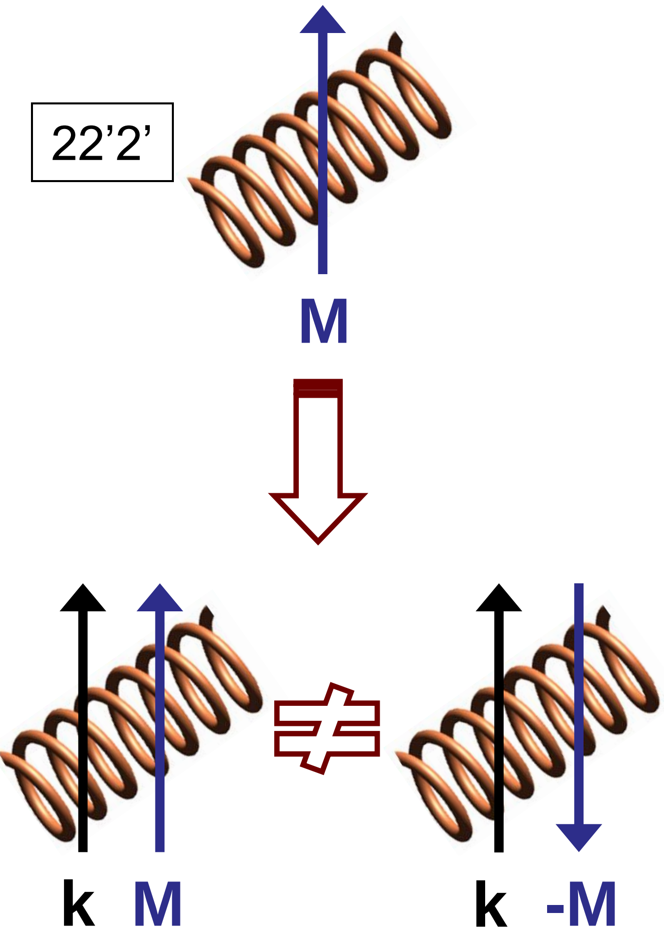
T-type DA



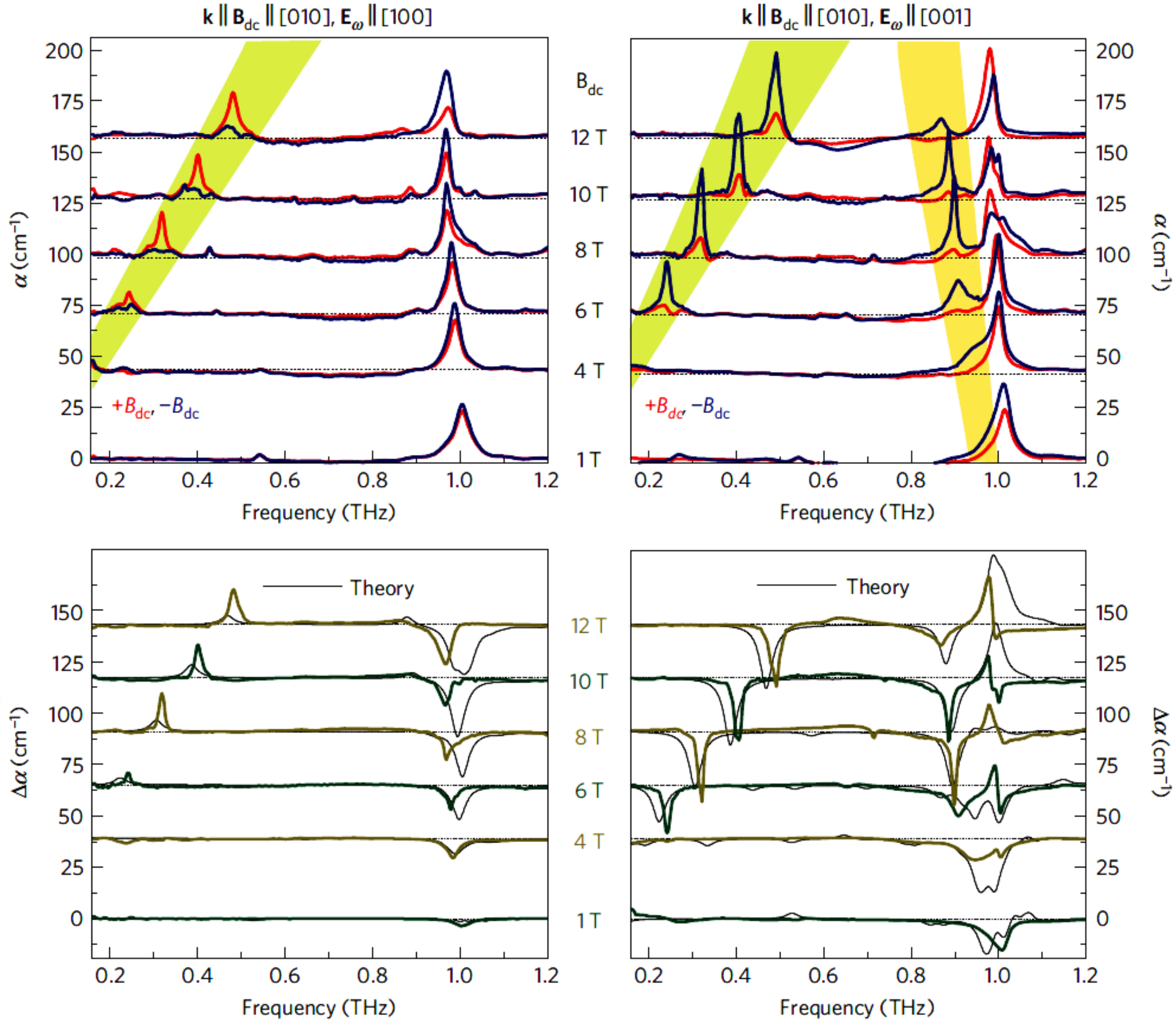
Kézsmárki, PRL (2011)

Multiferroic $Ba_2CoGe_2O_7$

22’2’

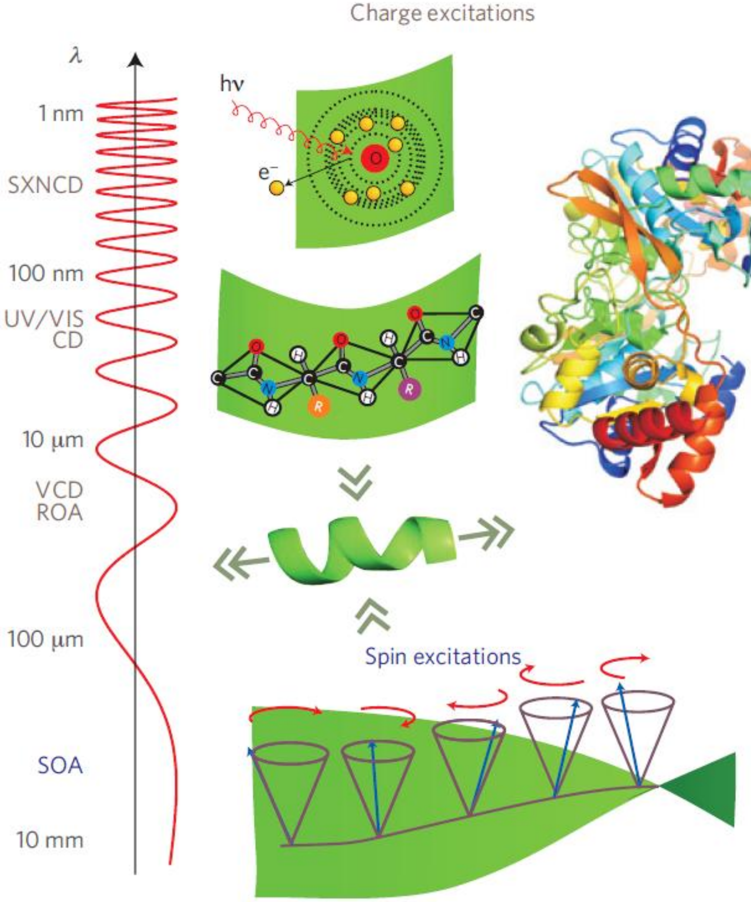


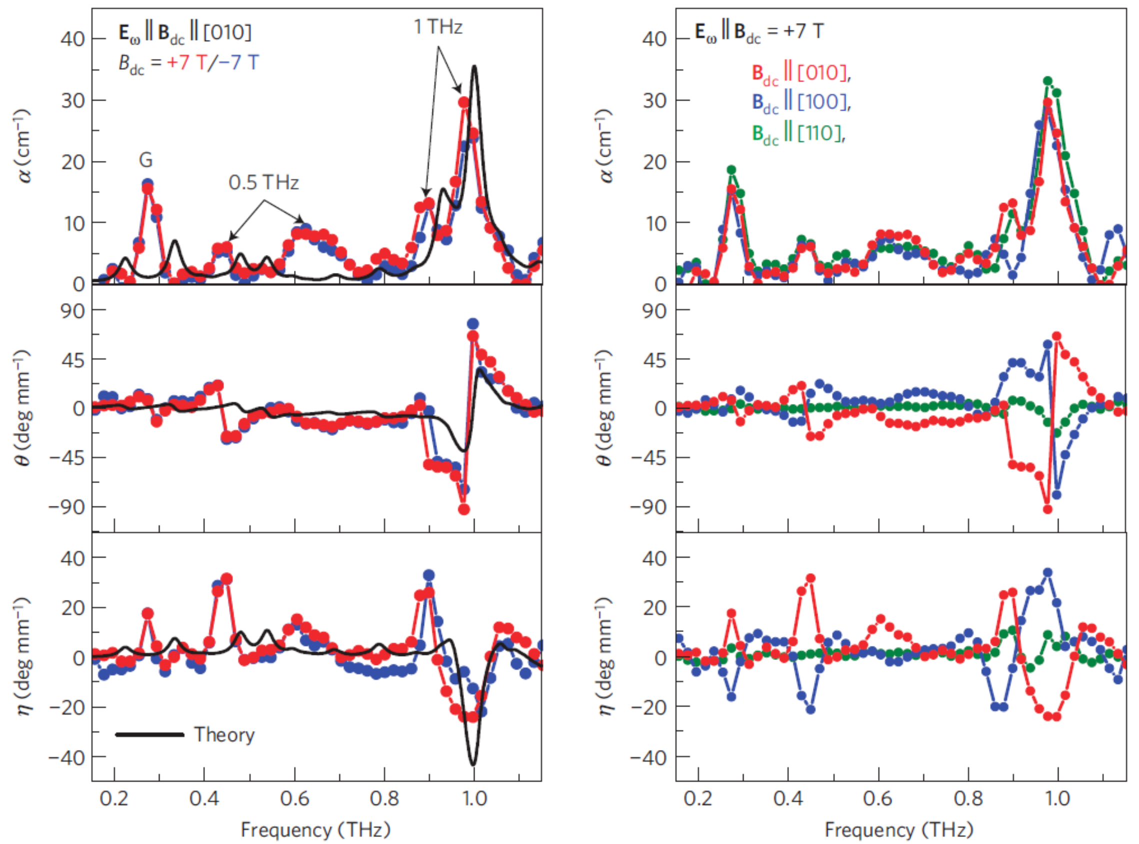
MC-type DA



Bordács, NatPhys (2012)

Multiferroic and Chiral State of $Ba_2CoGe_2O_7$

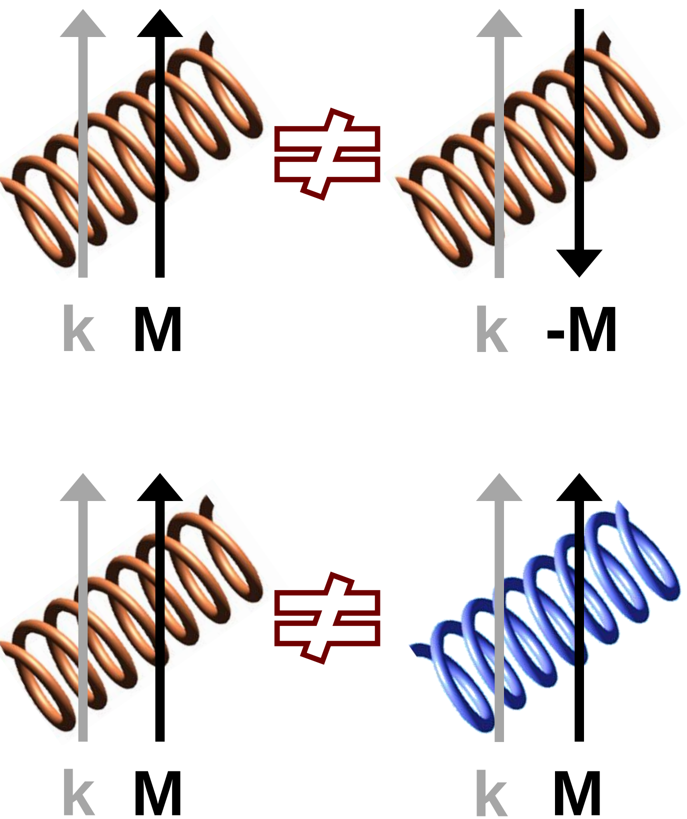




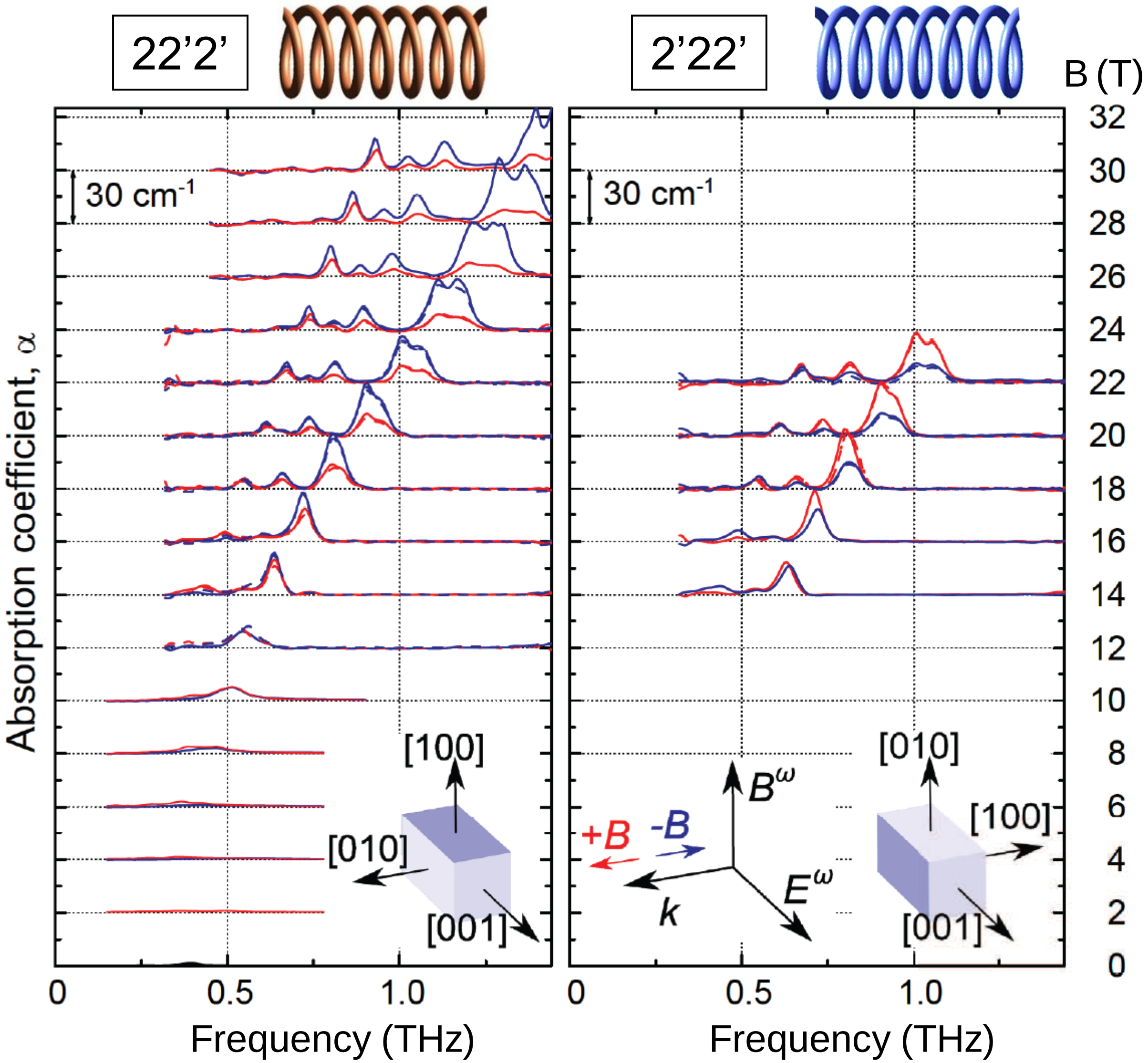
Bordács, NatPhys (2012)

Multiferroic and Chiral State of $Ca_2CoSi_2O_7$

$Ca_2CoSi_2O_7$



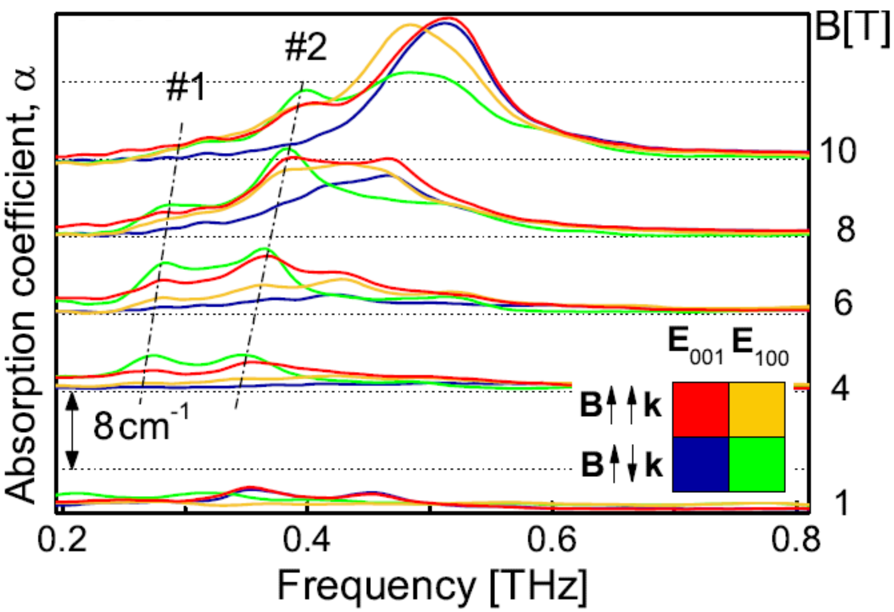
MC-type DA



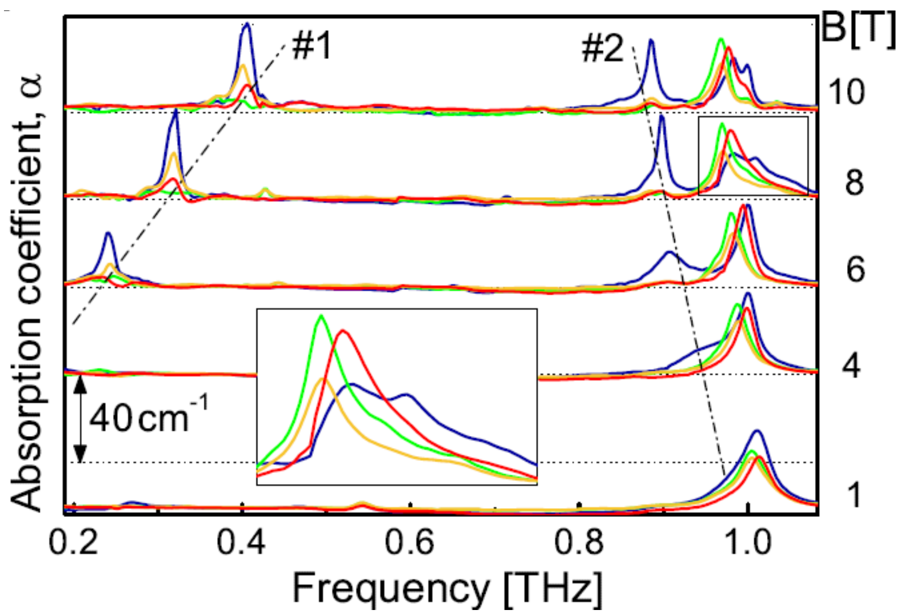
Kézsmárki, NatCommun (2014)

Multiferroic $Ba_2CoGe_2O_7$

$Ca_2CoSi_2O_7$



$Ba_2CoGe_2O_7$

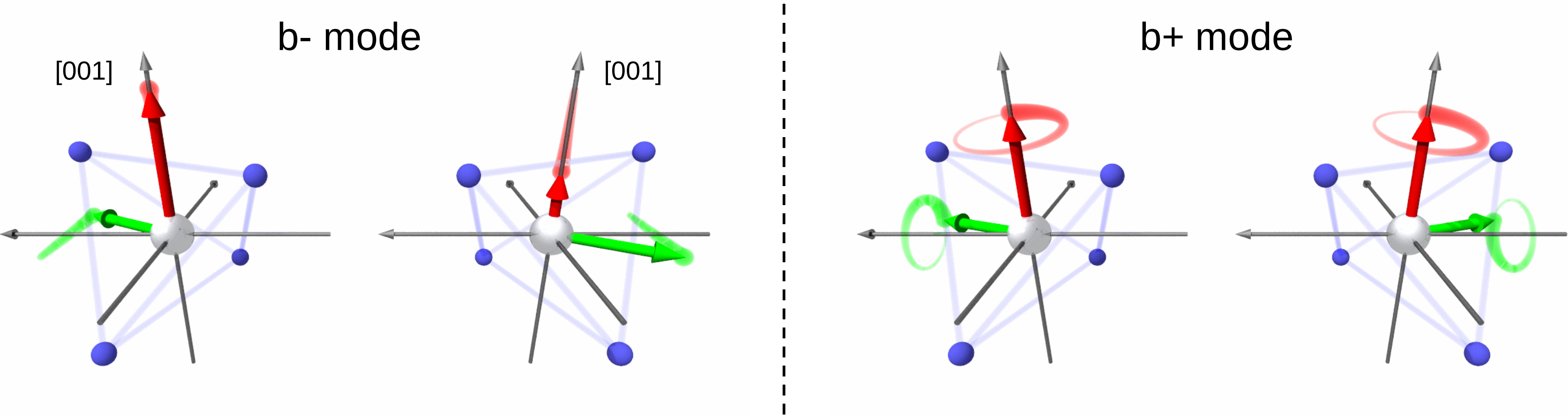


- Four different values of the refractive index for a given axis of propagation: forward and backward (±k) propagation and two orthogonal polarizations,
- Magnons with nearly optimal magnetoelectric ratio, $|\gamma| = \frac{c}{\sqrt{\epsilon_i^\infty}}$,
- Connection with dc ME effect: $\chi_{ij}^{me}(0) = \frac{c}{2\pi} \cdot \int_0^\infty \frac{\Delta\alpha(\omega)}{\omega^2} d\omega \quad \Leftarrow \quad \Re\chi(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\Im\chi(\omega')}{\omega' - \omega} d\omega'$

Kézsmárki, NatCommun (2014)

Multiferroic $Ba_2CoGe_2O_7$

S=3/2 spin: $$\mathcal{H} = \underbrace{J\sum_{\langle i,j\rangle}\left(S_i^x S_j^x + S_i^y S_j^y\right) + J_z \sum_{\langle i,j\rangle} S_i^z S_j^z}_{\text{J, } J_z \text{ exchange interaction}} + \underbrace{\sum_i \Lambda\left(S_i^z\right)^2}_{\Lambda \text{ single-ion anisotropy}}$$



- b- mode is the Goldstone mode (ω=0) ↔ dc magnetoelectric effect
- b+ would be the other Goldstone mode in the lack of magnetic anisotropy

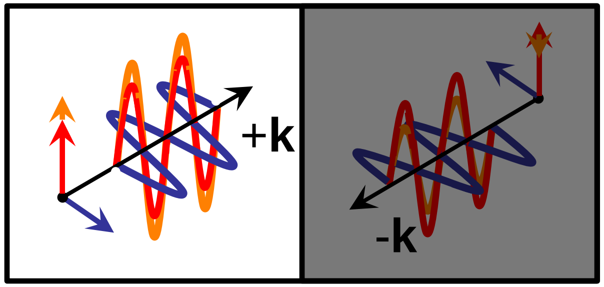
Penc, PRL (2012)

Outline

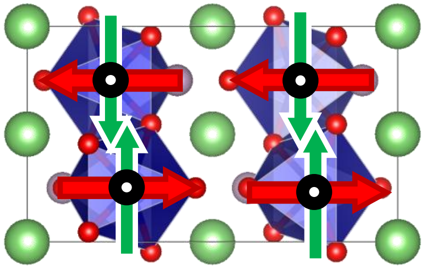
Static & optical magnetoelectric effects in multiferroics

$$\begin{bmatrix} D \\ B \end{bmatrix} = \begin{bmatrix} \hat{\varepsilon} & \hat{\chi}^{em} \\ \hat{\chi}^{me} & \hat{\mu} \end{bmatrix} \begin{bmatrix} E \\ H \end{bmatrix}$$

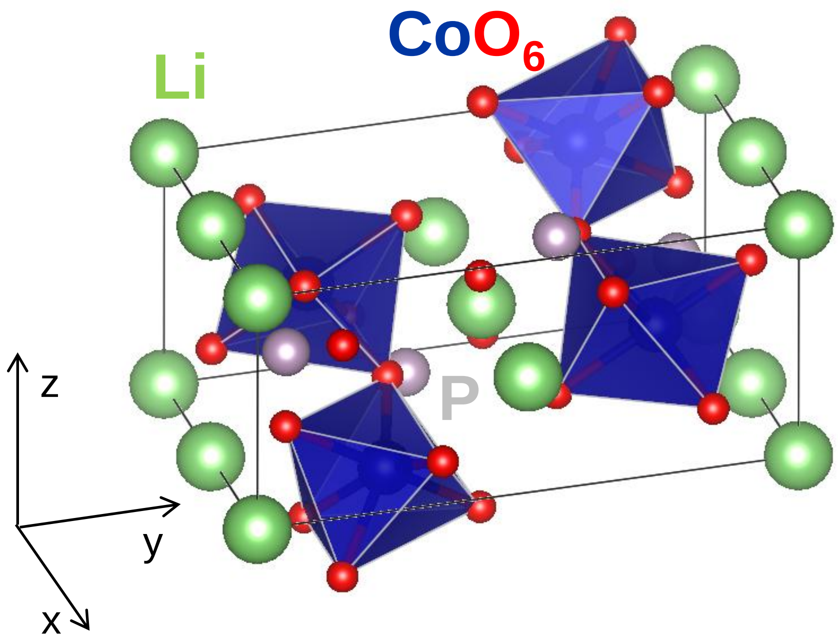
Quadrochroism & one-way trasparency via the optical magnetoelectric effect



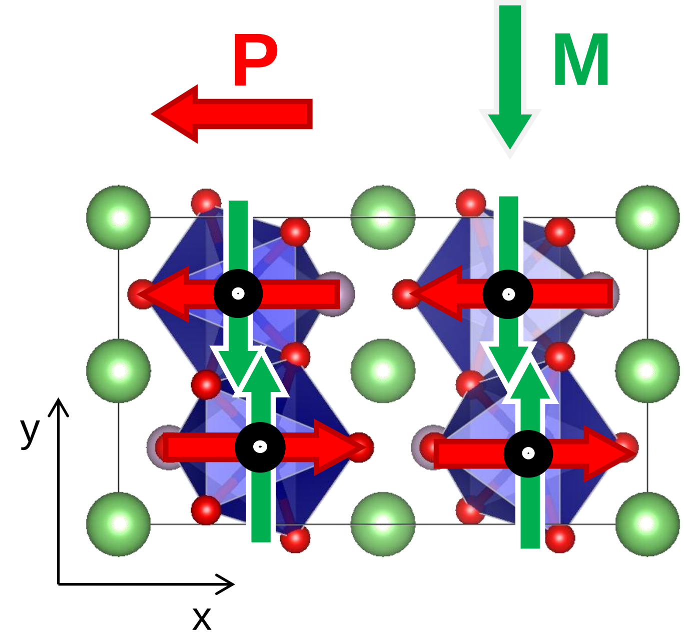
Target compounds: $Ba_2CoGe_2O_7$, $LiCoPO_4$, GaV_4S_8



Multiantiferroic $LiCoPO_4$



- orthorhombic Pmna (point group: mmm)
- distorted chessboard layers of **CoO_6** octahedra
- highly distorted **CoO_6** octahedra $\Rightarrow$
- **antiferroelectricity** (along x)

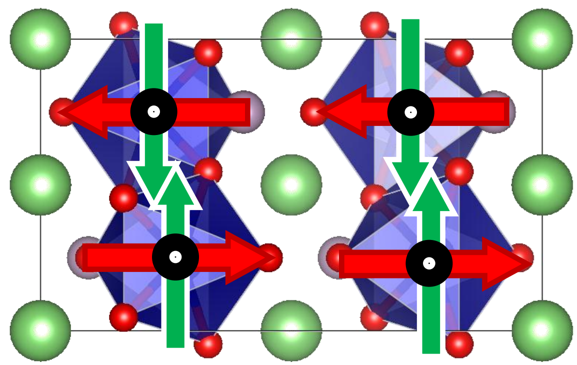


- magnetic order develops below T_N=21K
- **antiferromagnetism** (along y)
- orthorhombic Pmna' (point group: mmm')

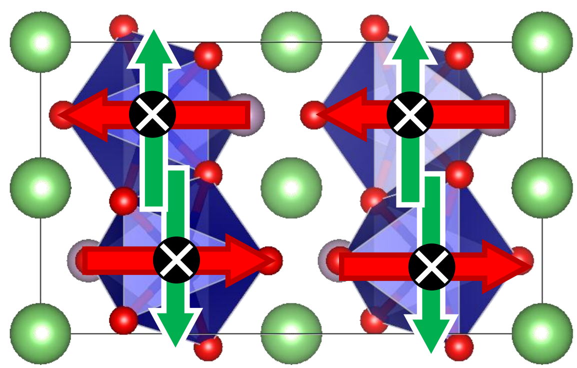
antiferroelectricity$_x$ × **antiferromagnetism$_y$** $\Rightarrow \pm\chi_{xy}^{me}$

Multiantiferroic $LiCoPO_4$

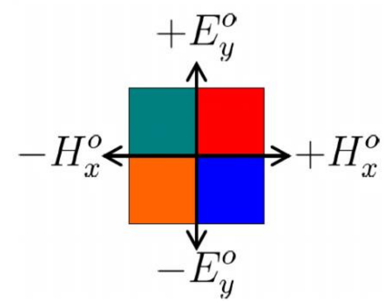
(red, orange) $\leftrightarrow \chi_{xy}^{me} > 0$



(blue, teal) $\leftrightarrow \chi_{xy}^{me} < 0$

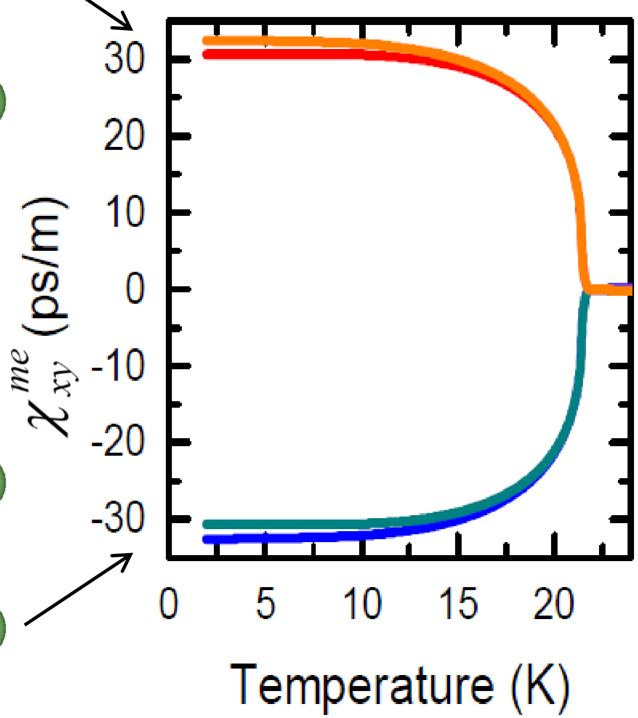


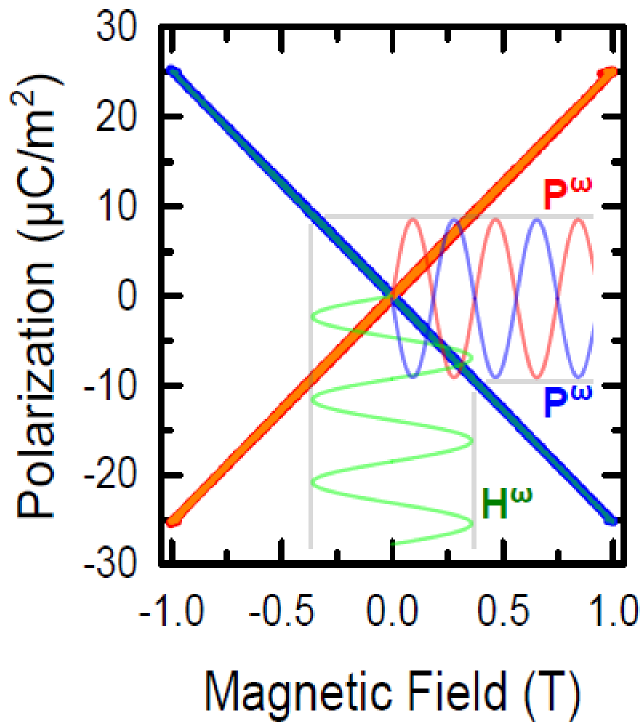
Magnetoelectric poling:



E^0=2 kV/cm

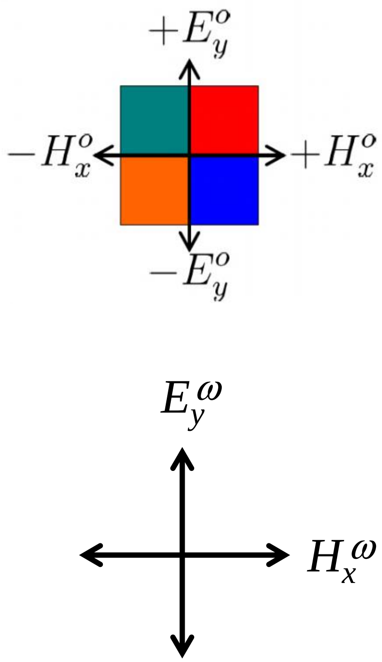
$\mu_0 H^0$=1 T

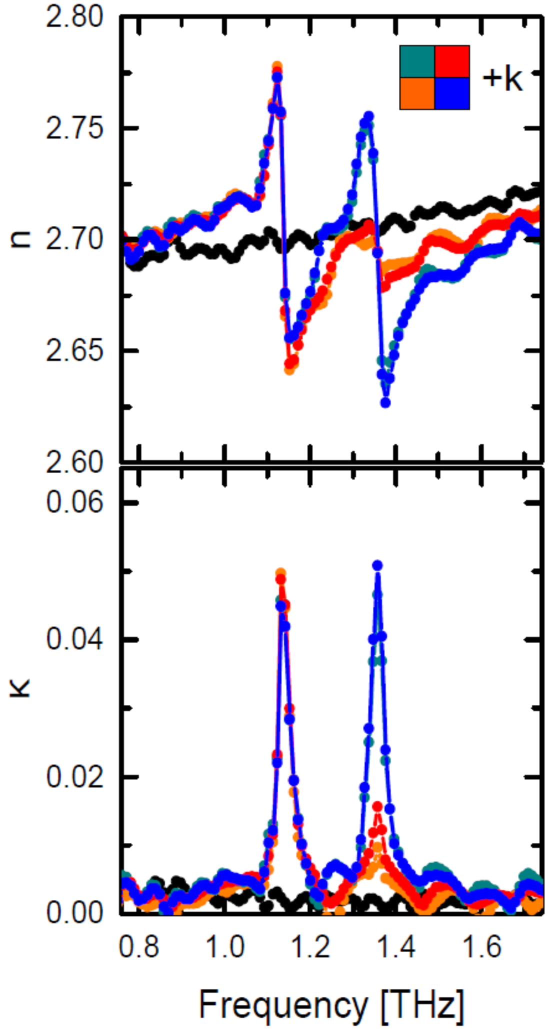


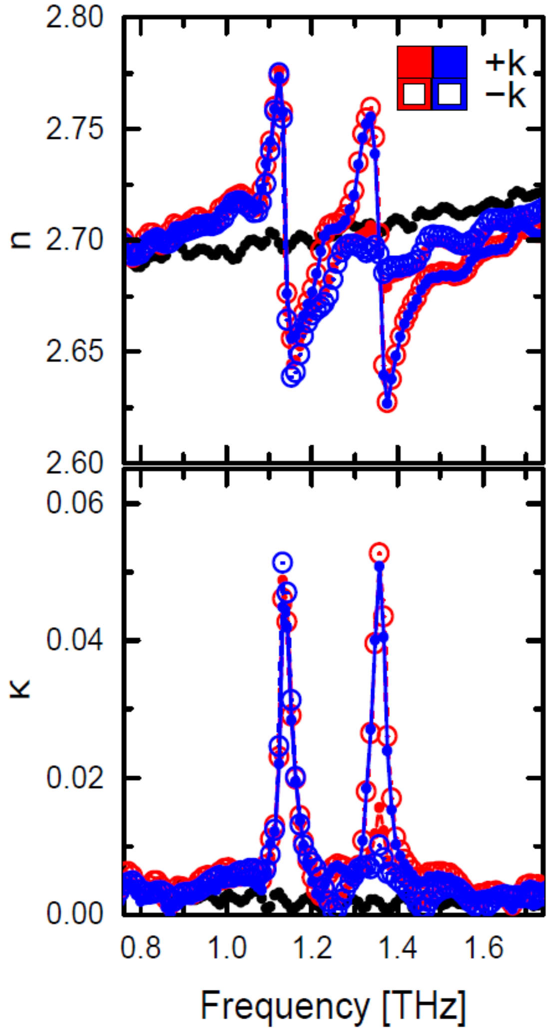


Sign of χ_{xy}^{me} depends on the sign of the poling $E^0 \times H^0$ field ☺

Multiantiferroic $LiCoPO_4$







Sign of $\chi_{xy}^{me}(\omega)$ depends on the sign of the poling $E^0 \times H^0$ field ☺

Remnant directional anisotropy in an antiferromagnet!

Outline

Static & optical magnetoelectric effects in multiferroics

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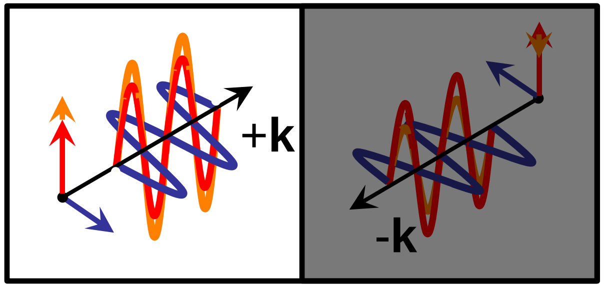
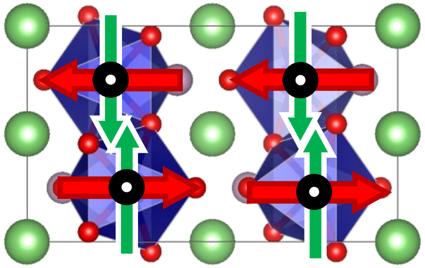
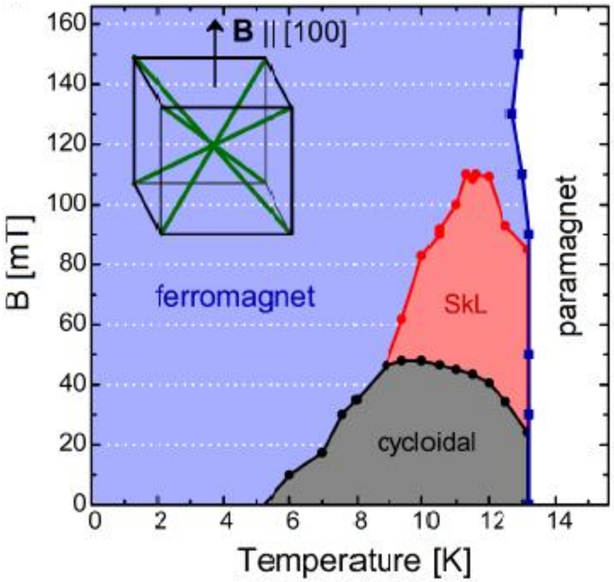
Quadrochroism & one-way trasparency via the optical magnetoelectric effect



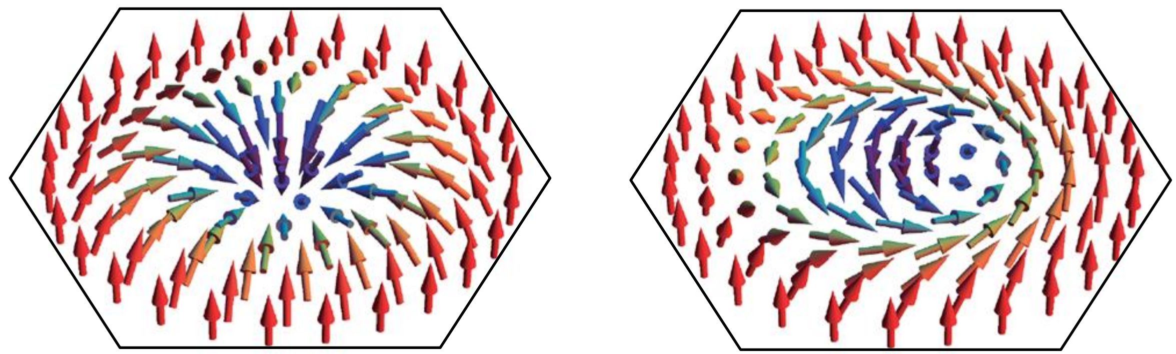
Target compounds: $Ba_2CoGe_2O_7$, $LiCoPO_4$, GaV_4S_8

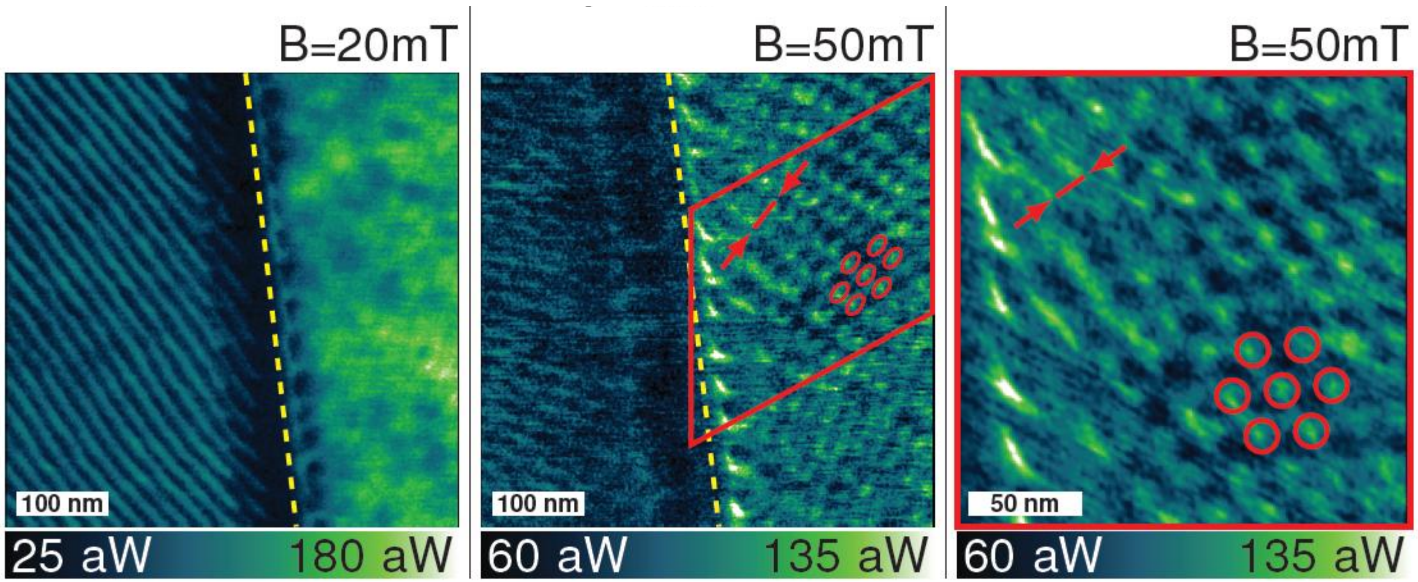


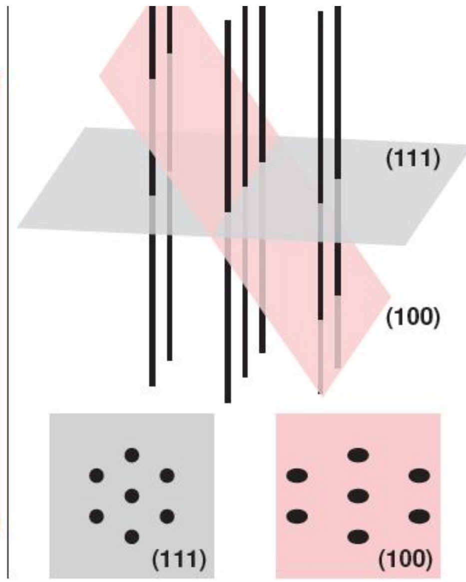
Multiferroic skyrmion host GaV_4S_8



Individual skyrmions of Néel and Bloch type:

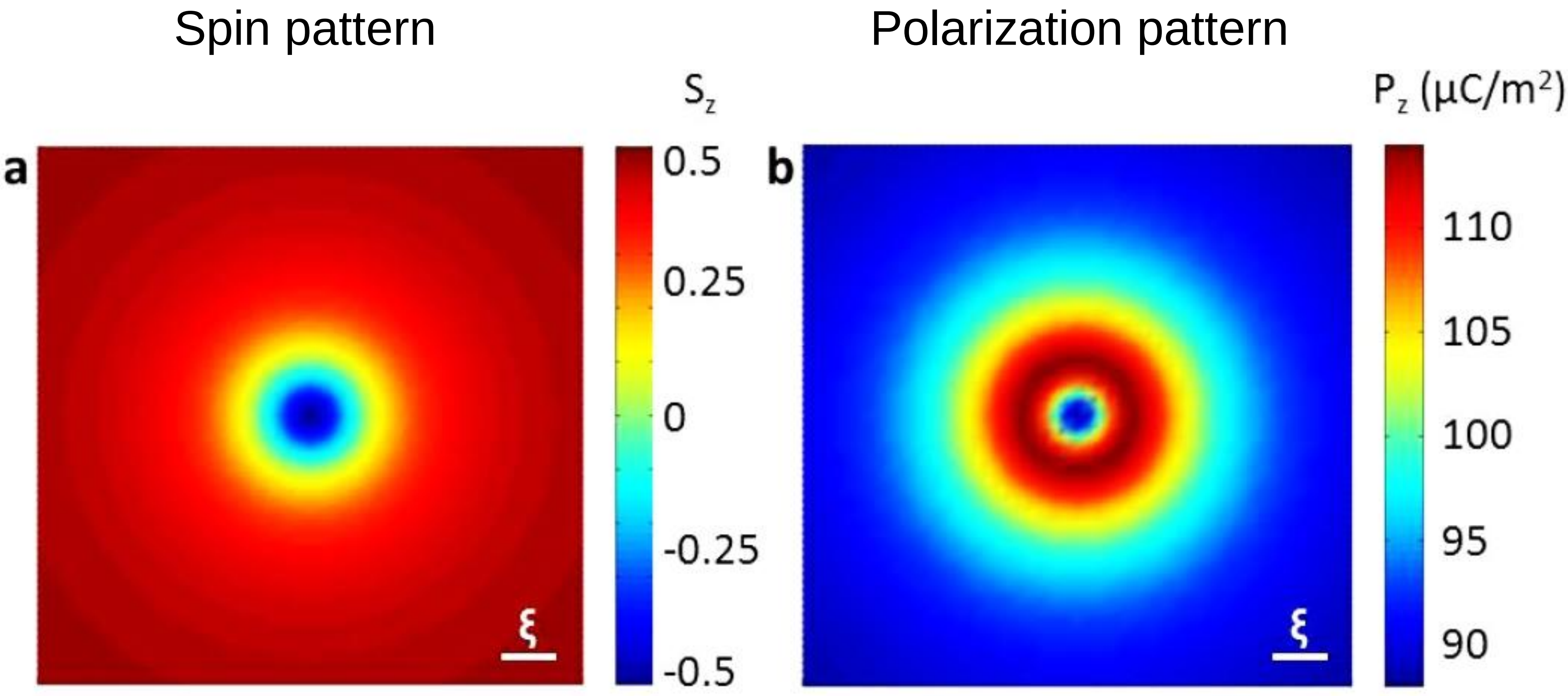






Kézsmárki, NatMater (2015)

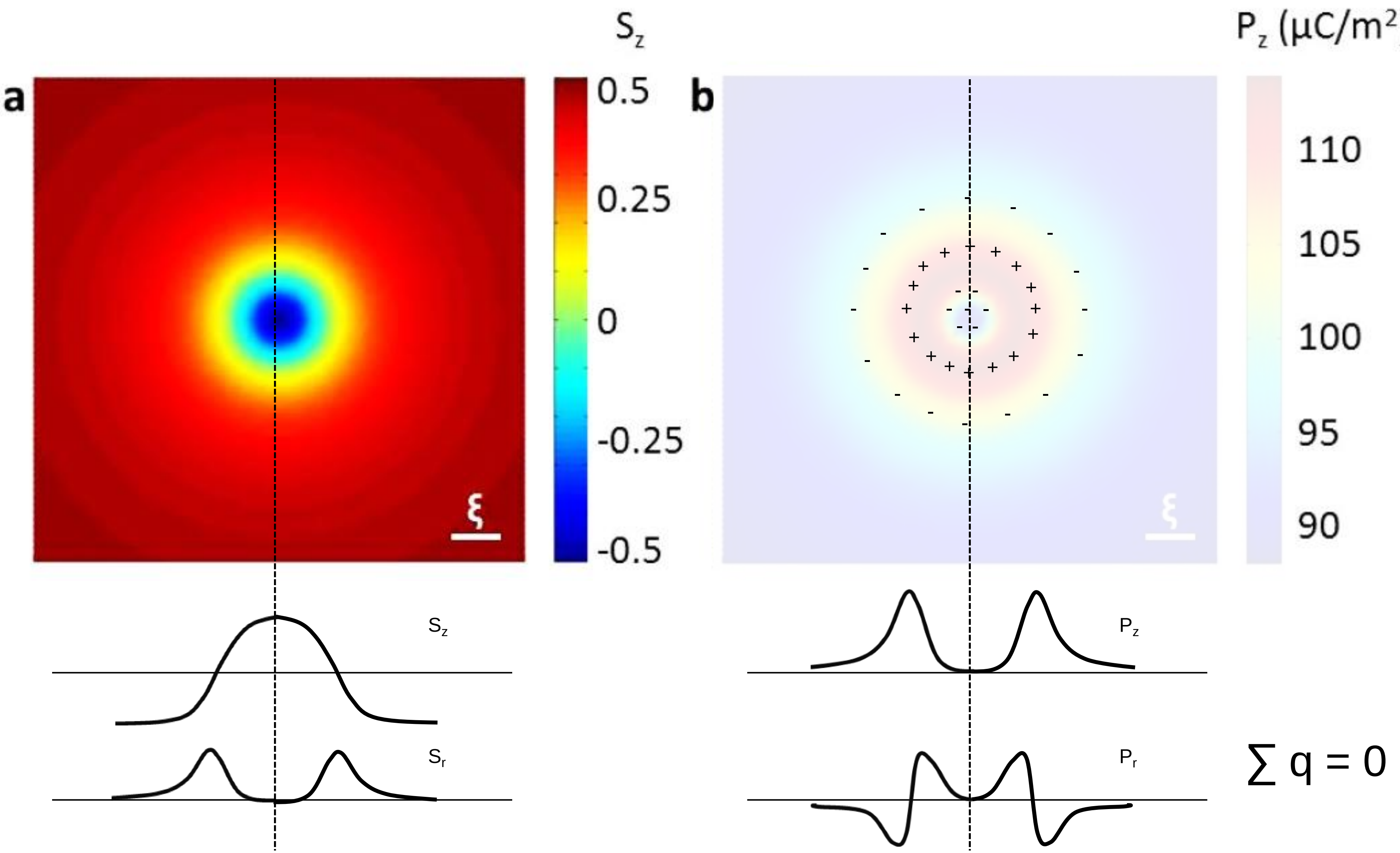
Multiferroic skyrmion host GaV_4S_8



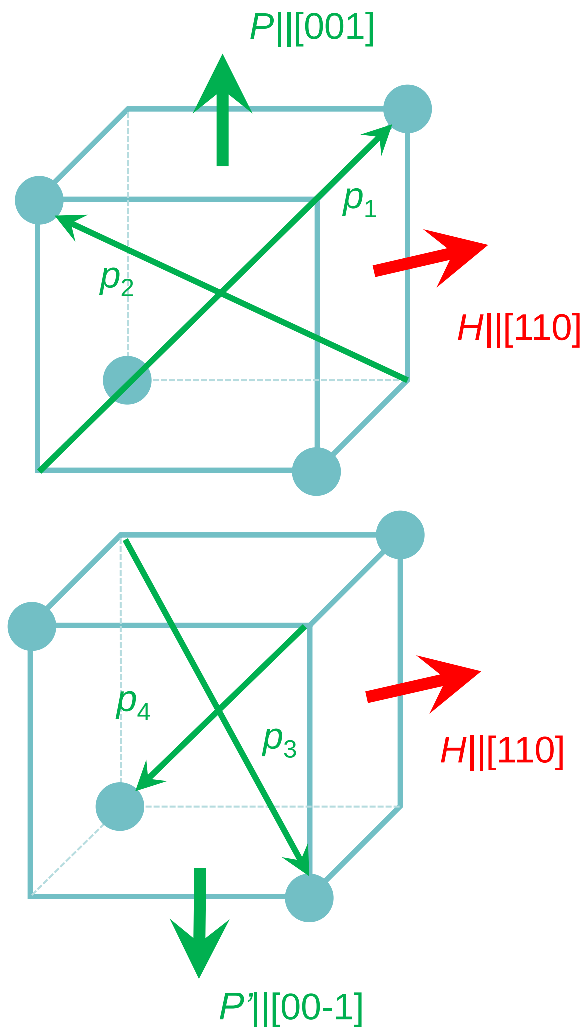
Ruff, SciAdvances (2015)

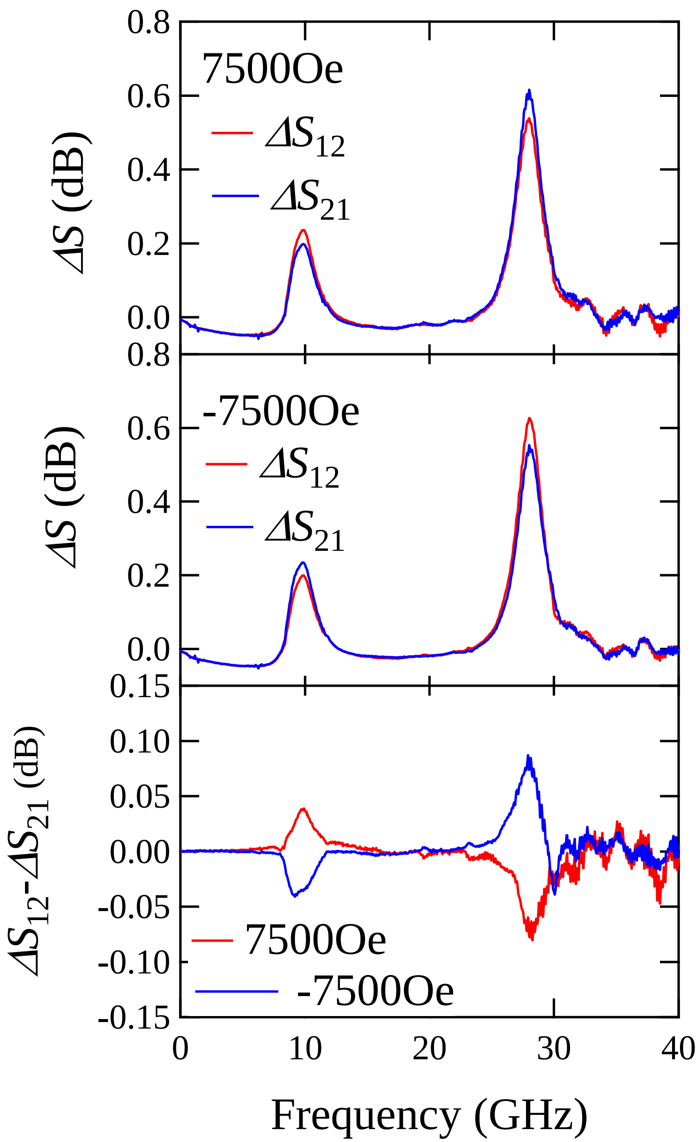
Multiferroic skyrmion host GaV_4S_8

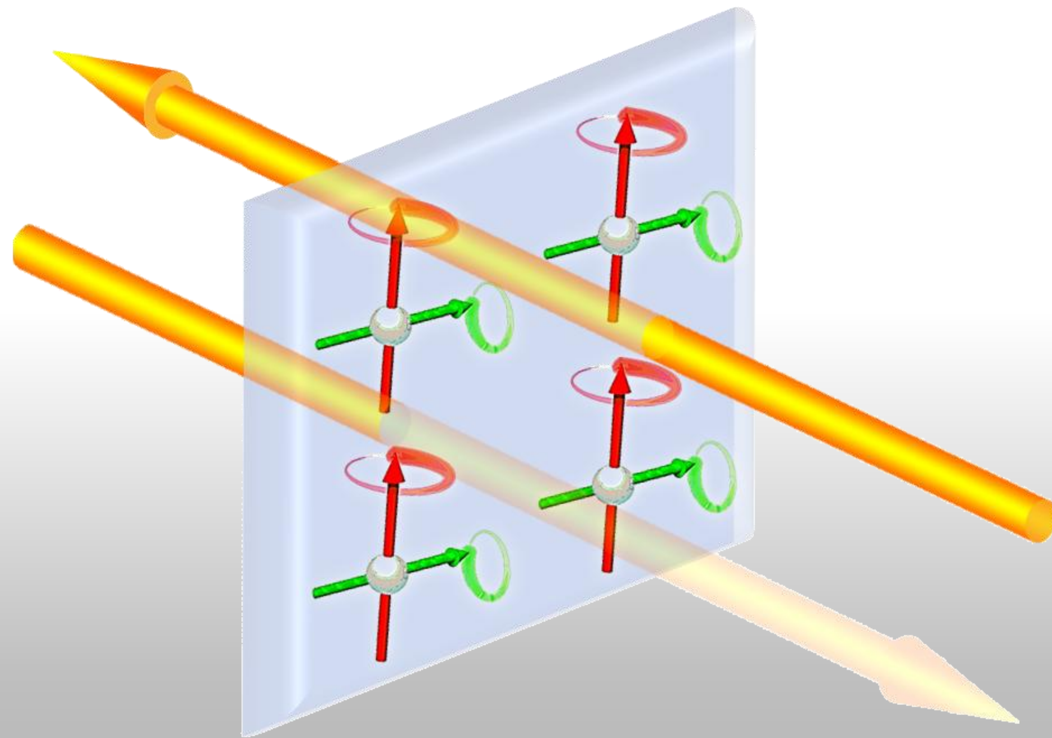
Spin pattern | Polarization pattern



Multiferroic skyrmion host GaV_4S_8







Thank you for your attention!

PhD and postdoc positions open

at the Istutute of electron correlation and magnetism of University of Augsburg, Department of Experimental Physics V.

kezsmark@mail.bme.hu