Terahertz spectroscopy of spin-phonon excitations in multiferroics

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Acknowledgments—collaborators

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Outline

Spin excitations in crystals

- Ferroic orders, multiferroics
- Properties of magnons / electromagnons
- Means of identifying electromagnons

Selected results

- Electromagnons
- Ultrafast dynamics

Perspectives and conclusions

Spin excitations in crystals

Ferroic orders

Magnetic (*B*, *H*):
6^{th} century BC – account on magnetite Fe_3O_4 (ferrimagnet, Thales of Miletus)
1930's – transition to an antiferromagnetic state observed (Landau, Néel)

$$B = \mu_0 \mu H$$

Electric (*D*, *E*):
1824 – discovery of pyroelectricity (D. Brewster, Rochelle salt)
1880 – Curie brothers discover the piezoelectric effect
1920 – hysteresis curve of Rochelle salt observed (Valasek)

$$D = \varepsilon_0 \varepsilon E$$

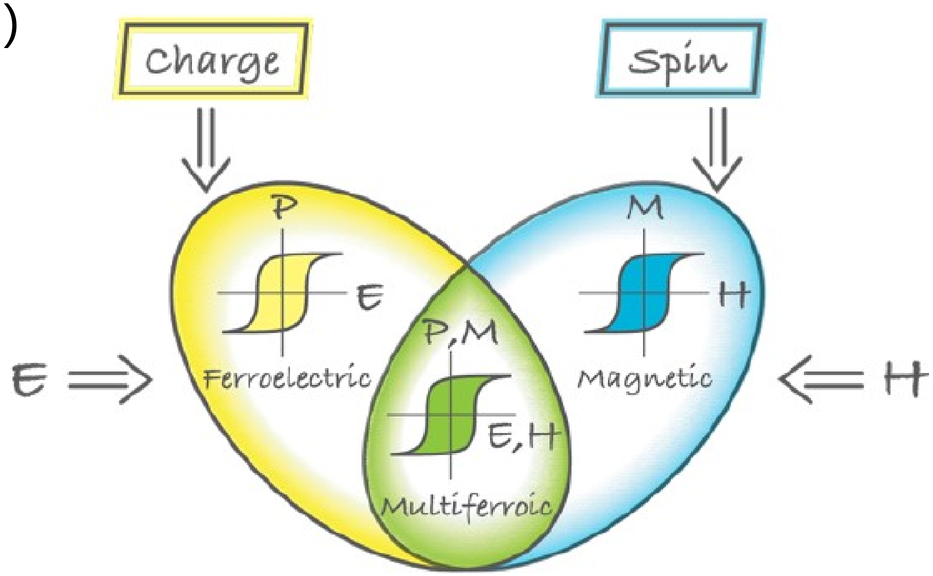
Elastic (σ, ε):
1969 – discovery of ferroelasticity (K. Aizu, Rochelle salt)

$$\sigma = E\epsilon$$

Multiferroics (magnetoelectric ones, ME)

First use of the word *multiferroic*: 2000 (according to Web of Science™)

- Two (+…?) ferroic Order Parameters
  - Ferromagnetism (also ferri-, etc.)
  - Ferroelectricity (etc.)
  - (Ferroelasticity)
  - (...)



- Most interesting: those with interaction between order parameters
- Applied electric field modifies magnetic ordering or vice versa

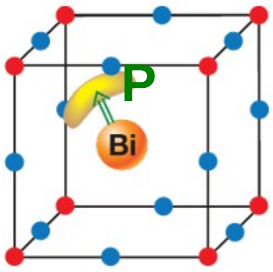
Attractive for prospective applications (spintronics, memories, sensors...)

Polarization and magnetization: ↑ or ↓ … four-state logic can be envisaged (states of *P*, *M*: ↑↓, ↓↑, ↓↓, ↑↑)

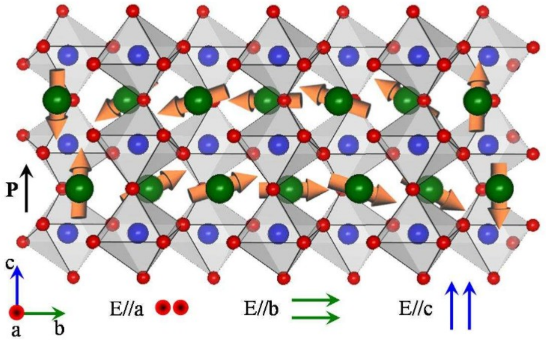
Classification of multiferroics

currently: tens of multiferroic compounds are known

	Type I	Type II
Critical temperatures T_C, T_N	usually above room temperature ☺	≤ 100 K
Ferroelectricity due to:	ions	spins
Spontaneous FE polarization	high ☺	low
ME coupling	low	high ☺
examples:	mixed perovskites; BiFeO$_3$	hexaferrites; TbMnO$_3$



BiFeO$_3$



TbMnO$_3$

*[D. Khomskii, Phys. **2**, 20 (2009)]

ME coupling

$$B = \mu_0 \mu H = \mu_0 H + M$$

$$D = \varepsilon_0 \varepsilon E = \varepsilon_0 E + P$$

- Static: ME effects

$$P_i = \sum \alpha_{ij} H_j + \sum \beta_{ijk} H_j H_k + \dots$$

$$M_i = \sum \alpha_{ij} E_j + \sum \beta_{ijk} E_j E_k + \dots$$

- Dynamic: typically in the GHz—THz ranges, may lead to electromagnons (EM)

- Link… sum rule (Kramers-Kronig relations):

The *static* ME effect is related with (*dynamic*) directional dichroism of low-*E* excitations*

$$\chi^{\mathrm{me}}_{\gamma\delta}(0) = \frac{c}{2\pi} \mathcal{P} \int_0^\infty \frac{\Delta\alpha(\omega)}{\omega^2} d\omega$$

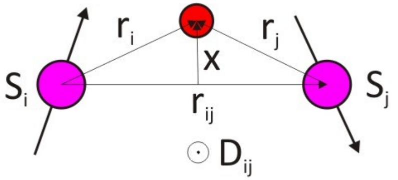
*[D. Szaller et al., PRB **89**, 184419 (2014)]

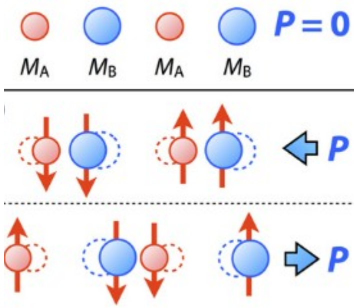
Microscopic origin of ME coupling

- FM properties linked to magnetic atoms (Fe, Co, Mn)
- Required for ME coupling: <u>time-reversal and space-inversion symmetries broken</u>

- Microscopic understanding <u>still incomplete</u>; some mechanisms were identified. Examples:

- **In type-I materials:**
  - <u>lone pairs</u> (outer 6s electrons) induce FE
  - <u>charge ordering</u> (breaks inversion symmetry → FE polarization)
- **In type-II materials:**
  - "<u>inverse Dzyaloshinskii-Moriya interaction</u>" (for spiral spin arrangements)
  - <u>exchange striction</u> (for collinear spins)

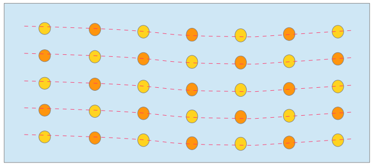




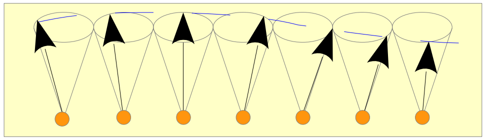
Static and dynamic ME couplings may have different origins.

reviews: Tokura *et al.*, Rep. Prog. Phys. **77**, 076501 (2014); Wang *et al.*, Comp. Mat. Sci. **112** (2016) 448

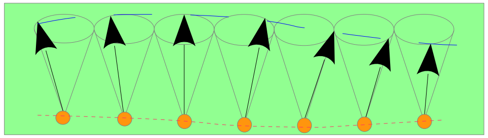
ME coupling induces electromagnons



- Phonons: in all crystals, “acoustic” / “optic” ones
- Active in infrared (also THz) and / or Raman spectra
- If infrared active: excited by *E*, resonances in *ε*(*ω*)



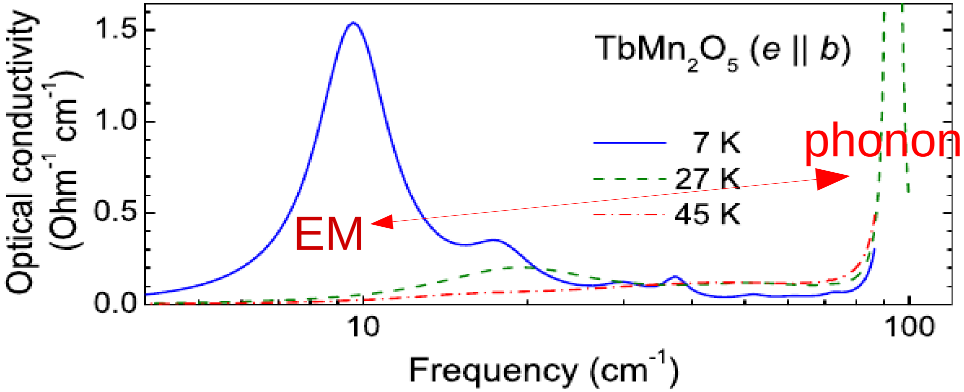
- Magnons: in FM, AFM, FiM; spin waves, due to exchange interaction
- Excited by *H*, resonance in *μ*(*ω*); *ε*(*ω*) is not affected



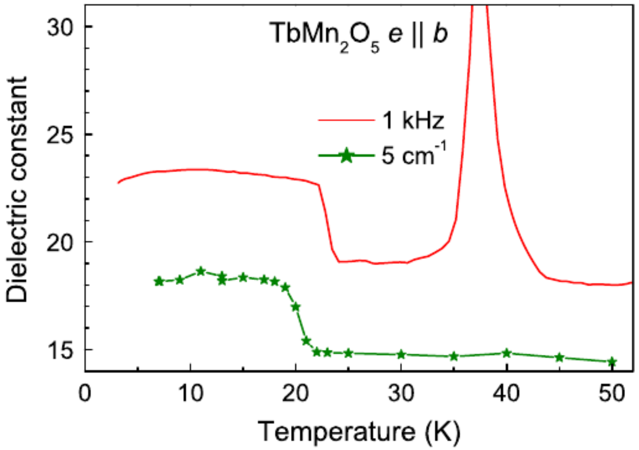
- Electromagnons: in multiferroics; due to spin-orbit interaction, several possible models
- Excited by *E*, resonance in both *μ*(*ω*) and *ε*(*ω*)

Characteristic features of electromagnons

- (i) diel. strength transfer



- (ii) step in *ε*(*T*)



from Sushkov *et al.*, J. Phys.: Cond. Matt. 20 (2008), 434210

- (iii) they occur in special points of the Brillouin zone ($\boldsymbol{q}=\pi/a$; $\boldsymbol{q}=\boldsymbol{q}_\mathrm{m}$; $\boldsymbol{q}=\pi/a-2\boldsymbol{q}_\mathrm{m}$ $\boldsymbol{q}_\mathrm{m}$... mg. structure modulation)

- (iv) sensitive to magnetic field

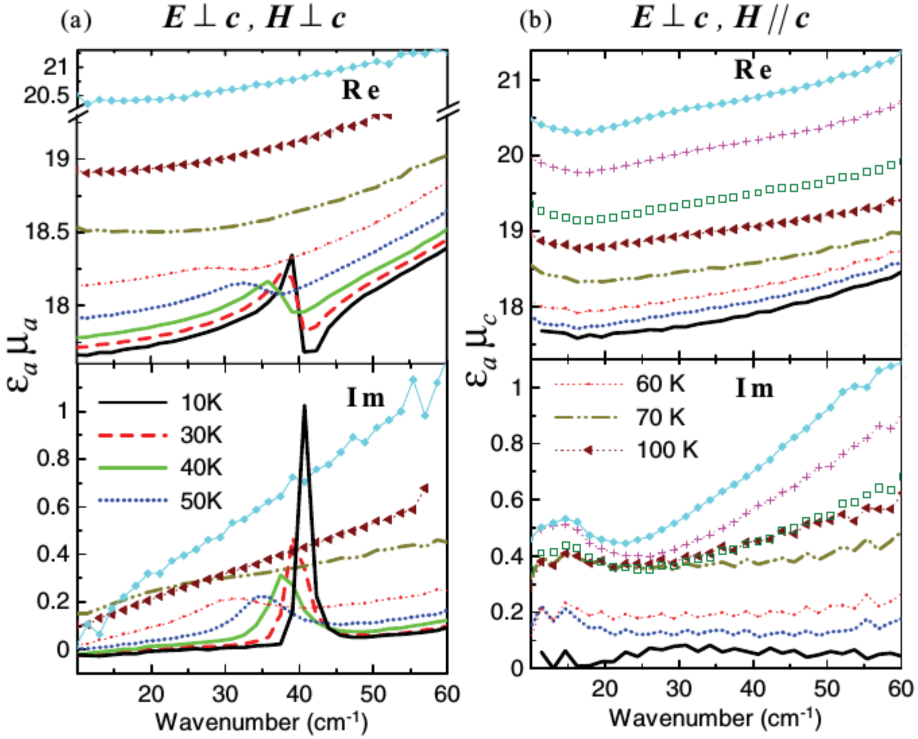
- (v) usually in the THz range

Discerning magnons from EMs

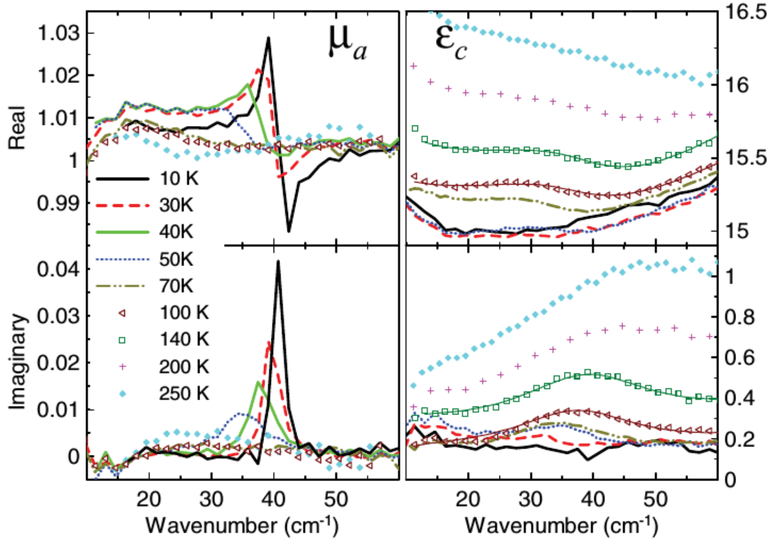
(i) measuring spectra along individual crystallographic directions

- Single crystals with various orientations needed
- Orientation of *E*, *H* with respect to cryst. axes important

Example: $YMnO_3$ (type I)



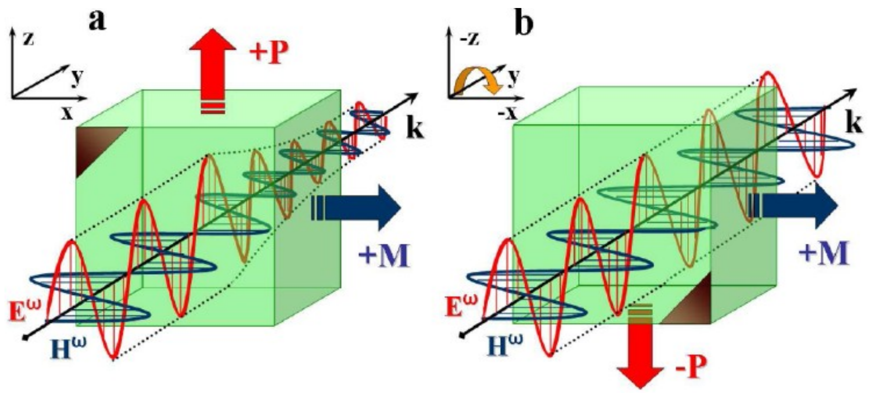
⇒ magnon (AFM reso- nance)



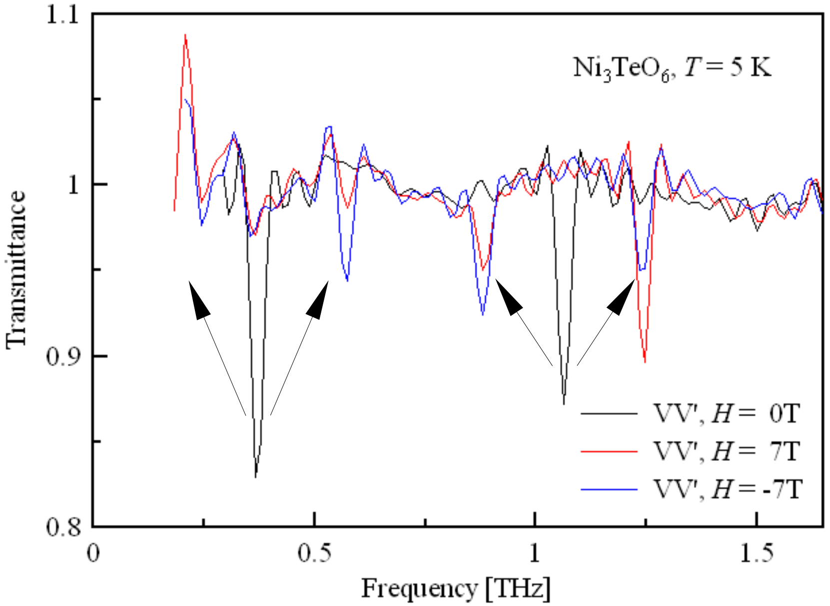
from C. Kadlec *et al.*,
PRB **84**, 174120 (2011)

Discerning magnons from EMs

(ii) directional dichroism... changes in absorption (of single crystals) upon reversal of ***k***-direction. Can be observed by switching ***M*** or ***P***. Typical of EMs.



Example: Ni_3TeO_6 (type II)



line splitting in mg. field, intensity depends on sign of H

Propagation of a EM wave: four solutions for the refractive index, depending on ***k*** and ***E***-direction

$$N_{\pm}^{\parallel}(\omega) \approx \pm 4\pi\chi'_{xz}(\omega) + \sqrt{\varepsilon_{zz}(\omega)\mu_{xx}(\omega)}$$

$$N_{\pm}^{\perp}(\omega) \approx \pm 4\pi\chi'_{zx}(\omega) + \sqrt{\varepsilon_{xx}(\omega)\mu_{zz}(\omega)},$$

(also called quadrochroism)

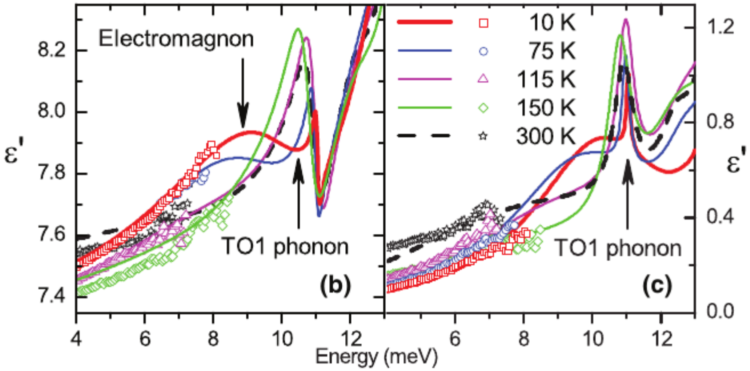
see Kézsmárki *et al.*, Nat. Commun. **5**, 3203 (2014)

Discerning magnons from EMs

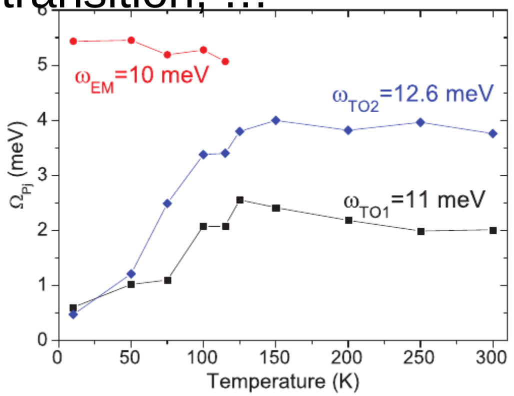
(iii) combination of THz (infrared) spectra and inelastic neutron scattering

Example: ε-Fe$_2$O$_3$

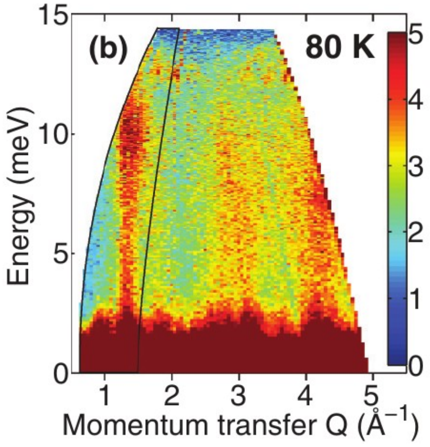
An excitation observed in THz (IR) spectra, ...



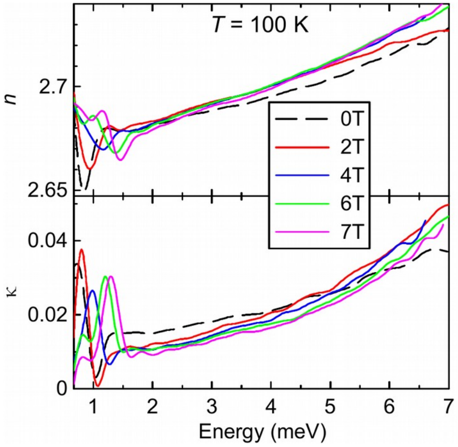
… acquiring its strength from phonons at a phase transition, …



…observed by neutrons at the same E, with lower intensity at higher Q,…



… and which depends on mg. field...



… is an EM;
the method is suitable for ceramics

C. Kadlec *et al.*,
PRB **88**, 104301 (2013)

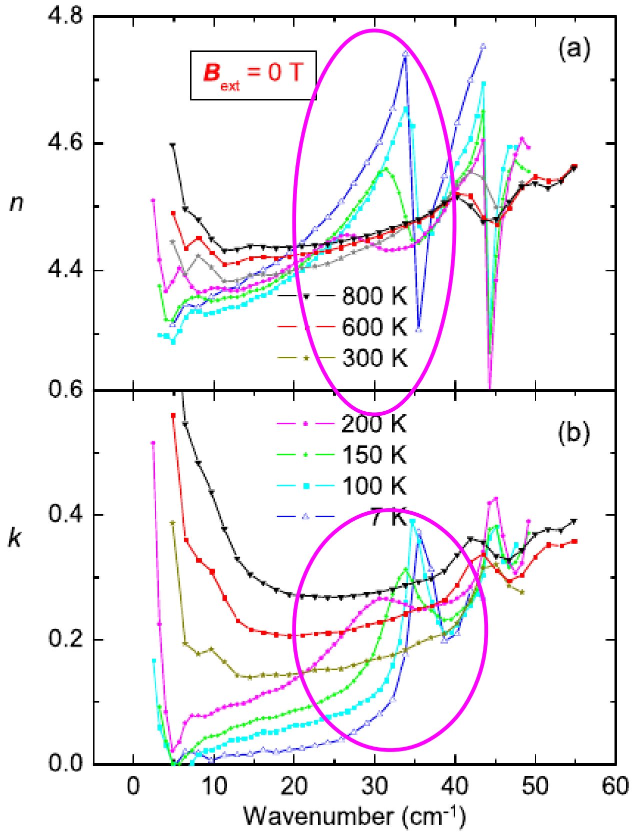
Discerning magnons from EMs

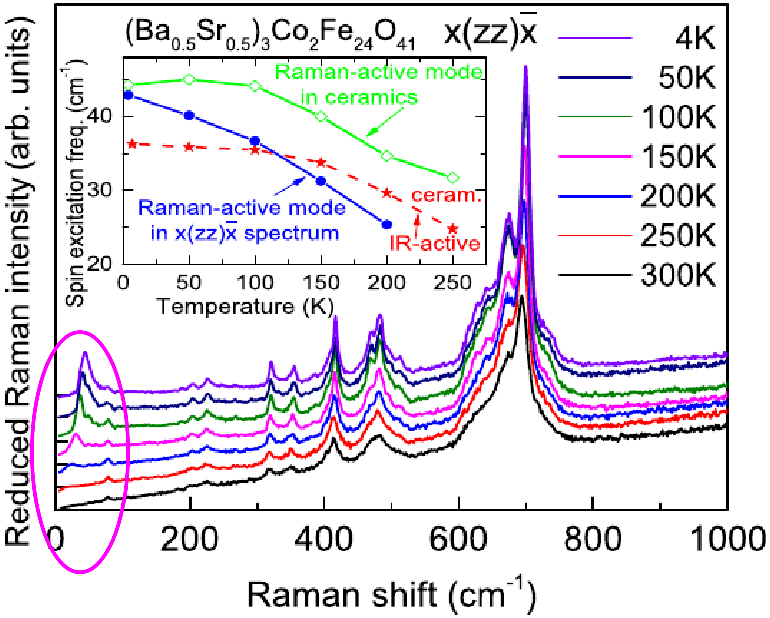
(iv) combination of THz (infrared) and Raman spectra

An excitation active in <u>both THz (IR) and Raman spectra</u> is an electromagnon...

S. Skiadopoulou *et al.*, PRB **91**, 174108 (2015); P. Rovillain *et al.*, PRB 8**1**, 054428 (2010)

THz:





samples: **Z-type hexaferrite**

…but it may be difficult to prove that a feature in both kinds of spectra is the same.

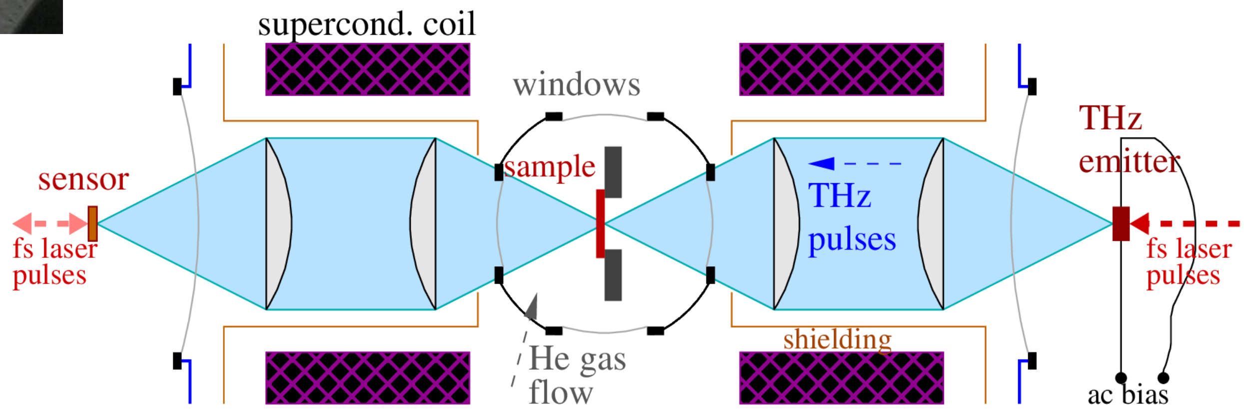
FK *et al.*, PRB **94**, 024419 (2016)

THz experiments in magnetic field

- Spectromag, Oxford inst.
- Temp. range: 2–260 K
- Mag. field range: 0–7 T
- Spectral range: 0.2–2.5 THz
- Sample diameter: 1–10 mm
- Available geometries:
- Voigt, $\boldsymbol{H} \perp \boldsymbol{k}_{\mathrm{THz}}$ (and $\boldsymbol{H}_{\mathrm{THz}} \perp \boldsymbol{H}$ or $\boldsymbol{H}_{THz} \parallel \boldsymbol{H}$)
- Faraday, $\boldsymbol{H} \parallel \boldsymbol{k}_{\mathrm{THz}}$

output: spectra of complex

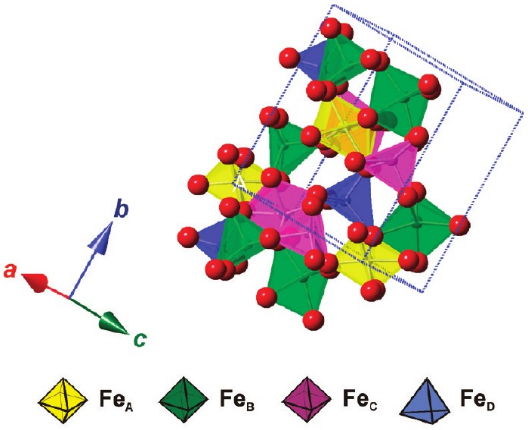
$$N(\nu) = \sqrt{\varepsilon(\nu)\mu(\nu)}$$



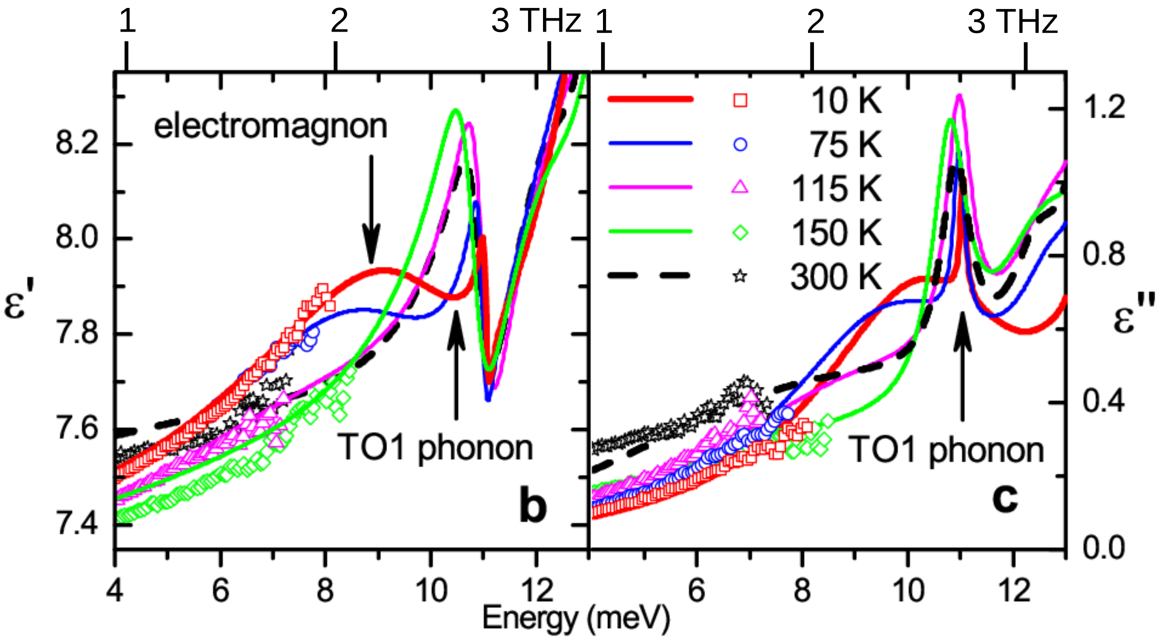
Selected results

EM in a type-I multiferroic: ε-Fe_2O_3

synthetic, rarer than α, γ phases
(hematite, maghemite)

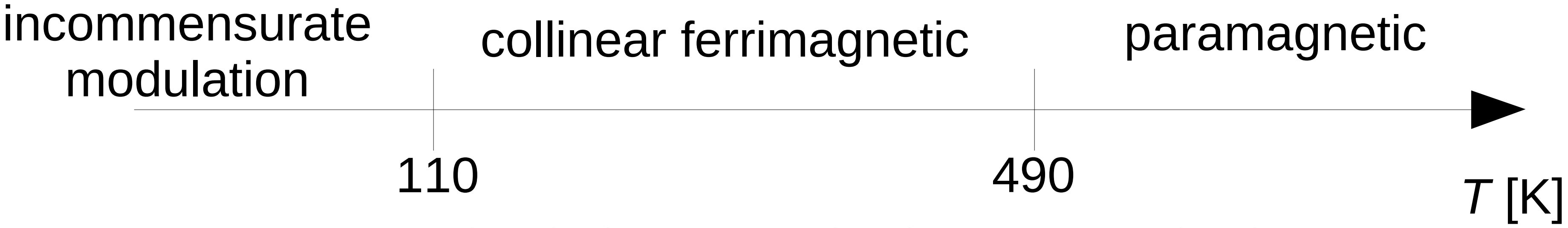


ε-Fe_2O_3



- 300 K: very high coercive field, $H_c \approx 2$ T
- single crystals unstable → <u>nanoparticles only;</u> sintered pellets used

Sequence of phase transitions



incommensurate modulation

collinear ferrimagnetic

paramagnetic

110

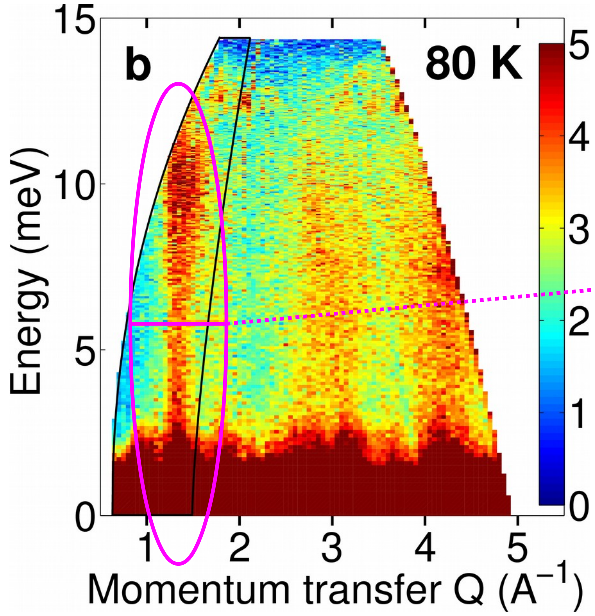
490

T [K]

From Tucek *et al.*, Chem. Mater. **22** (2010); APL **99**, 253108 (2011)

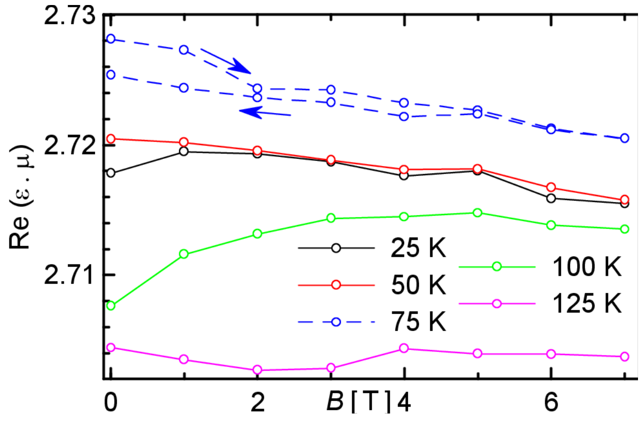
EM in ε-Fe_2O_3—further experiments

EM also observed in neutron scattering:



- Sensitivity of THz spectra to mag. field:

refractive index at 1.2 THz:



- Activation of EM: due to incommensurate modulation
- Electromagnons not restricted to type-II multiferroics
- Possibility to identify electromagnons in polycrystalline samples

C. Kadlec *et al.*, PRB **88**, 104301 (2013)

$CaMn_7O_{12}$: EM in a paramagnetic phase

T

Cubic, *Im*$\overline{3}$, metallic conductivity

T_{CO} = 450 K: charge ordering

Trigonal, *R*$\overline{3}$, insulating

T_{inc} = 250 K: onset of orbital ordering

Trigonal + *incommens. spin modulation*, ***q*** || *c*

T_{N1} = 90 K

FE, AFM, helical spin structure along *c*, $\boldsymbol{q}_m$ || *c*

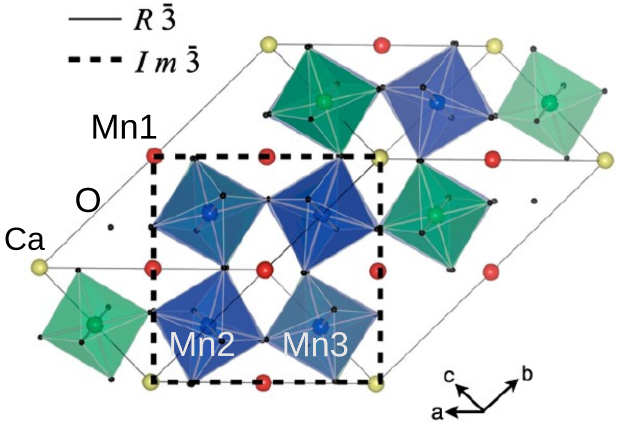
T_{N2} = 48 K

two mag. modulations $\boldsymbol{q}_{m1,2}$ || *c*; **P_s up to 3 mC/m^2**

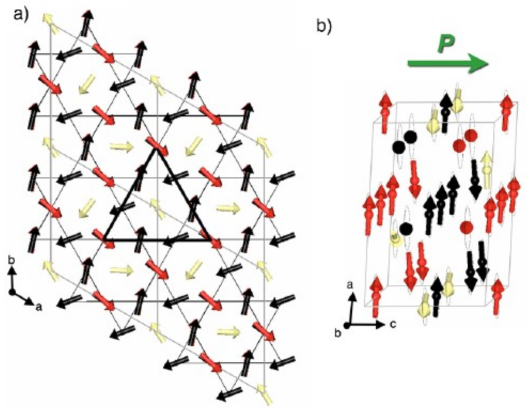
~4 times higher than in $TbMnO_3$

Perovskite with four ABO_3 units,

$(CaMn^{3+}_3)(Mn^{3+}_3Mn^{4+})\ O_{12}$:

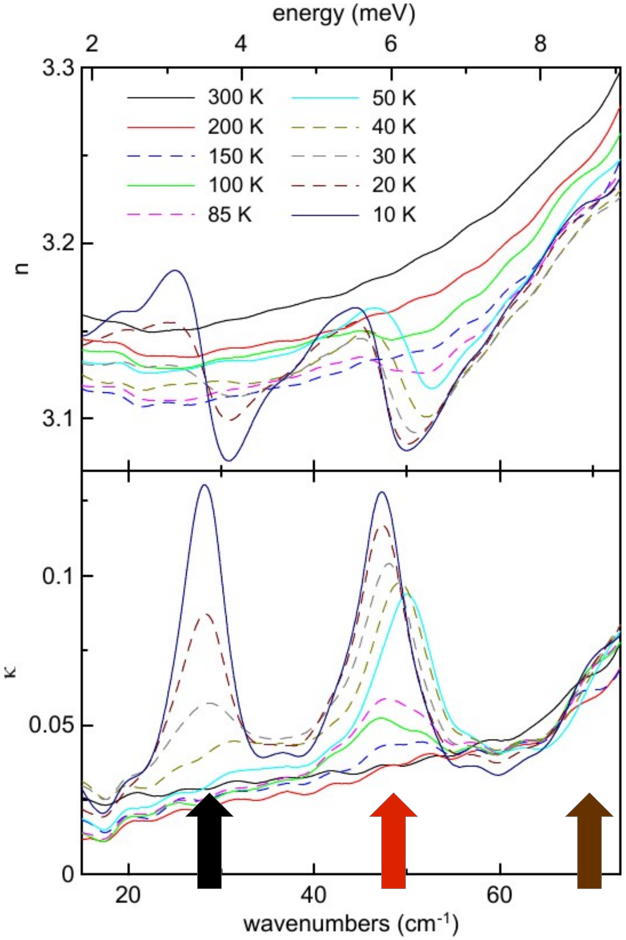


mg. structure—spins of Mn ions:



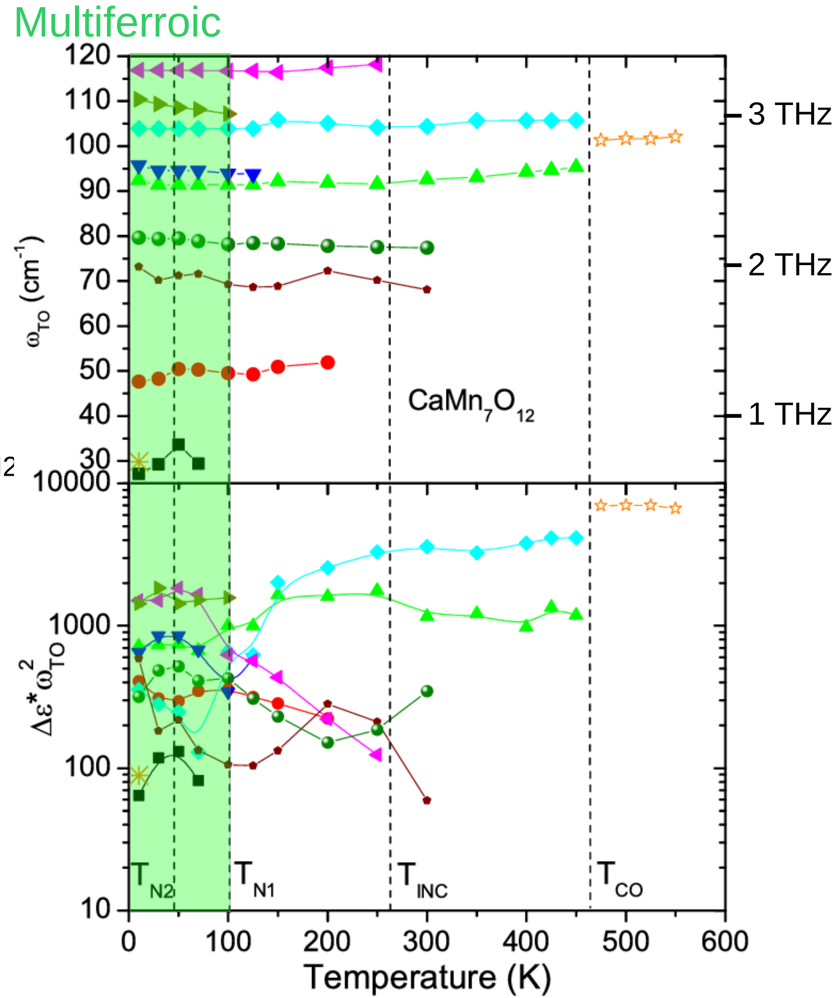
From R. D. Johnson *et al.*,
PRL **108**, 067201 (2012)

THz spectra of $CaMn_7O_{12}$



New strong modes appear below T_{N1}, T_{N2} near 25; 50; 70 cm^{-1}.

Higher-frequency phonons lose strength… EMs



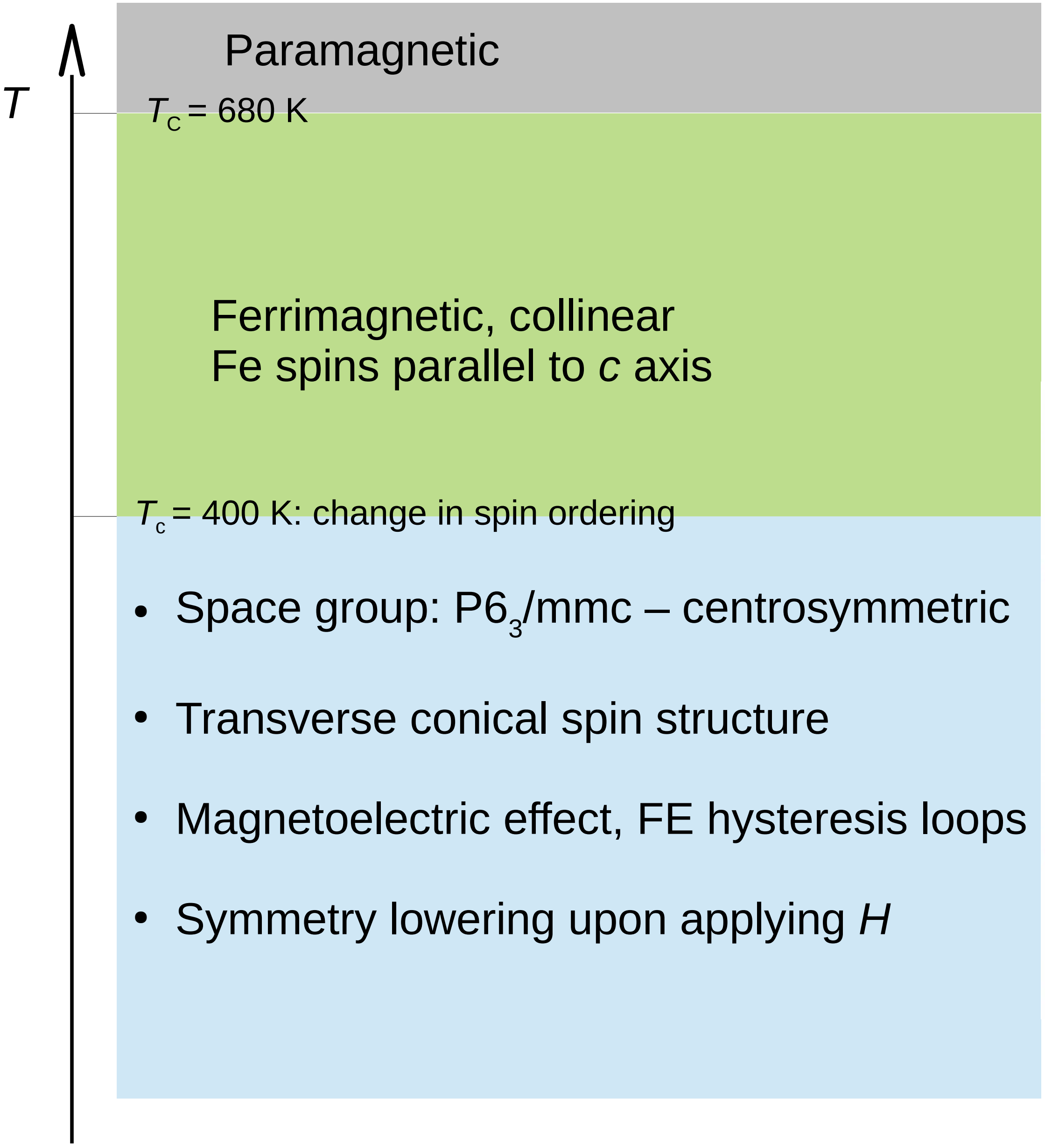
Mode near 50 cm^{-1}: anomaly at T_{N1}; above T_{N1}: weaker

but exists up to 200 K (in the paramagnetic phase)

FK *et al.*,
PRB **90**, 054307 (2014)

“Paraelectromagnon”, appears due to short-range dynamic correlations

Z-hexaferrite $(Ba_{0.2}Sr_{0.80})_3Co_2Fe_{24}O_{41}$



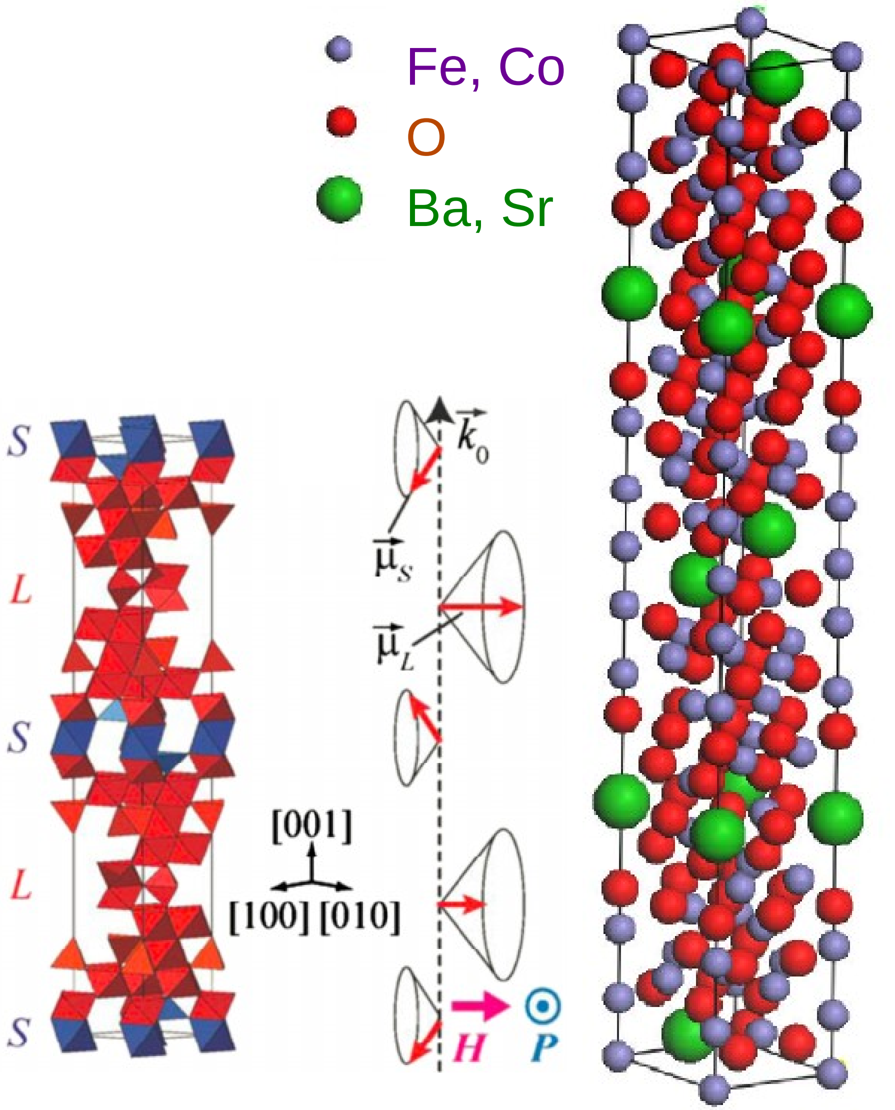
Paramagnetic

T_C = 680 K

Ferrimagnetic, collinear
Fe spins parallel to *c* axis

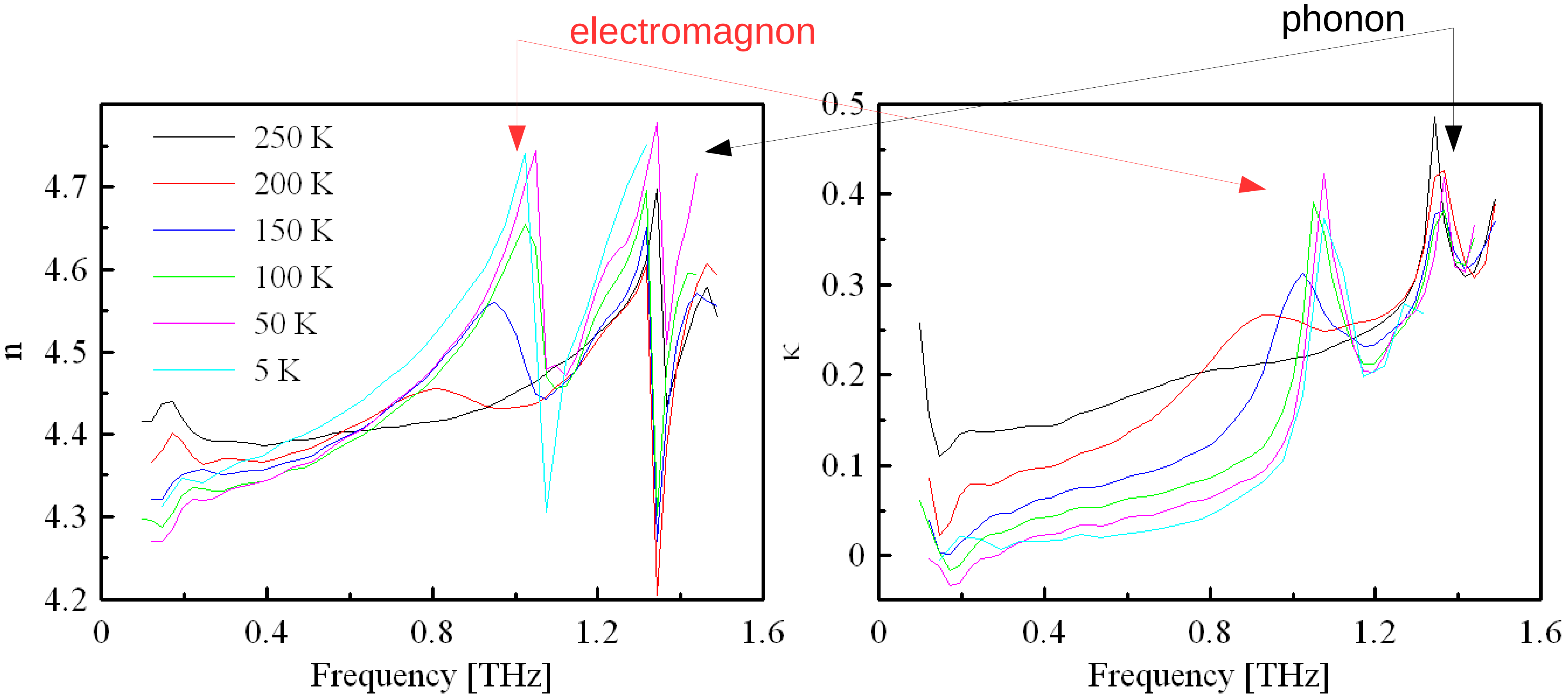
T_c = 400 K: change in spin ordering

- Space group: $P6_3/mmc$ – centrosymmetric
- Transverse conical spin structure
- Magnetoelectric effect, FE hysteresis loops
- Symmetry lowering upon applying *H*



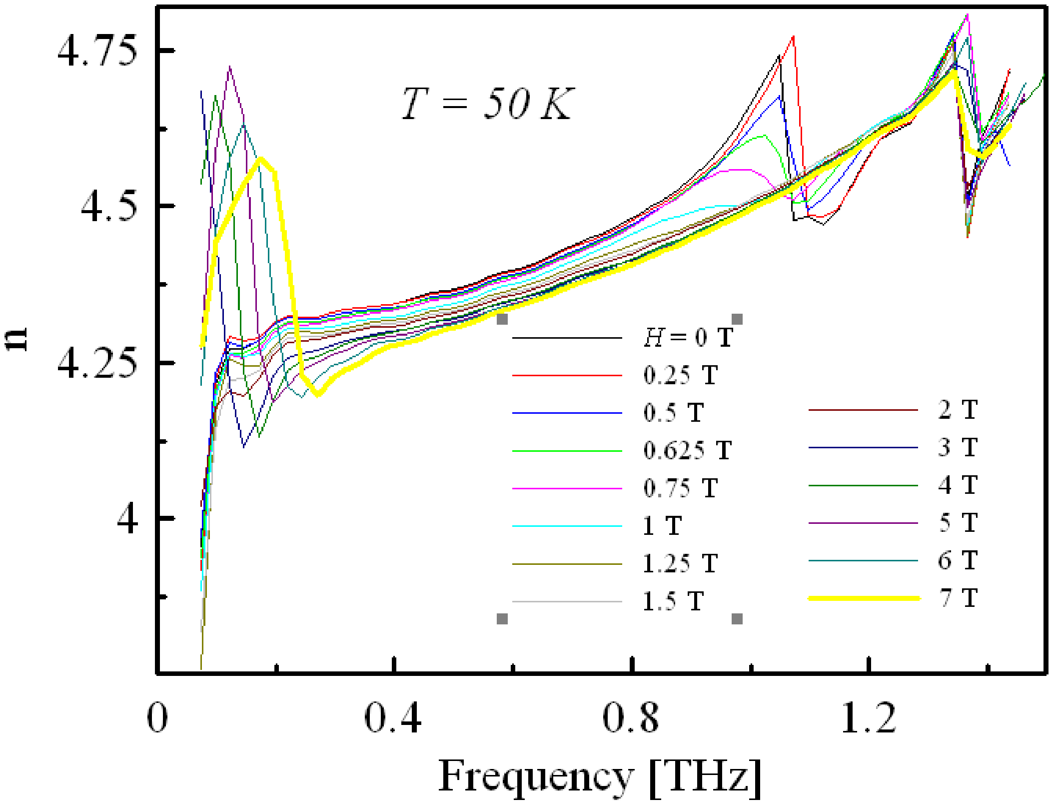
Z-hexaferrite: *T*-dependent THz spectra

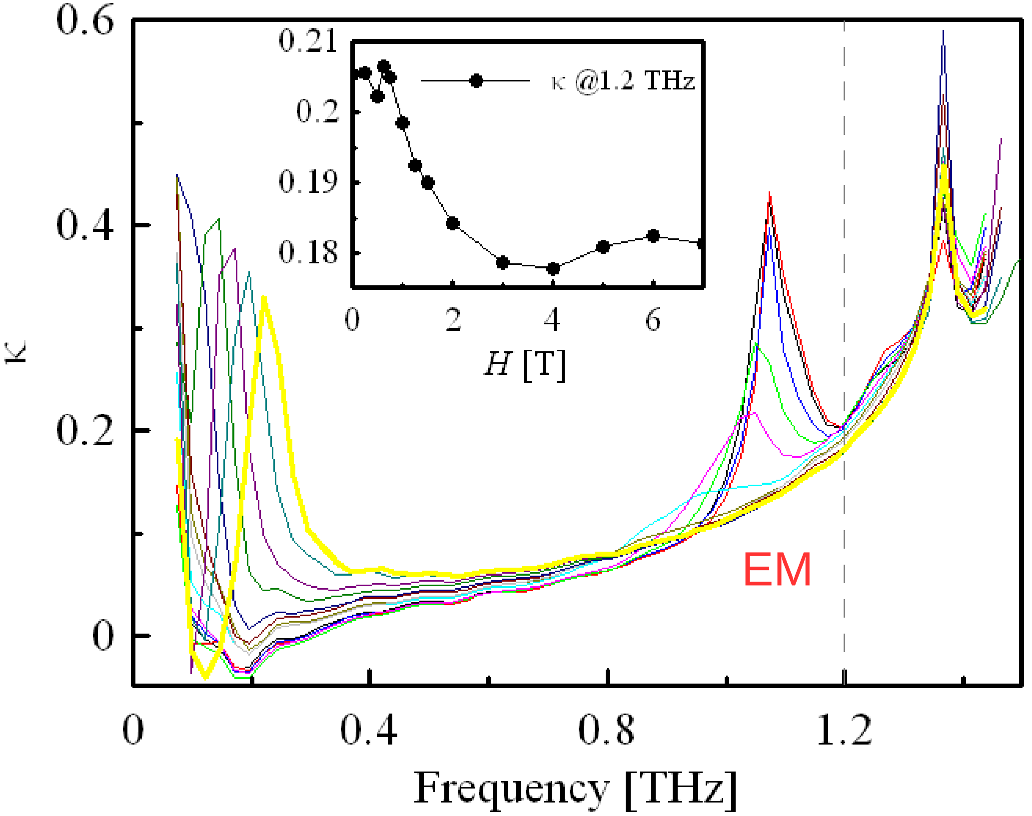
Below: spectra of $N = n + ik$; $\varepsilon \neq N^2$ since $\mu \neq 1$;
contributions to *ε, μ* cannot be easily distinguished

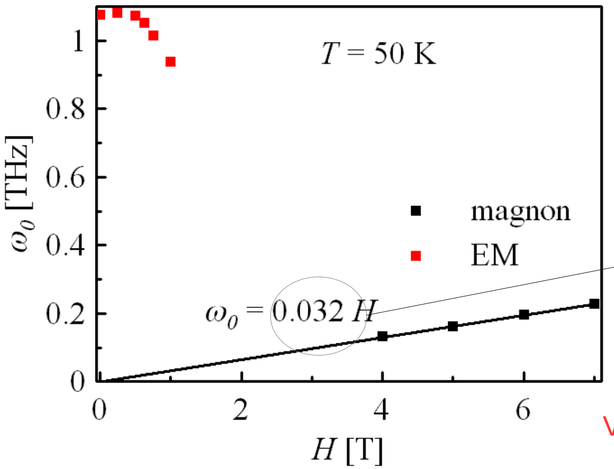


- Phonon: area of the peak in ε” clearly smaller at 50 K than at 250 K … transfer of strength?
- Low-frequency increase in *κ* – can be understood in magnetic field

Z-hexaferrite spectra in magnetic field







Corresponds to gyromag. ratio, free el.: 0.028 THz/T

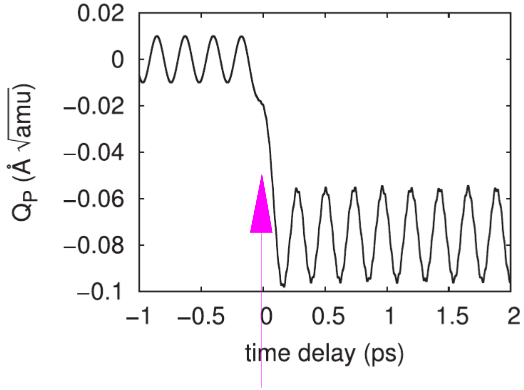
In a single crystal, Voigt geom.: only appears if $B_{THz} \perp B_{ext}$

Observed effects of magnetic field:

1. up to *H* = 2 T: shifts and suppresses the magnon near 1 THz
2. for *H* > 2 T: makes the low-frequency resonance visible in THz range (same field dependence for *T* = 5–250 K)

Perspectives: ultrafast control of polarization / magnetization?

- Discussed up to now: linear properties (low incident intensity)
- Increased intensity: <u>possibility to reach a non-linear regime</u>.
  - Single-mode effects (absorption bleaching, frequency shift...)
  - Inter-mode coupling—may offer new functionality

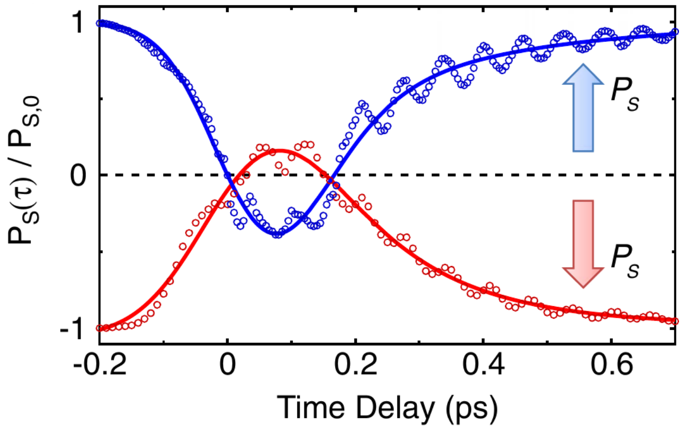


IR pump at $t = 0$

Switching of FE polarization—**predicted theoretically** for perovskites in 2015

Generalized mode coordinates: Q_P, Q_{IR}; combined terms in E surface: $Q_P Q^2_{IR} + Q_{IR} Q^2_P$ etc.

A. Subedi, PRB **92**, 214303 (2015)



- Experimental realization—LiNbO$_3$, measurement of time-resolved Second harmonic generation (after excitation by mid-infrared pulses)

- **Transient polarization switching achieved**

R. Mankowsky *et al.*, PRL **118**, 197601 (2017)

Conclusions

- ME multiferroics: promising new functionality
- Electromagnons: mixed phonon—magnon excitations in multiferroics
- Four methods of identifying EMs (two require single crystals)
- Prospective advances due to nonlinearities and inter-mode coupling

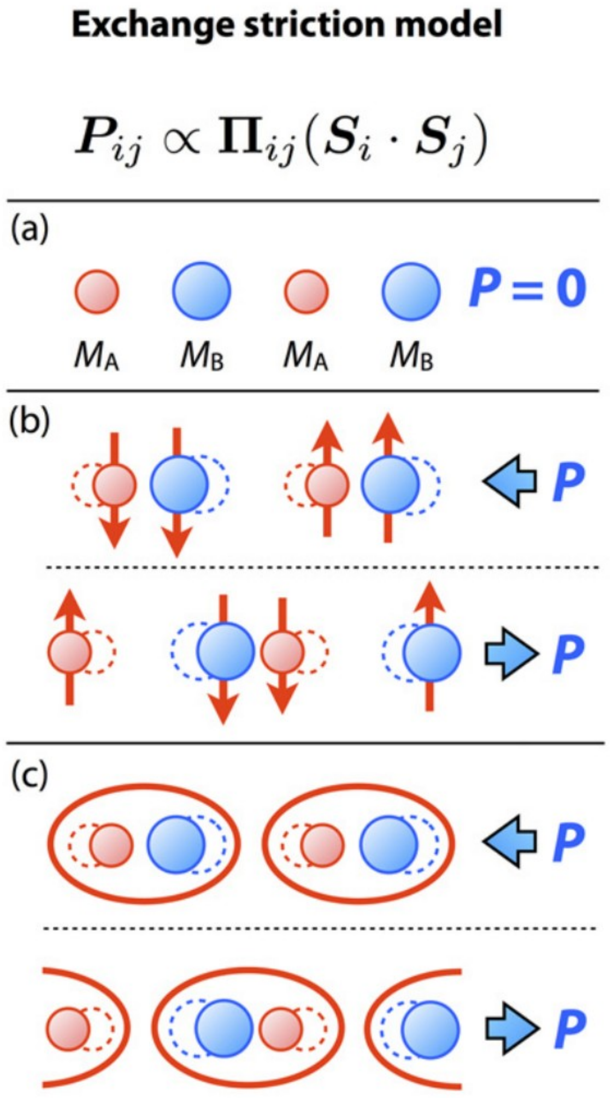
Microscopic origin of ME coupling

- In Type-II multiferroics: 3 basic microscopic mechanisms leading to ME coupling:
  1. Exchange striction (spin-Peierls instability)
  2. Inverse Dzyaloshinski-Moriya interaction (spin-current model)
  3. Spin-dependent p-d hybridization

See Tokura Y. *et al.*, Rep. Prog. Phys. **77** (2014), 076501

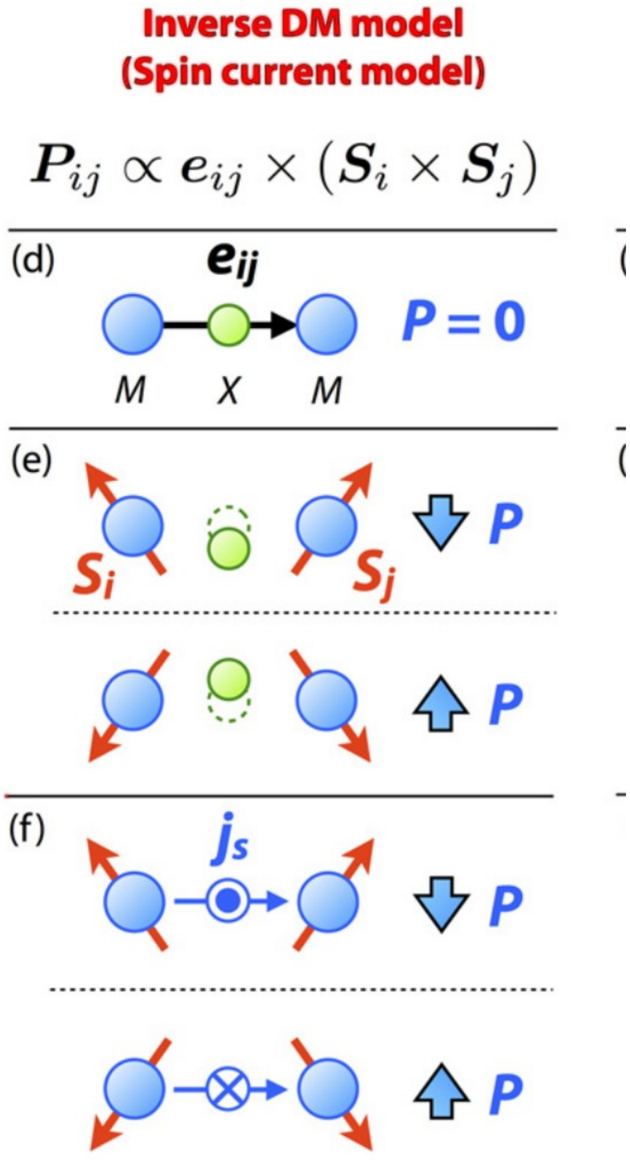
1. Exchange-striction mechanism

- Especially in structures with collinear spins
- AFM exchange coupling between spins, modulated by atoms' displacements
- Polarization induced by dimerization – spin-Peierls mechanism



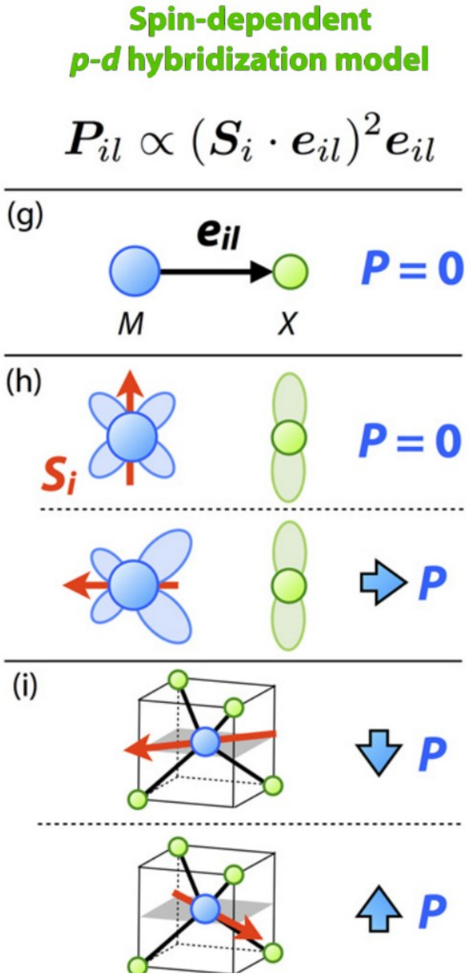
2. Inverse Dzyaloshinskii-Moriya interaction

- Inverse D.-M. interaction: acting among magnetic ions M linked by a ligand atom X
- Vector product… $P \neq 0$ only if S_i, S_j are not parallel – spiral or conical structures
- Antisymmetric exchange interaction due to spin-orbit coupling
- Magnetic ordering leads to lateral shifts of ligand atoms – induces polarization *P*



3. Spin-dependent *p-d* hybridization

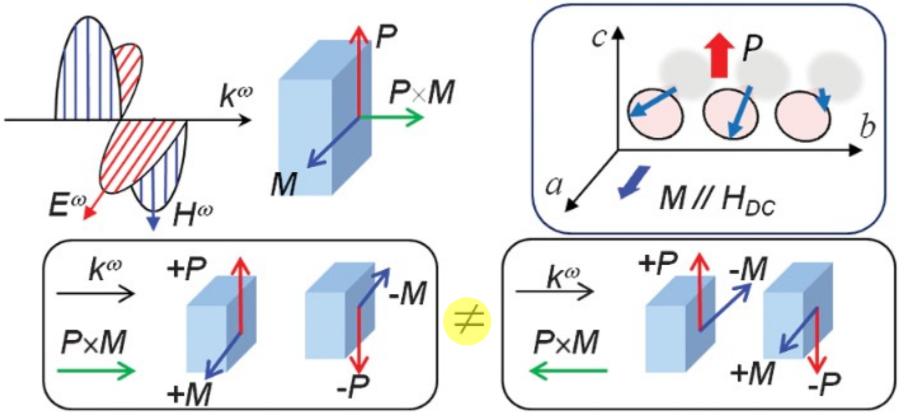
- M: magnetic ion, *d*-type orbital, X: ligand ion, p-type orbital
- Covalent bond between M, X
- Covalency depends on spins due to relativistic spin-orbit interaction → bond deformation
- If deformations do not cancel out: macroscopic *P* (noncentrosymmetric or triangular lattices)



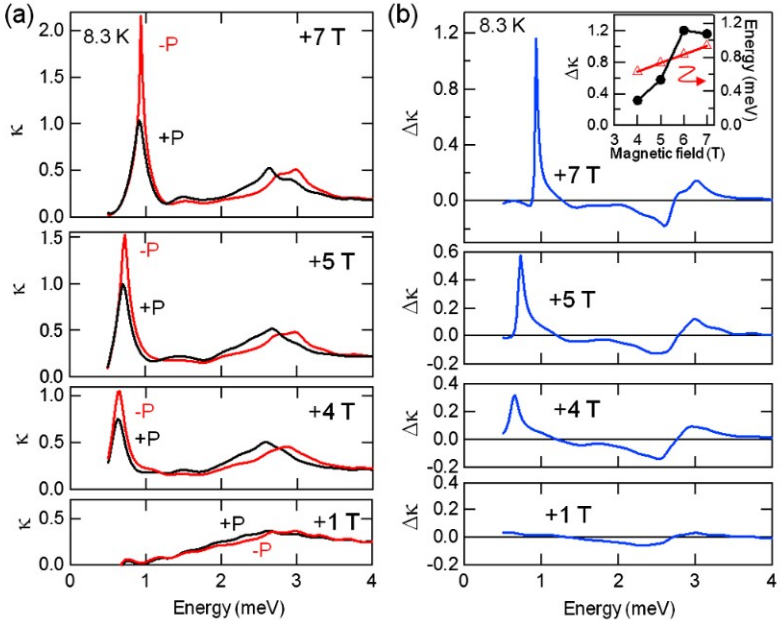
Nonreciprocal directional dichroism

- $Gd_{0.5}Tb_{0.5}MnO_3$ single crystal
- Shows el. polarization *P* and magnetization *M*
- Magnetic field applied: up to 7 T, Voigt geometry
- Electric field applied: electric contacts, Ag paste

THz transmission spectroscopy – experimental configuration:



H-dependent THz absorption:



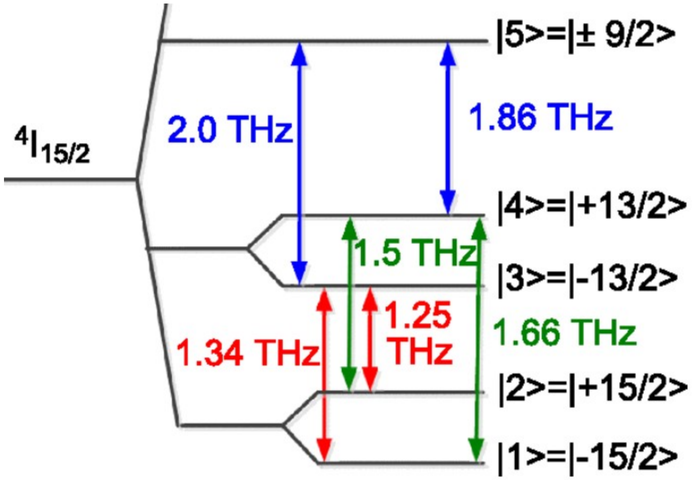
THz absorption strongly depends on the *P*, *M* states
Spectral weight transfer between two EMs of different origins

Y. Takahashi *et al.*, PRL **111**, 037204 (2013)

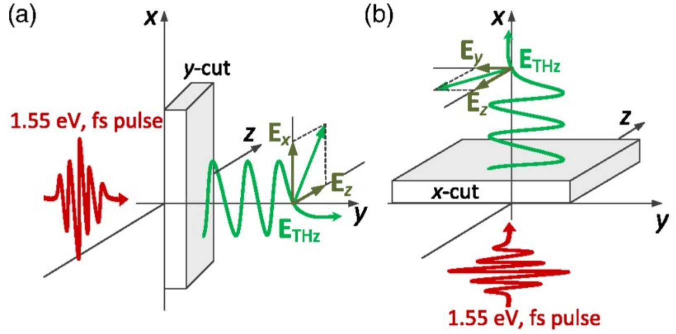
Selective excitation of mg. / el. dipoles

- Er FeO$_3$ single crystals
- optical excitation, THz emission
- femtosecond laser, λ = 800 nm

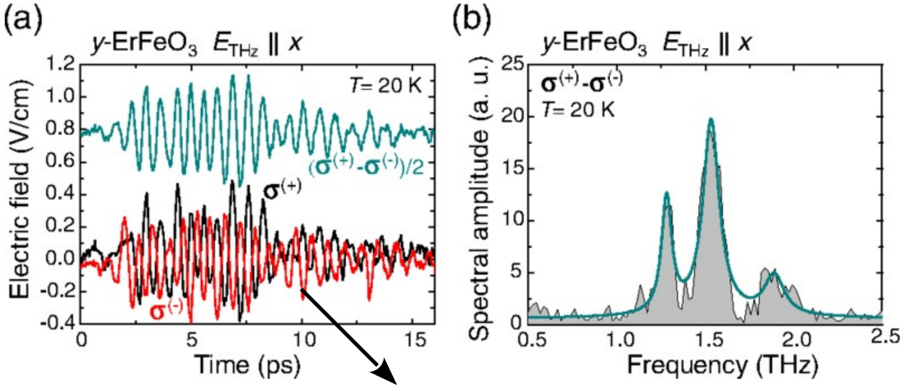
Er^{3+} energy levels:



Experimental configurations:



Emitted lines depending on circular polarization:



different frequencies for $\sigma^{(+)}$, $\sigma^{(-)}$

Possibility to activate THz-range el. / mg. dipoles by laser pulses

R. V. Mikhaylovskiy *et al.*, PRL **118**, 017205 (2017)