Terahertz and Raman Spectroscopies of Quantum Magnets.

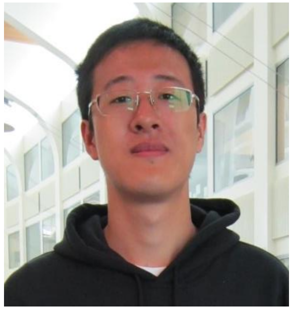
Rolando Valdés Aguilar
Guest Researcher, NIST Gaithersburg

Team

OSU PHYSICS

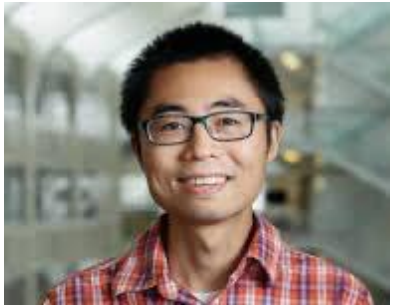

Evan Jasper

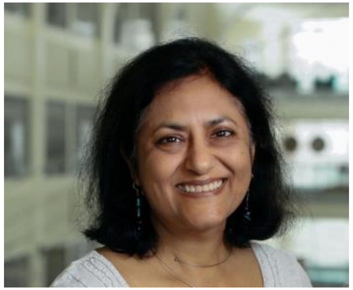

Daniel Heligman


Yufei Li


Chase Lyon


Alex Giovannone


Yuan-Ming Lu


Nandini Trivedi

NIST GAITHERSBURG

Jeff R. Simpson
Kevin F. Garrity
Maria Muñoz
Tehseen Adel

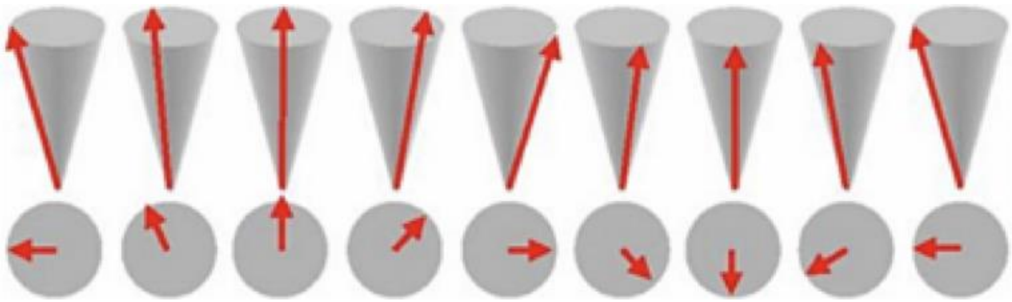

Angela Hight Walker


Thuc Mai

Magnons

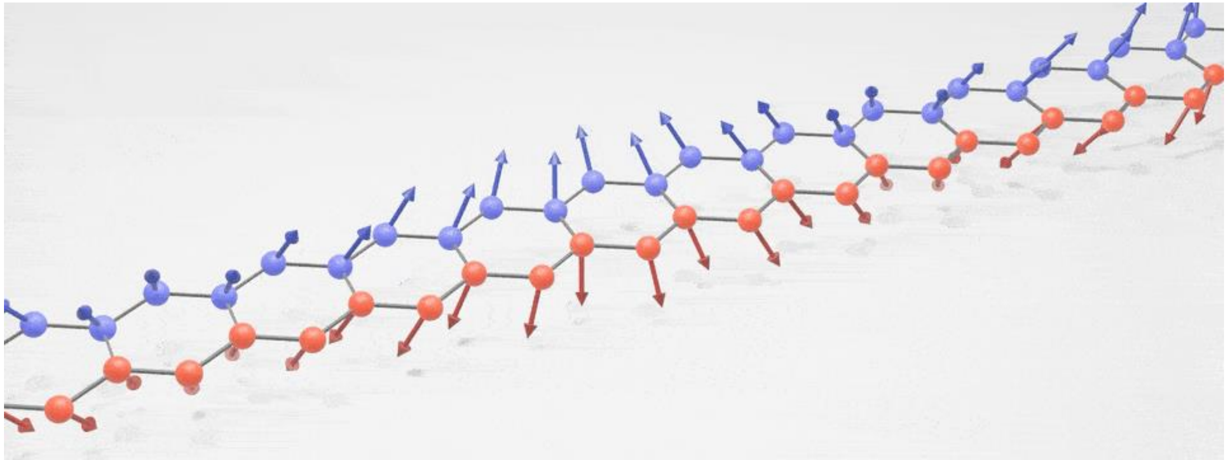
Spin waves (aka magnons) are elementary excitations in a magnetic system with long-range magnetic order.

E.g. spins precess around the direction of ordered moment (usually parallel to the external field)



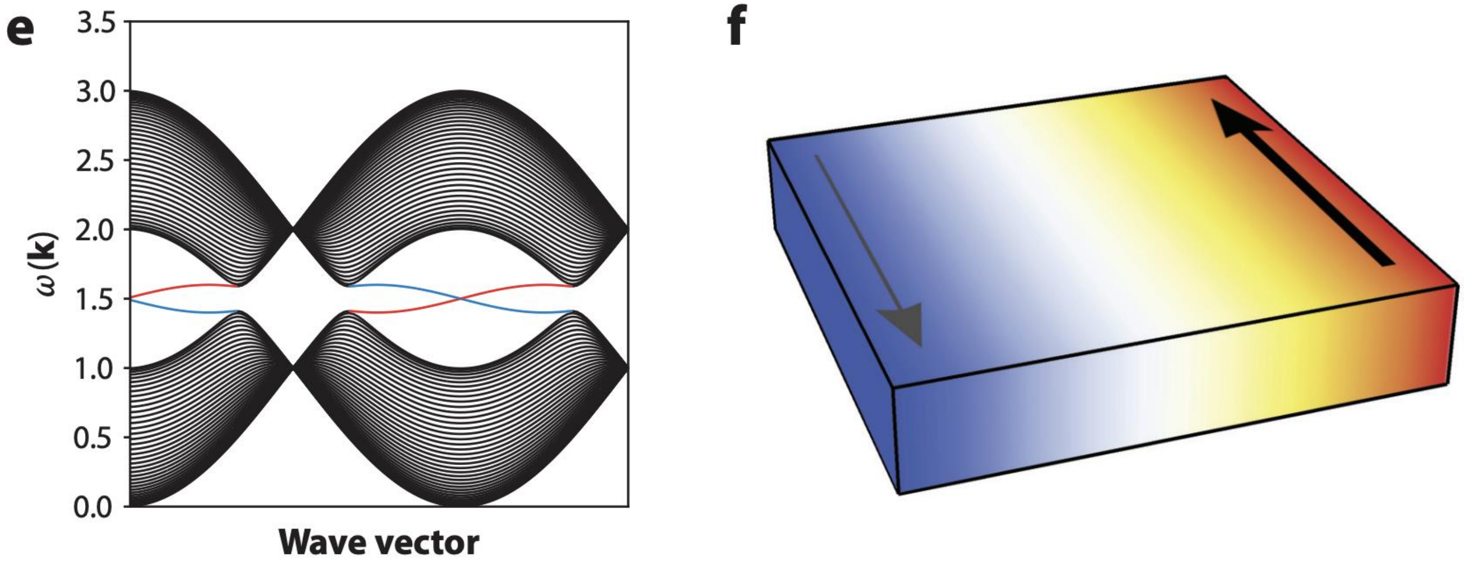
Spin waves can be probed by neutrons and light scattering excitations, and thermal/spin transport

Magnons



Credit: Sean Kelley/NIST

Topological Magnons



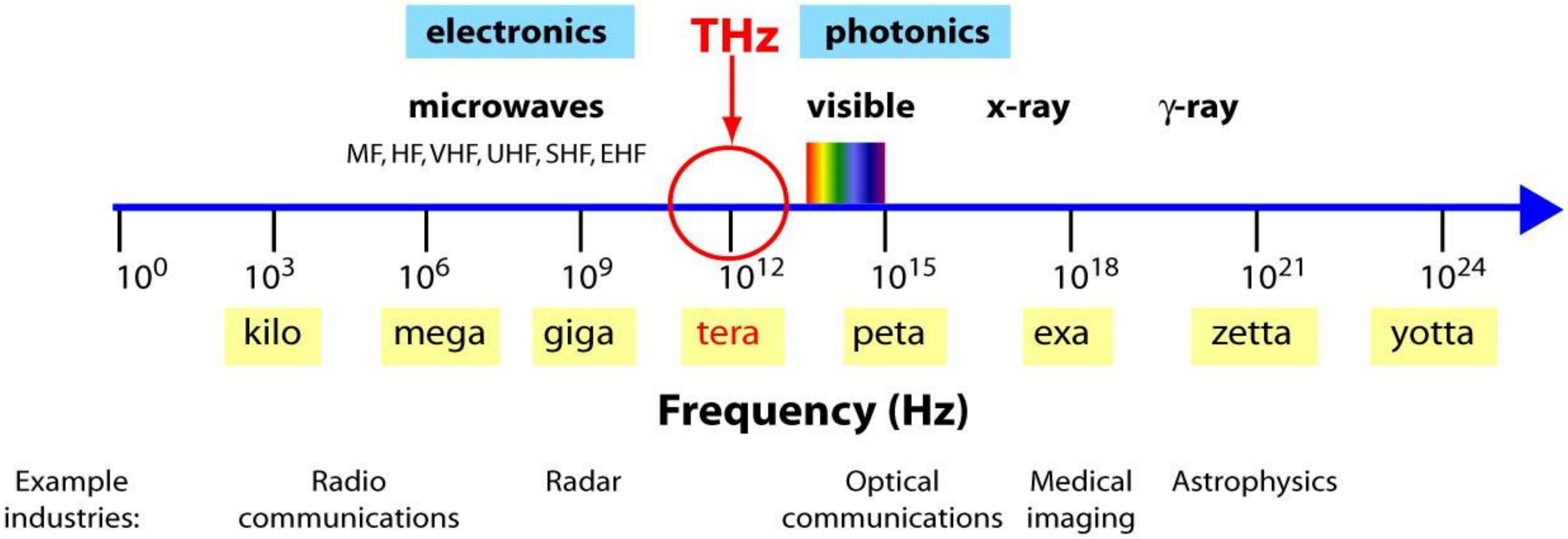
Like in topological insulators, surface/edge states are protected from backscattering.
Longer coherence lengths.

Can information be shared?

Annu. Rev. Condens. Matter Phys. **13**, 171 (2022)

Terahertz Spectroscopy

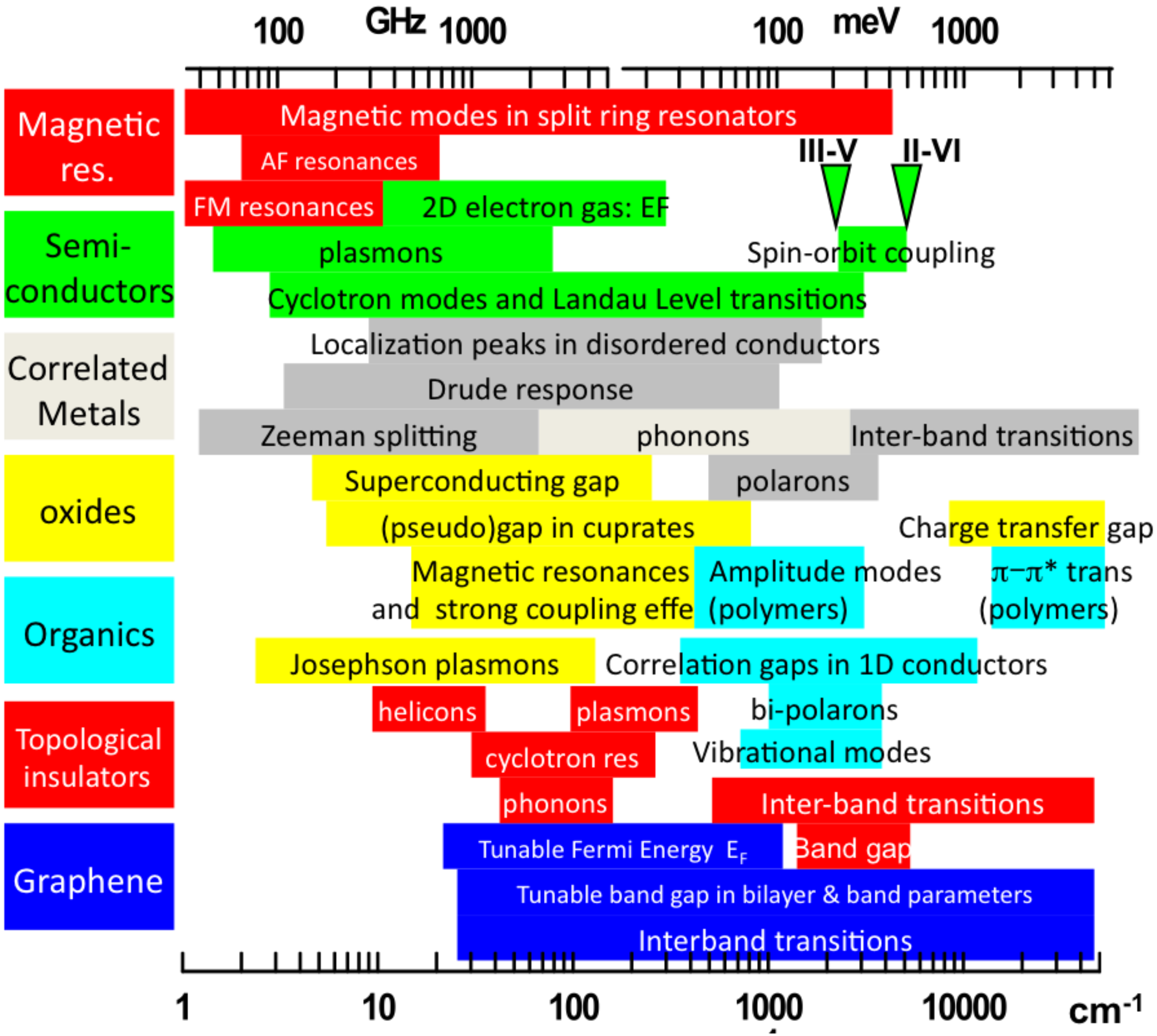
Terahertz Spectrum



1 THz ~ 1 ps ~ 300μm ~ 33 cm^{-1} ~4.1 meV ~ 47.6^{0}K

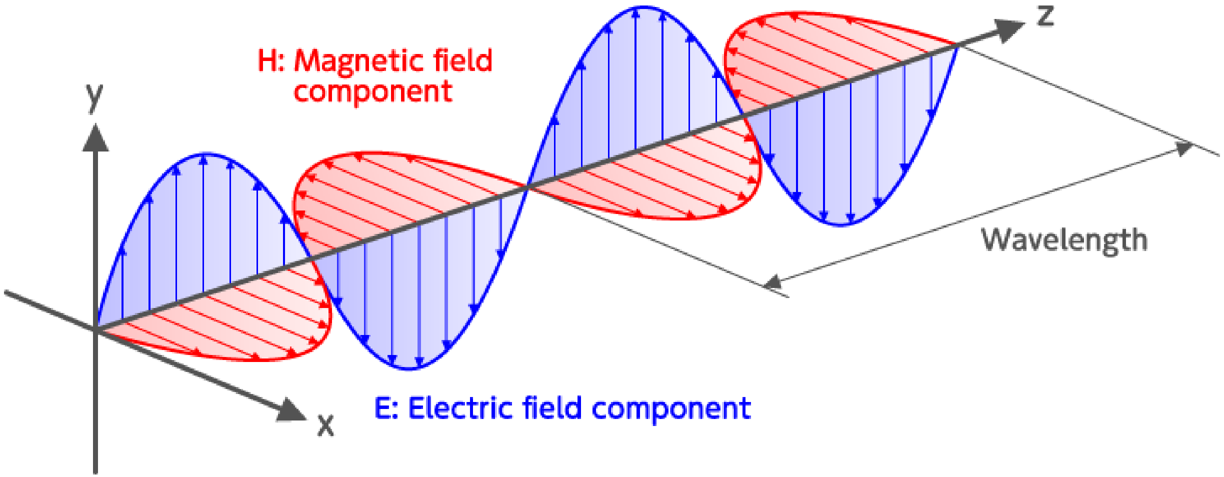
Natural Energy/Frequency/Time Scales in Materials

- 1 THz = 4.1 meV = 1 ps = 48 K = 33 cm^{-1}
- Momentum relaxation time in metals is ~ 100's fs to 10's ps
- Energy gaps in superconductors ~ few meV
- (Anti)-Ferromagnetic Resonances ~ few to 100's GHz
- Spin-orbit energy in transition metal oxides ~ few meV to 100's meV



From D.N. Basov

Electromagnetic Waves

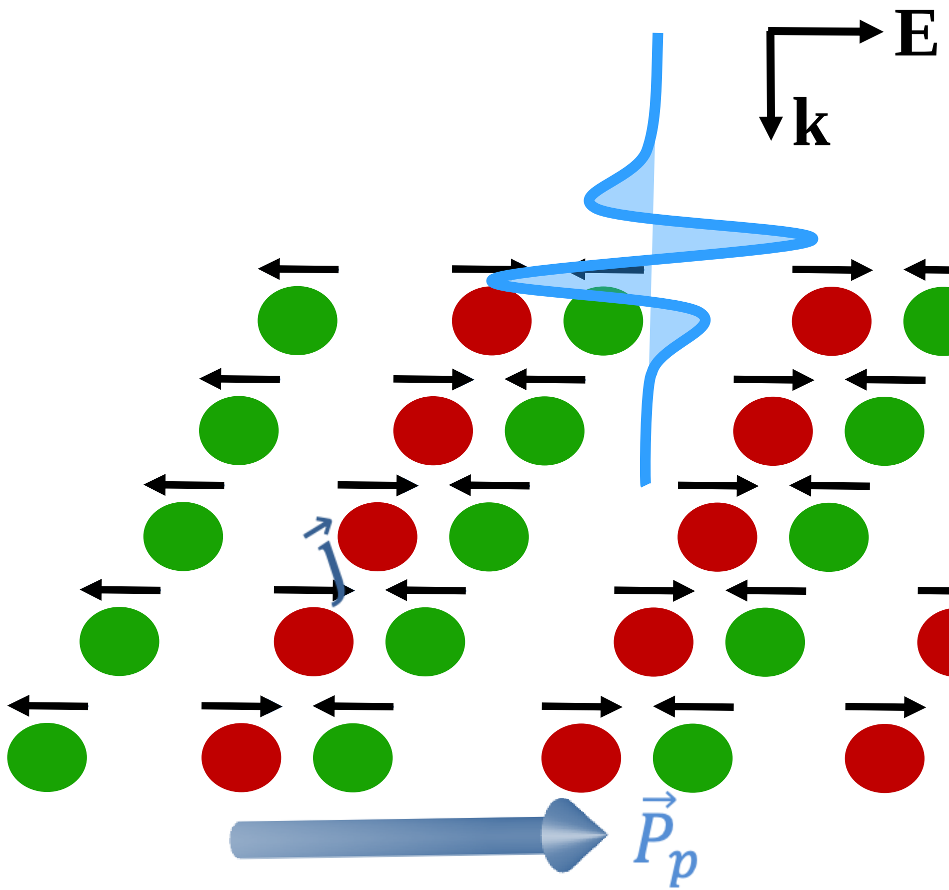


$$\mathbf{P} = \chi_e \mathbf{E},$$
$$\mathbf{M} = \chi_m \mathbf{H},$$

Electric field can accelerate charges, excite polarization waves.
Magnetic field can excite magnetization waves.

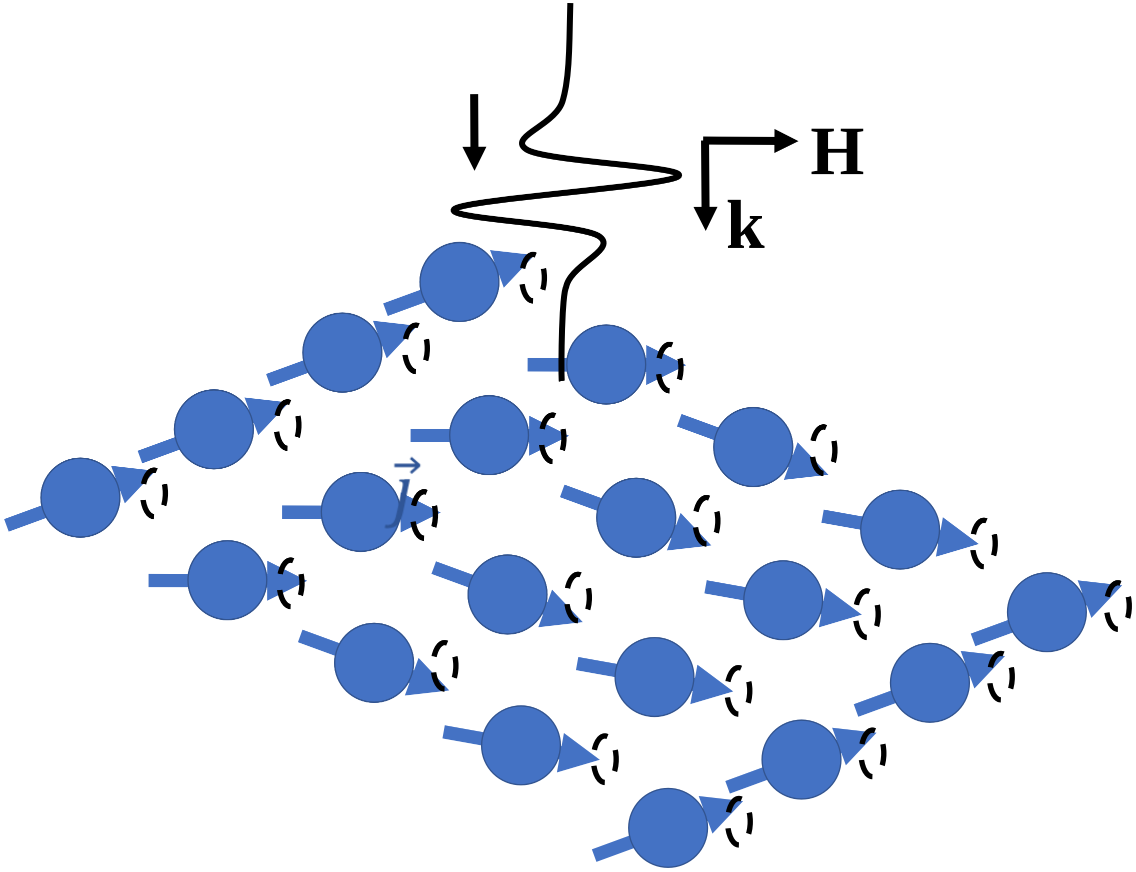
Note that $p = h/\lambda$ is the momentum of the wave. Long wavelength means small momentum.

Lattice Vibration (phonon)

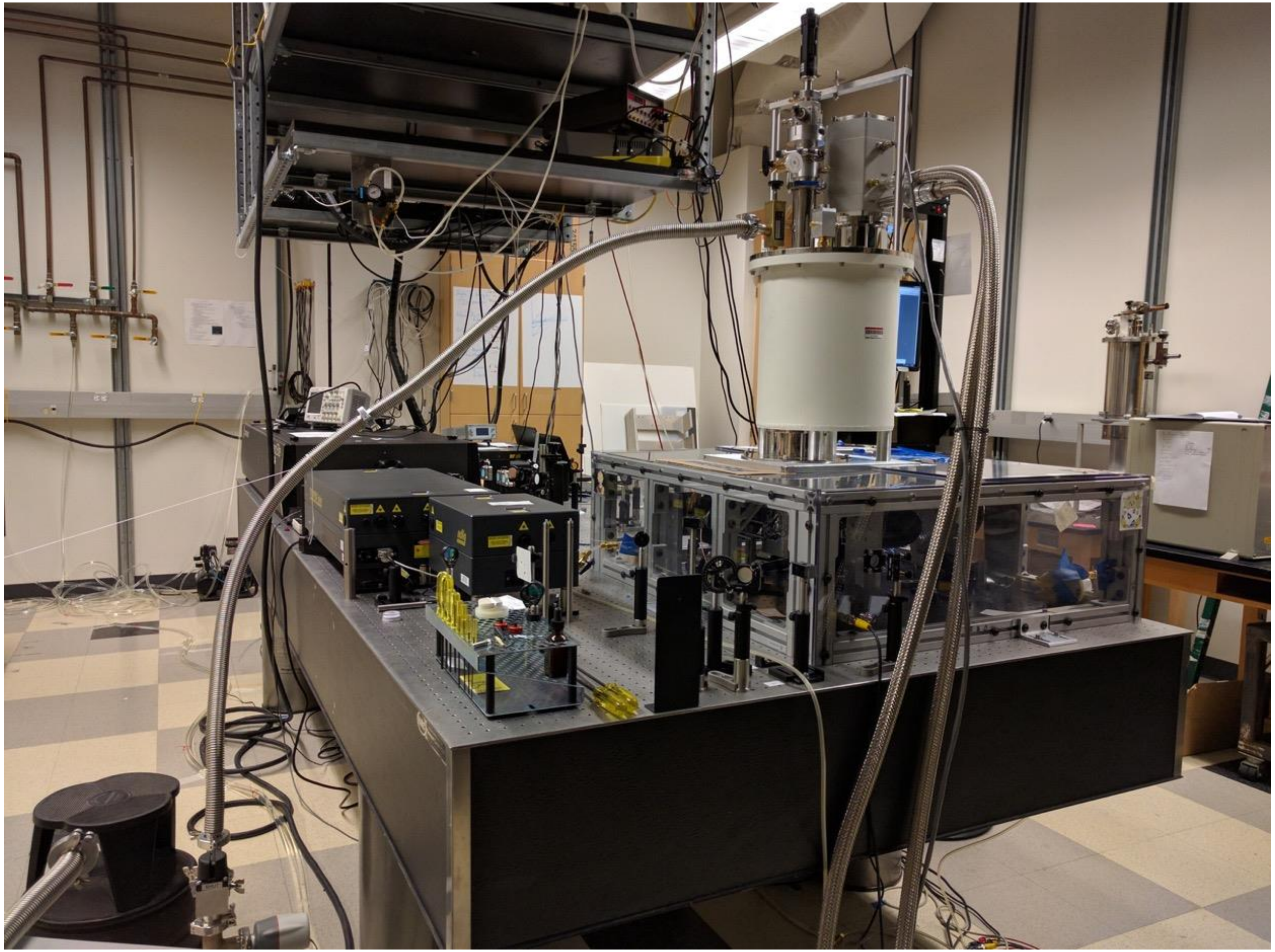


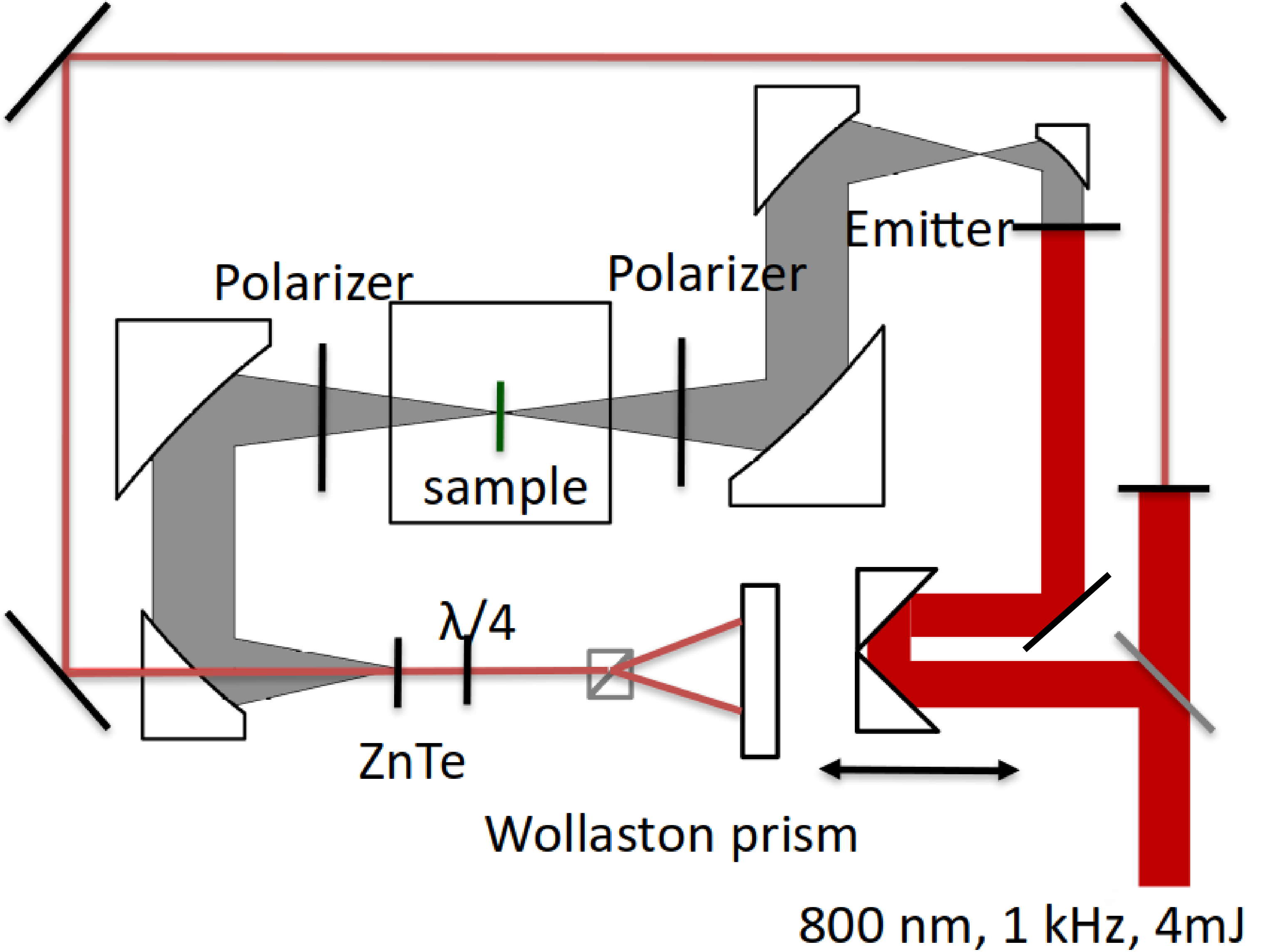
$$\mathbf{P} = \chi_e \mathbf{E}$$

Spin Wave (magnon)



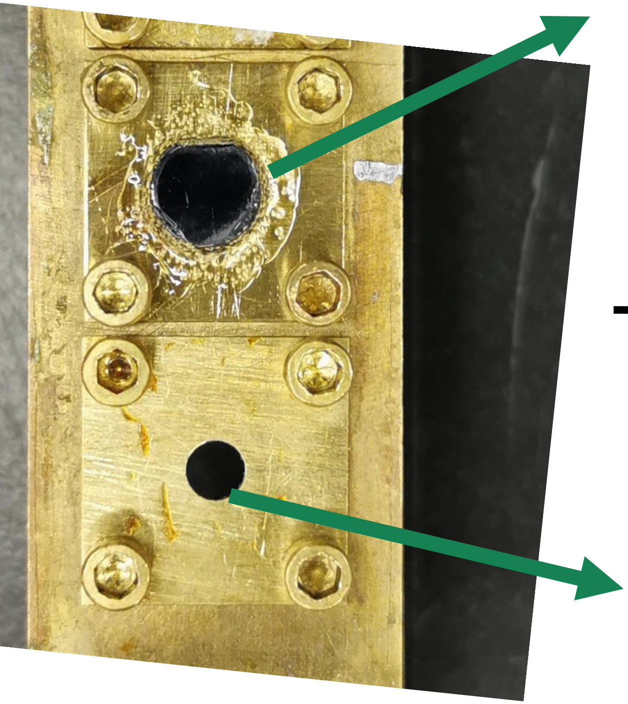
THz Laboratory



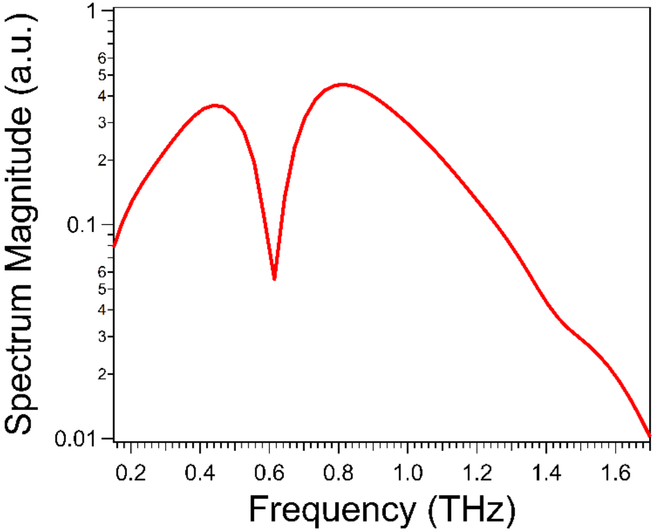

Emitter
Polarizer
Polarizer
sample
λ/4
ZnTe
Wollaston prism
800 nm, 1 kHz, 4mJ

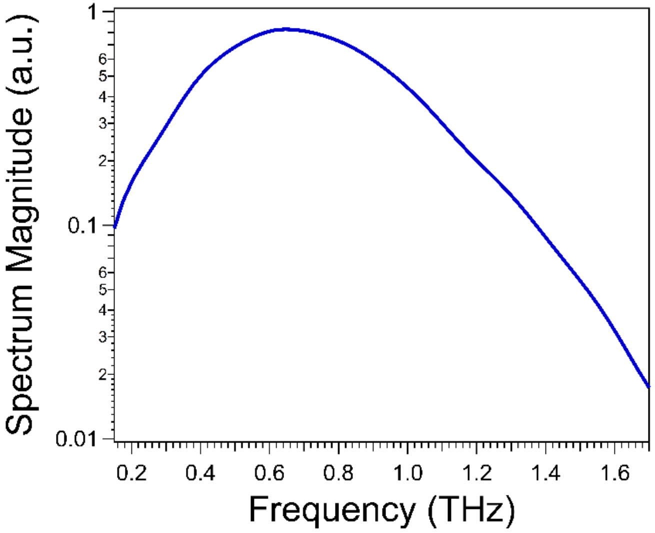
Time-domain terahertz spectroscopy

sample

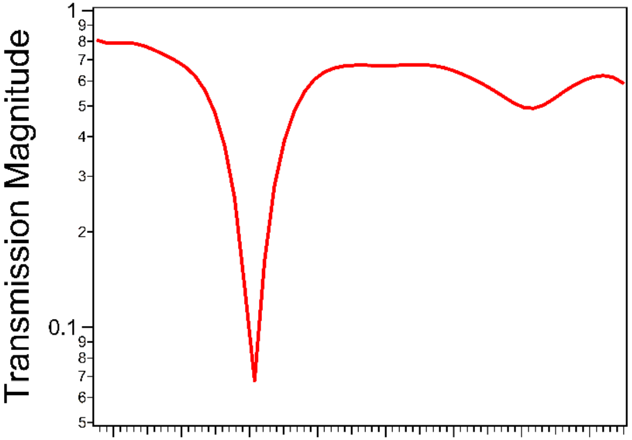


aperture

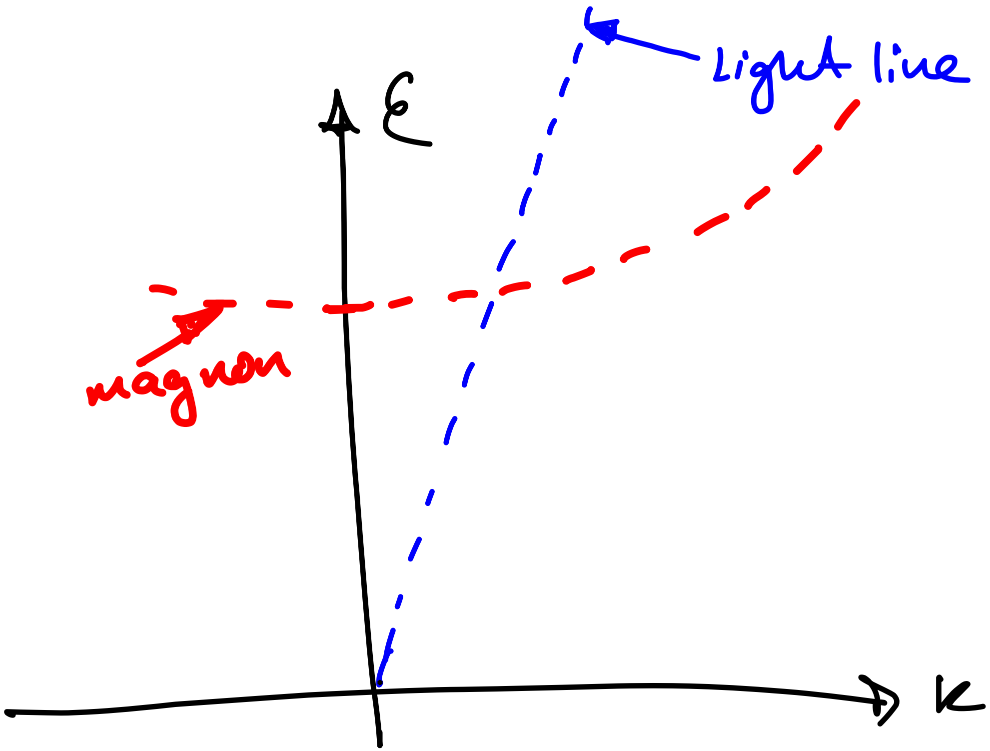


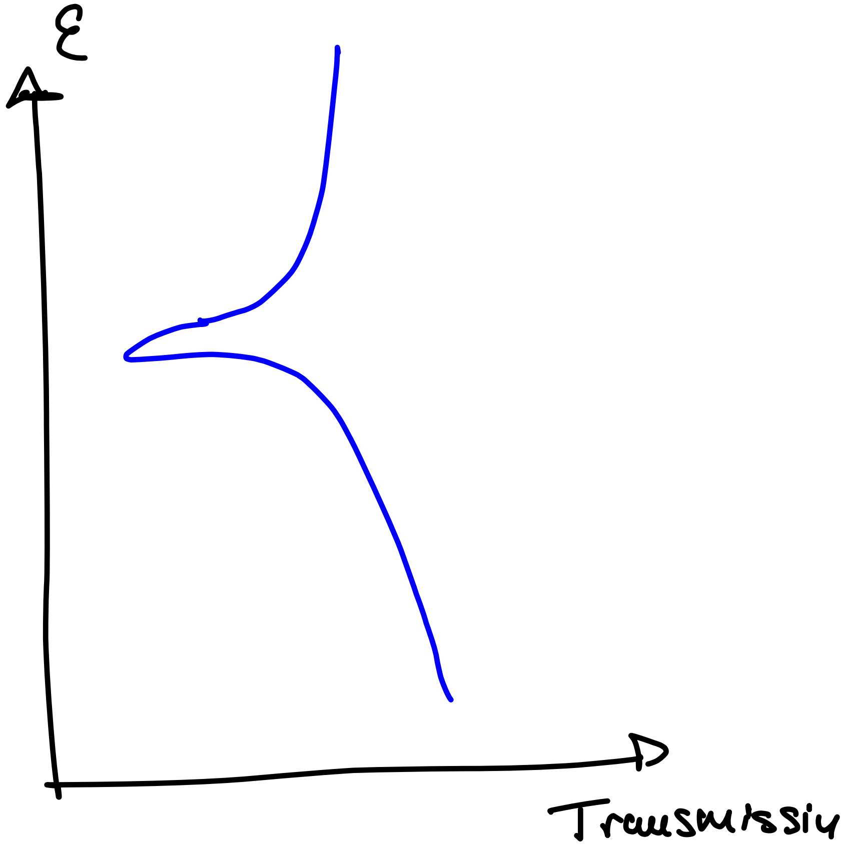


=



Magnon Polaritons





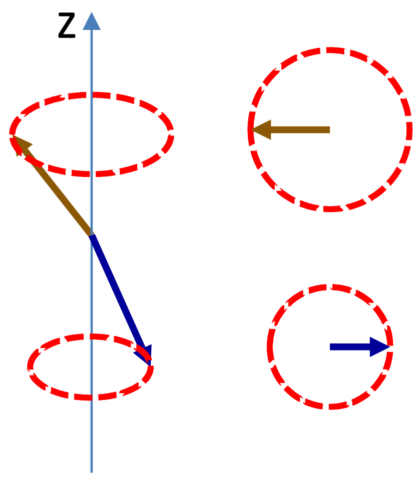
Two sublattices AFM + Mean field

$$\mathcal{F} = -\boldsymbol{H}\bullet(\boldsymbol{M_1}+\boldsymbol{M_2})+\lambda\boldsymbol{M_1}\bullet\boldsymbol{M_2}+K_x(M_{1x}^2+M_{2x}^2)+K_y(M_{1y}^2+M_{2y}^2)$$

Uniaxial Anisotropy $K_x = K_y$

Side view

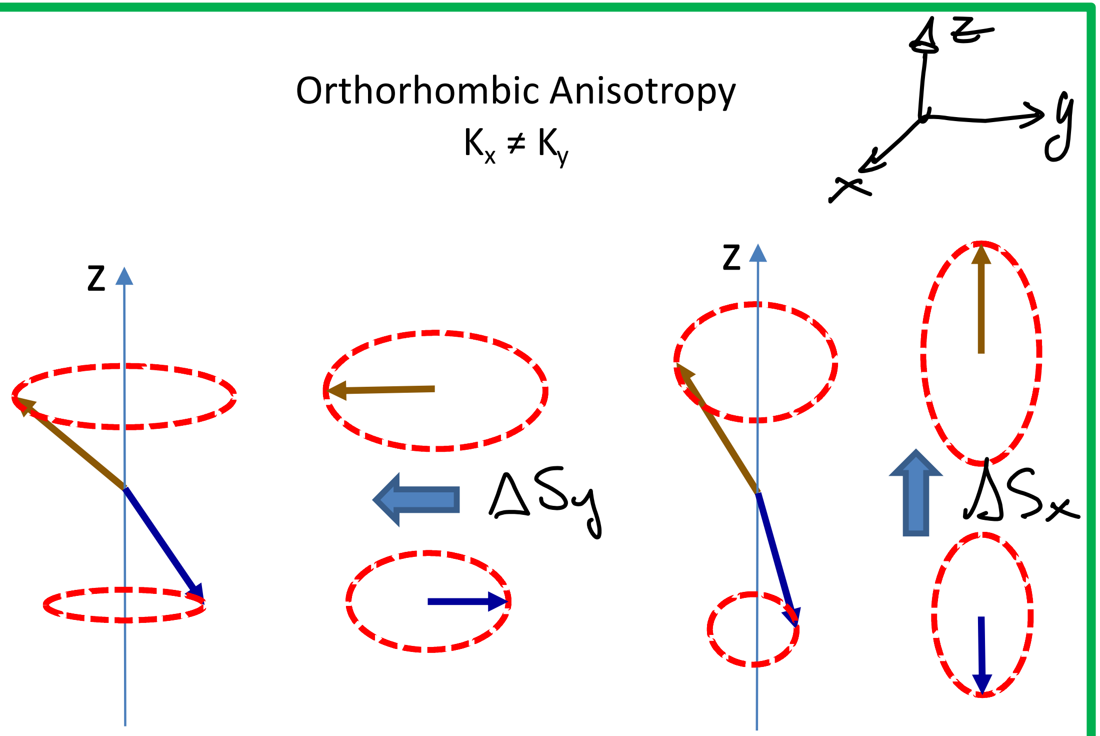
Top view



Circular Mode

Orthorhombic Anisotropy

$K_x \neq K_y$



Elliptical Modes

K_x , $K_y > 0$

z – easy axis

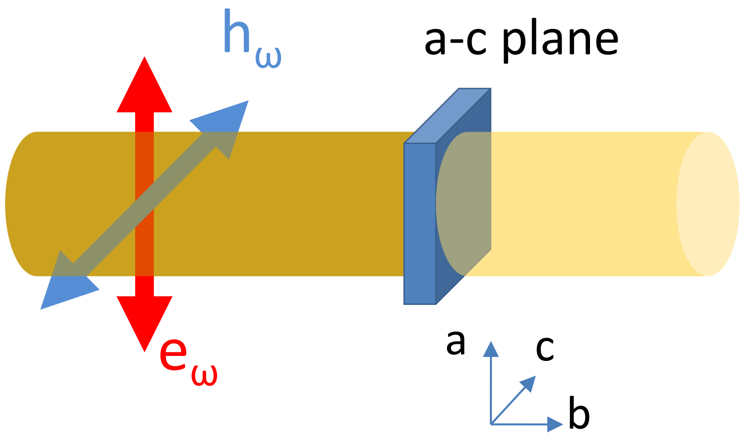
e_ω

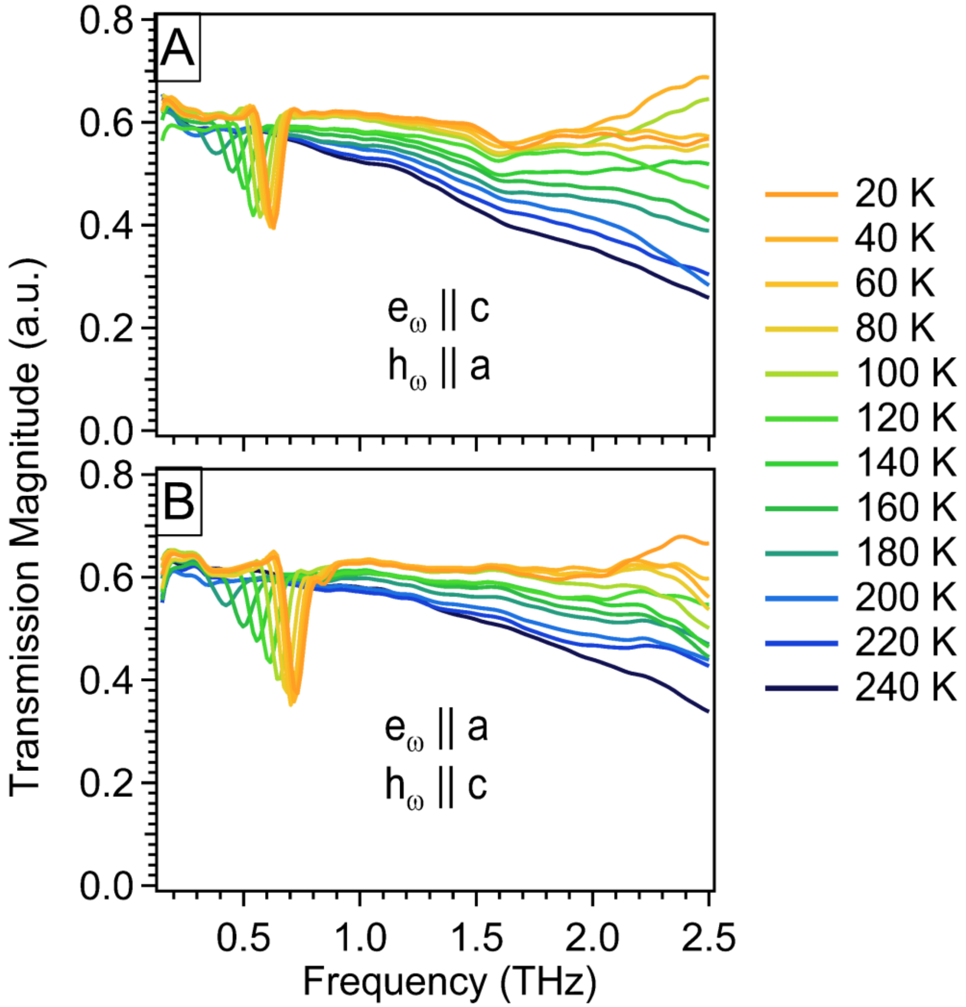
h_ω

$\underbrace{g h_\omega \Delta S}_{\text{magnetic dipole}}$

Keffer and Kittel (Physical Review V. 85, N. 2, Jan 15, 1952)

1 THz ~ 4 meV ~ 44 K ~ 33 cm^{-1}

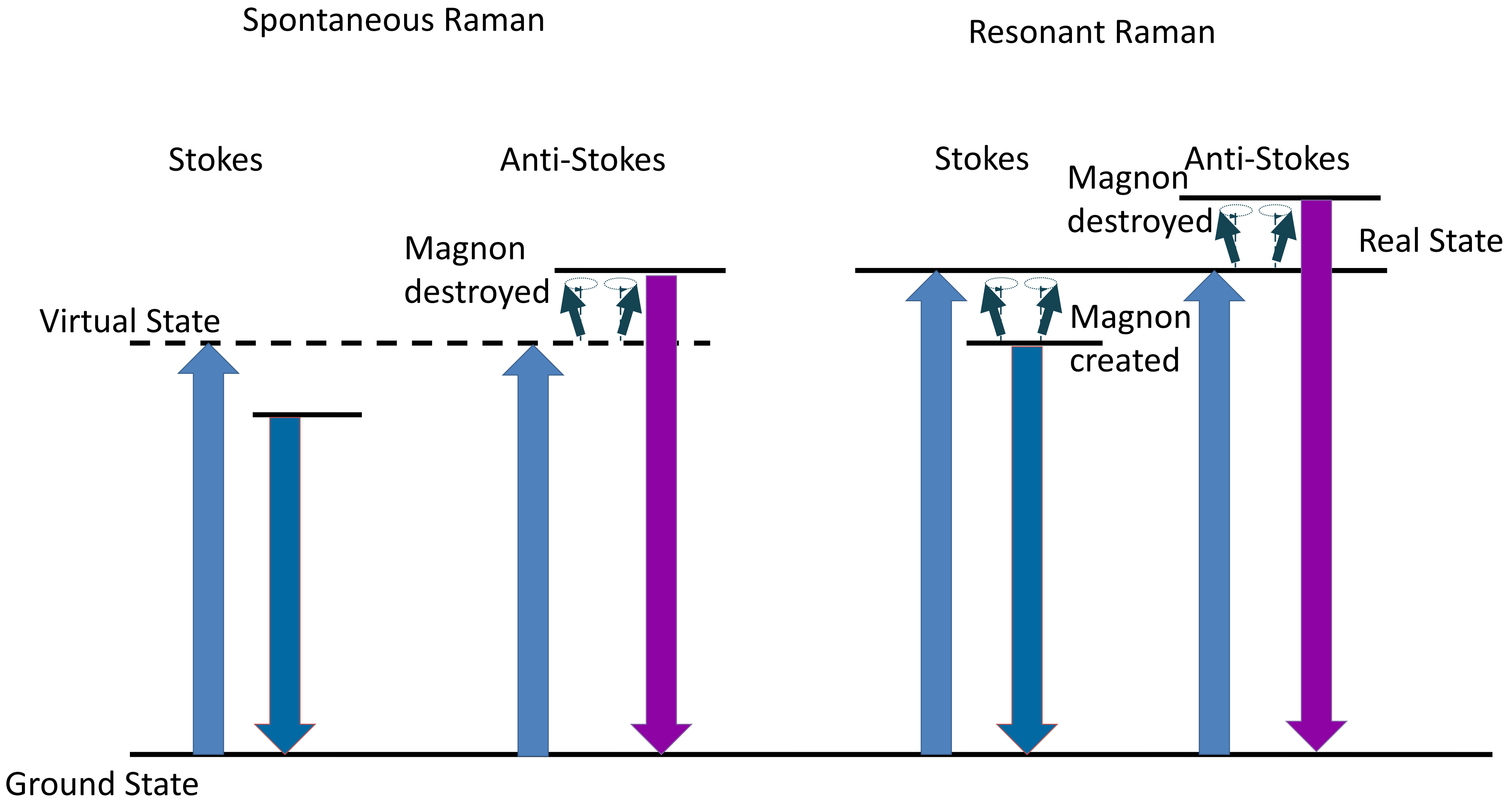




T.T. Mai, PhD Thesis (2019).

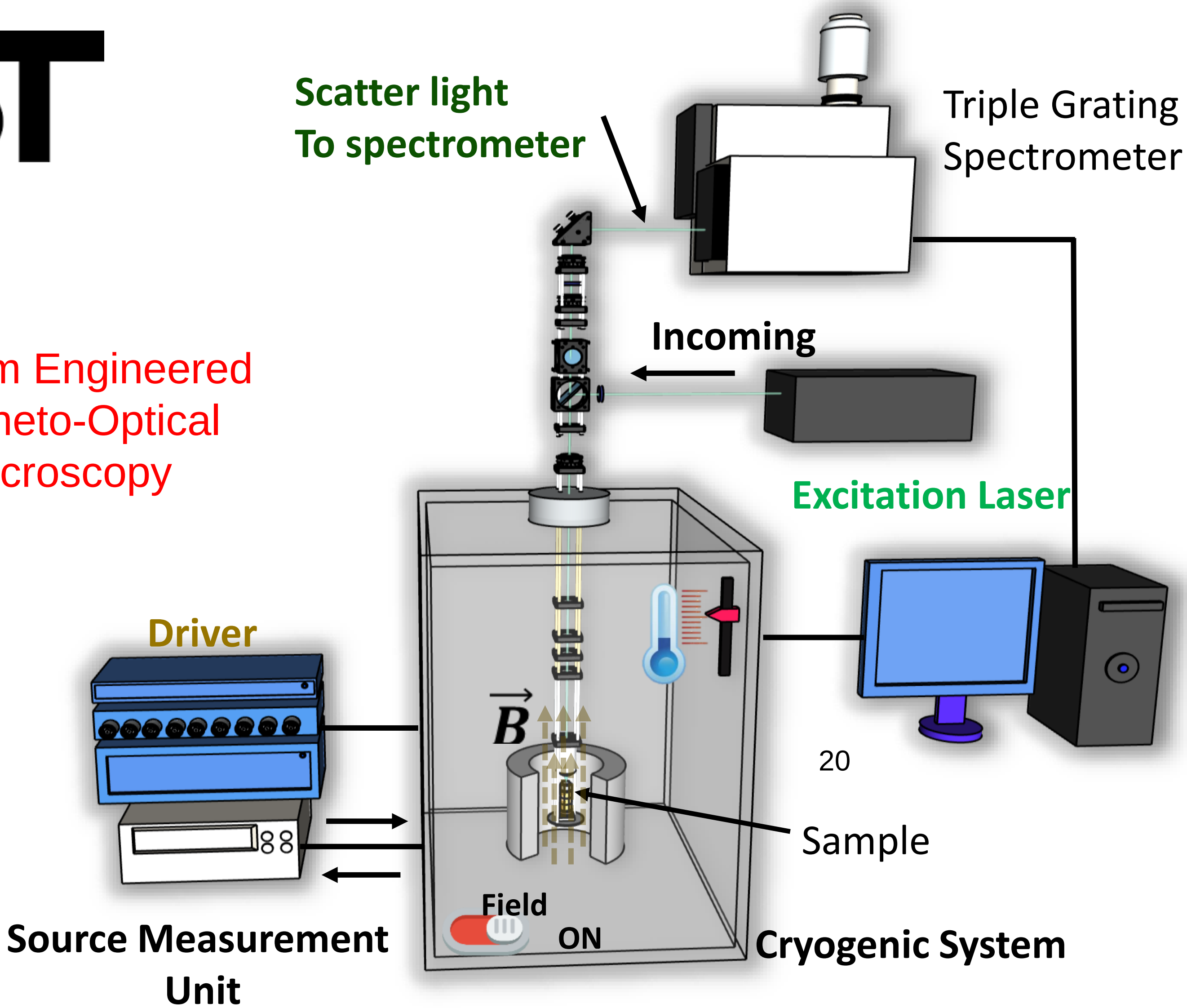
Raman Spectroscopy

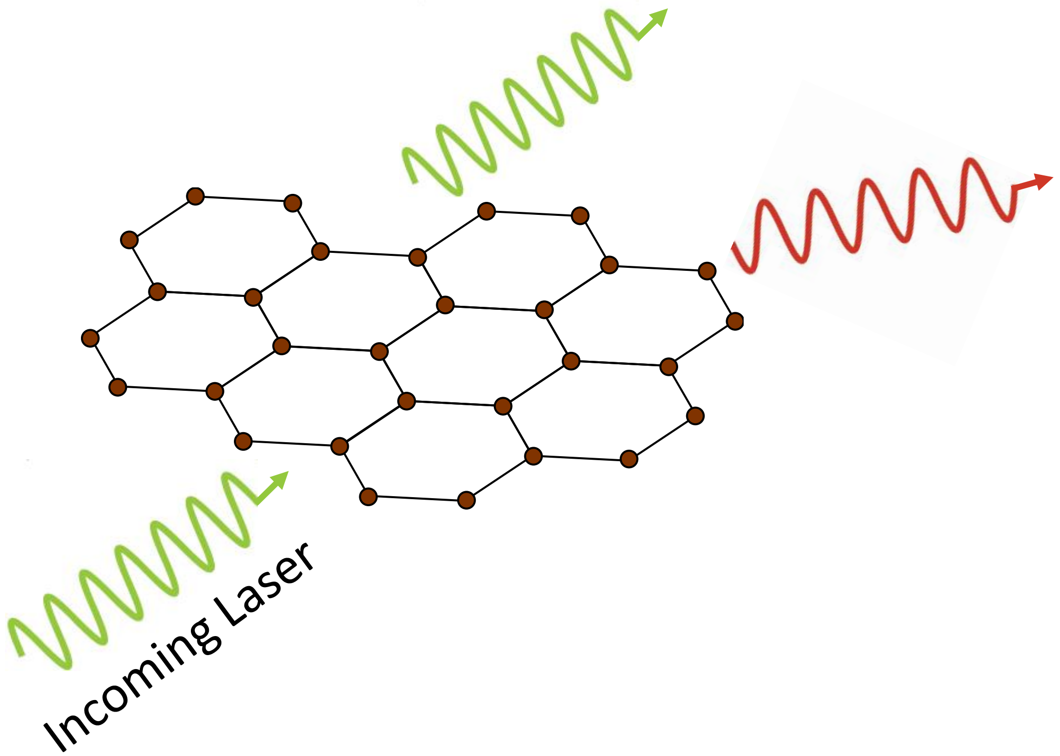
Raman Spectroscopy

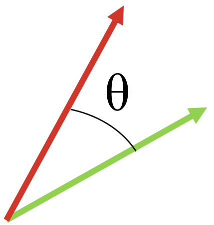


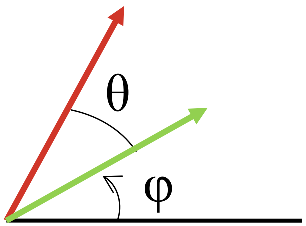
Custom Engineered Magneto-Optical Microscopy

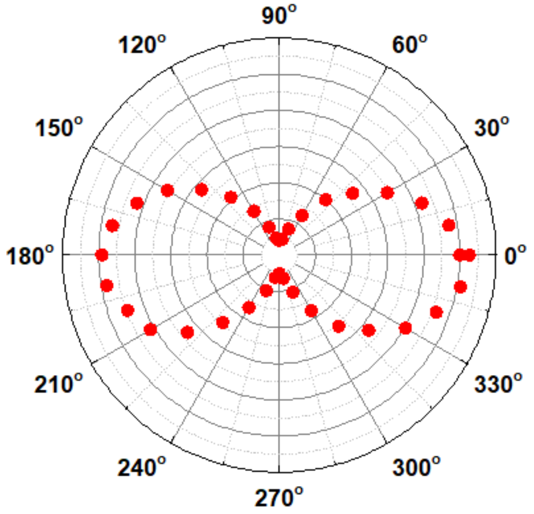
Angela Hight Walker



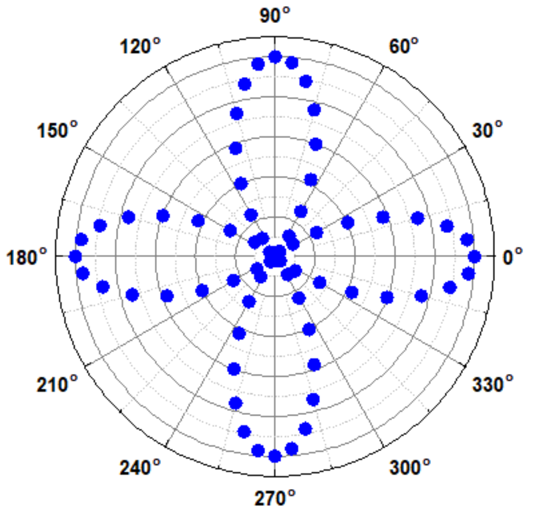








Angle θ



Angle φ

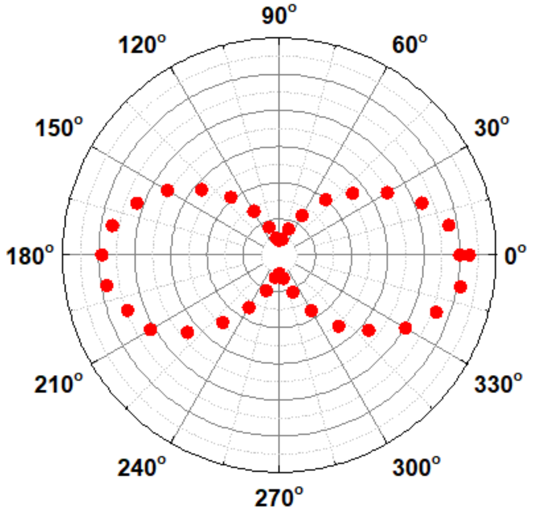
The symmetry of the scattering mode determines the shape of the polar plots. E.g.

$$A_g \doteq \begin{pmatrix} b & 0 & d \\ 0 & c & 0 \\ d & 0 & a \end{pmatrix} \qquad B_g \doteq \begin{pmatrix} 0 & f & 0 \\ f & 0 & e \\ 0 & e & 0 \end{pmatrix}$$

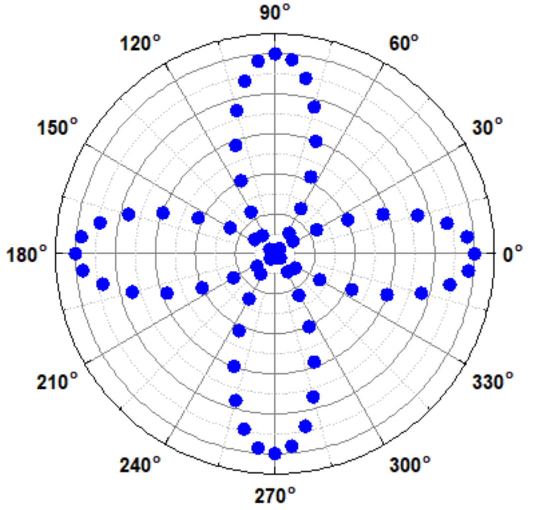
$$I_R \propto \left|\varepsilon_s \cdot R \cdot \varepsilon_i\right|^2$$

$$\varepsilon_i \doteq \begin{pmatrix} \cos(\theta) \\ \sin(\theta) \\ 0 \end{pmatrix} \qquad \varepsilon_s \doteq \begin{pmatrix} \cos(\theta+\varphi) \\ \sin(\theta+\varphi) \\ 0 \end{pmatrix}$$

By controlling polarization of incoming and scattered photons we can figure out (in principle) the matrix representation of the Raman tensor.



Angle θ



Angle φ

Character Table of the group D_{2h}(mmm)*

D_{2h}(mmm)	#	1	2_z	2_y	2_x	-1	m_z	m_y	m_x	functions
A_g	Γ_1^+	1	1	1	1	1	1	1	1	x^2,y^2,z^2
B_{1g}	Γ_3^+	1	1	-1	-1	1	1	-1	-1	xy,J_z
B_{2g}	Γ_2^+	1	-1	1	-1	1	-1	1	-1	xz,J_y
B_{3g}	Γ_4^+	1	-1	-1	1	1	-1	-1	1	yz,J_x
A_u	Γ_1^-	1	1	1	1	-1	-1	-1	-1	.
B_{1u}	Γ_3^-	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	Γ_2^-	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	Γ_4^-	1	-1	-1	1	-1	1	1	-1	x

$$A_g \doteq \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

$$B_{1g} \doteq \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Note here that this irrep also transforms as J_z, i.e. as an angular momentum along the z axis →**magnetic moment**.

These transform as polar vectors (electric dipoles).

More interesting case where irreps have complex characters.

Character Table of the group C_{3i}(-3)*

C_{3i}(-3)	#	1	3^+	3^-	-1	-3^+	-3^-	functions
A_g	Γ_1^+	1	1	1	1	1	1	x^2+y^2, z^2, J_z
^1E_g ^2E_g	Γ_3^+ Γ_2^+	1 1	w^2 w	w w^2	1 1	w^2 w	w w^2	$(xz,yz),(x^2-y^2,xy),(J_x,J_y)$
A_u	Γ_1^-	1	1	1	-1	-1	-1	z
^1E_u ^2E_u	Γ_3^- Γ_2^-	1 1	w^2 w	w w^2	-1 -1	$-w^2$ $-w$	$-w$ $-w^2$	(x,y)

$w = \exp(2i\pi/3)$

$$A_g \doteq \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix}$$

$$^1E_g \doteq \begin{pmatrix} c & d & e \\ d & -c & f \\ e & f & 0 \end{pmatrix} \quad (\text{‘}x\text{’})$$

$$^2E_g \doteq \begin{pmatrix} d & -c & -f \\ -c & -d & e \\ -f & e & 0 \end{pmatrix} \quad (\text{‘}y\text{’})$$

These are treated as ‘degenerate’, i.e. 2 components of 2-dimensional irrep.

But this is incorrect.

Same issue with ^1E_u and ^2E_u

Character Table of the group C_{3i}(-3)*

C_{3i}(-3)	#	1	3^+	3^-	-1	-3^+	-3^-	functions
A_g	Γ_1^+	1	1	1	1	1	1	x^2+y^2, z^2, J_z
^1E_g ^2E_g	Γ_3^+ Γ_2^+	1 1	w^2 w	w w^2	1 1	w^2 w	w w^2	$(xz,yz),(x^2-y^2,xy),(J_x,J_y)$
A_u	Γ_1^-	1	1	1	-1	-1	-1	z
^1E_u ^2E_u	Γ_3^- Γ_2^-	1 1	w^2 w	w w^2	-1 -1	$-w^2$ $-w$	$-w$ $-w^2$	(x,y)

$w = \exp(2i\pi/3)$

We can tell because the 3-fold rotations (+ and -) do not have the same characters, i.e. they do not belong the same class.

Which means there must be a way to distinguish the representations that have w and w^2 characters.

Table C.2: $\overline{3}$. $|G| = 6$.

class	1	3^-	3^+	$\overline{1}$	$\overline{3}^-$	$\overline{3}^+$	
order	1	3	3	2	6	6	
$\mathrm{A_g}$	1	1	1	1	1	1	$J_z,\, z^2,\, x^2+y^2$
$^1\mathrm{E_g}$	1	$\frac{-1+\mathrm{i}\sqrt{3}}{2}$	$\frac{-1-\mathrm{i}\sqrt{3}}{2}$	1	$\frac{-1+\mathrm{i}\sqrt{3}}{2}$	$\frac{-1-\mathrm{i}\sqrt{3}}{2}$	$J_x - \mathrm{i}J_y,\, xz - \mathrm{i}yz,\, x^2 - y^2 + 2\mathrm{i}xy$
$^2\mathrm{E_g}$	1	$\frac{-1-\mathrm{i}\sqrt{3}}{2}$	$\frac{-1+\mathrm{i}\sqrt{3}}{2}$	1	$\frac{-1-\mathrm{i}\sqrt{3}}{2}$	$\frac{-1+\mathrm{i}\sqrt{3}}{2}$	$J_x + \mathrm{i}J_y,\, xz + \mathrm{i}yz,\, x^2 - y^2 - 2\mathrm{i}xy$
$\mathrm{A_u}$	1	1	1	-1	-1	-1	z
$^1\mathrm{E_u}$	1	$\frac{-1+\mathrm{i}\sqrt{3}}{2}$	$\frac{-1-\mathrm{i}\sqrt{3}}{2}$	-1	$\frac{1-\mathrm{i}\sqrt{3}}{2}$	$\frac{1+\mathrm{i}\sqrt{3}}{2}$	$x - \mathrm{i}y$
$^2\mathrm{E_u}$	1	$\frac{-1-\mathrm{i}\sqrt{3}}{2}$	$\frac{-1+\mathrm{i}\sqrt{3}}{2}$	-1	$\frac{1+\mathrm{i}\sqrt{3}}{2}$	$\frac{1-\mathrm{i}\sqrt{3}}{2}$	$x + \mathrm{i}y$

If we consider time-reversal symmetry, then

$x + iy$ | $x - iy$

$J_x + iJ_y$ | $J_x - iJ_y$

are distinguishable.

Then, the Raman matrices become:

$$^1E_g \doteq \begin{pmatrix} c & 2ic & d \\ 2ic & -c & -id \\ d & -id & 0 \end{pmatrix} \qquad ^2E_g \doteq \begin{pmatrix} c & -2ic & d \\ -2ic & -c & id \\ d & id & 0 \end{pmatrix}$$

Character Table of the group T_h(m-3)*

T_h(m-3)	#	1	3^+	3^-	2	-1	-3^+	-3^-	m	functions
Mult.	-	1	4	4	3	1	4	4	3	.
A_g	Γ_1^+	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
^1E_g ^2E_g	Γ_2^+ Γ_3^+	1 1	w w^2	w^2 w	1 1	1 1	w w^2	w^2 w	1 1	$(2z^2-x^2-y^2, x^2-y^2)$
T_g	Γ_4^+	3	0	0	-1	3	0	0	-1	(xz,yz,xy),(J_x,J_y,J_z)
A_u	Γ_1^-	1	1	1	1	-1	-1	-1	-1	.
^1E_u ^2E_u	Γ_2^- Γ_3^-	1 1	w w^2	w^2 w	1 1	-1 -1	-w $-w^2$	$-w^2$ -w	-1 -1	.
T_u	Γ_4^-	3	0	0	-1	-3	0	0	1	(x,y,z)

w = exp(2iπ/3)

$$A_g \doteq \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$$

$$^1E_g \doteq \begin{pmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & -2b \end{pmatrix}$$

$$^2E_g \doteq \begin{pmatrix} -\sqrt{3}b & 0 & 0 \\ 0 & \sqrt{3}b & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Same as before, time reversal can distinguish both E_g representations, producing:

$$^1E_g \doteq \begin{pmatrix} b & 0 & 0 \\ 0 & be^{i\frac{2\pi}{3}} & 0 \\ 0 & 0 & be^{-i\frac{2\pi}{3}} \end{pmatrix} \qquad ^2E_g \doteq \begin{pmatrix} b & 0 & 0 \\ 0 & be^{-i\frac{2\pi}{3}} & 0 \\ 0 & 0 & be^{i\frac{2\pi}{3}} \end{pmatrix}$$

$MnTe_2$

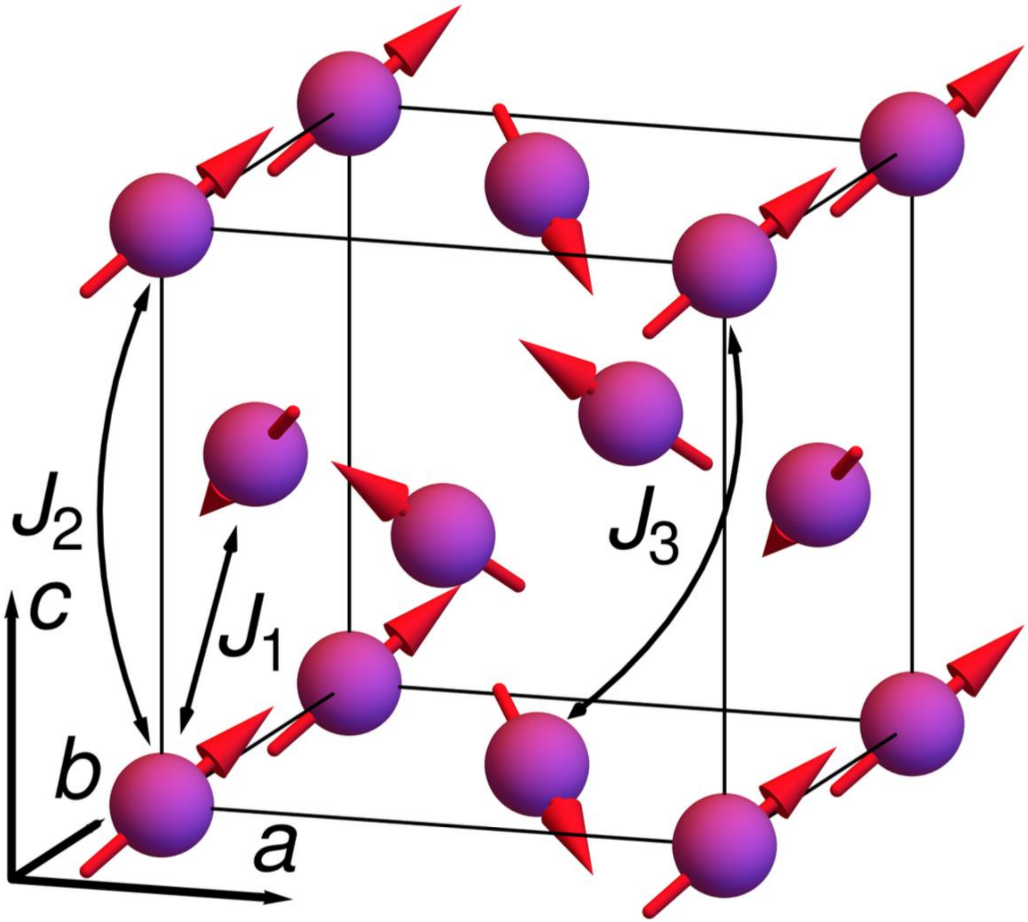
Transition temperature ~ 87 K

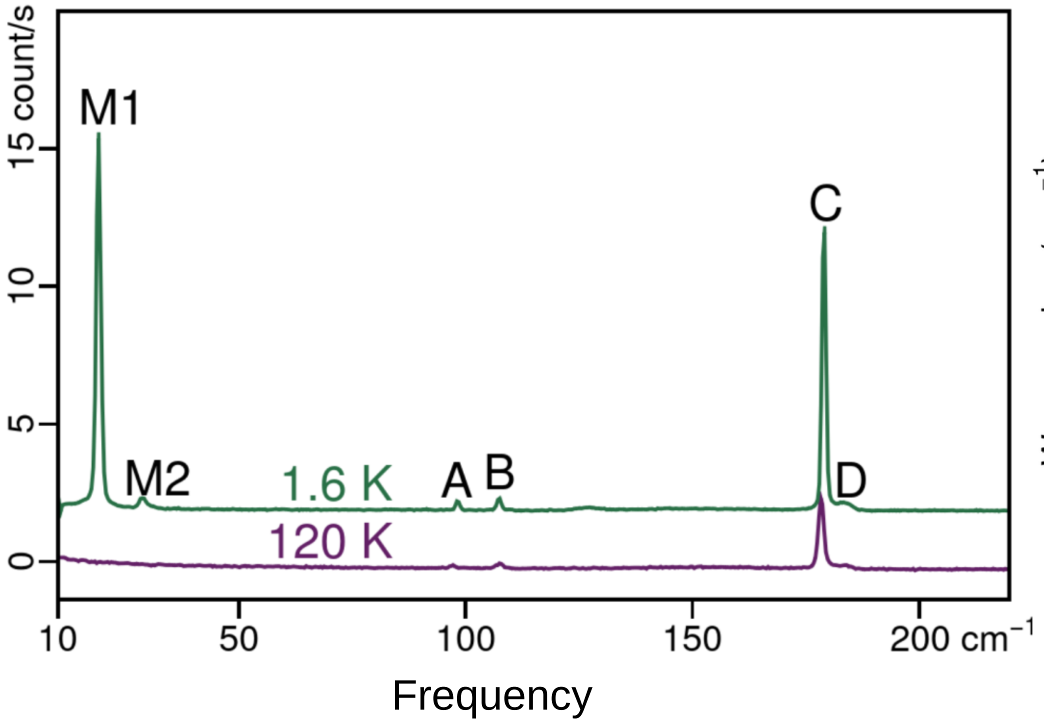
Noncollinear magnetic structure

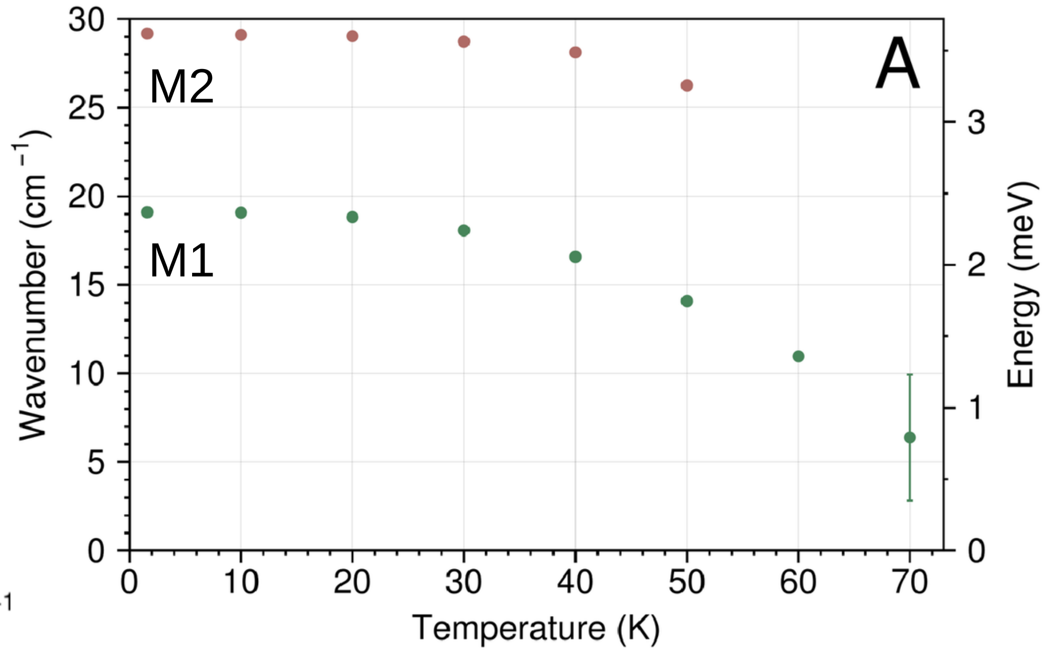
Space group $Pa\bar{3}$

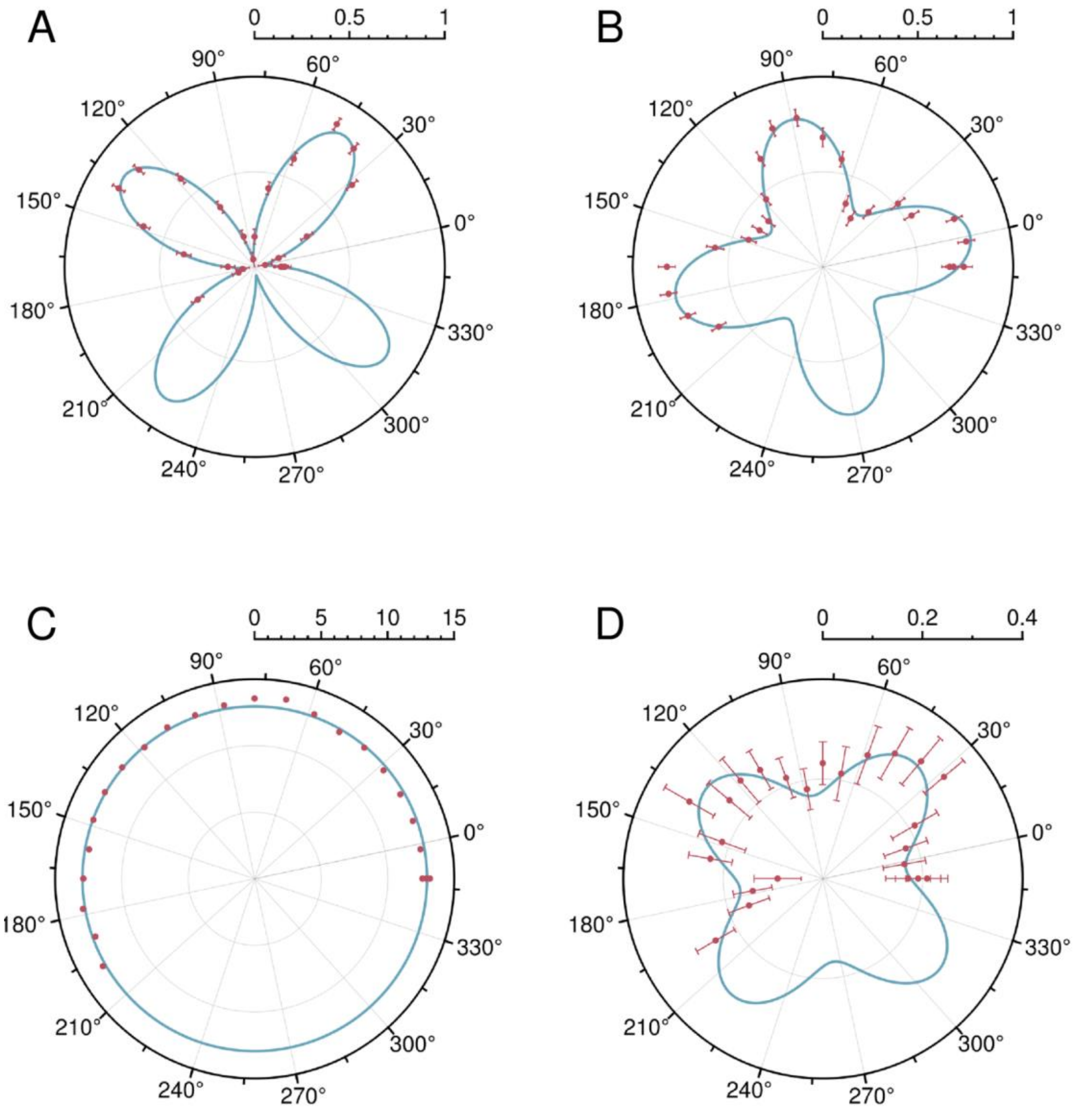
Point group $m\bar{3}$

S = 5/2

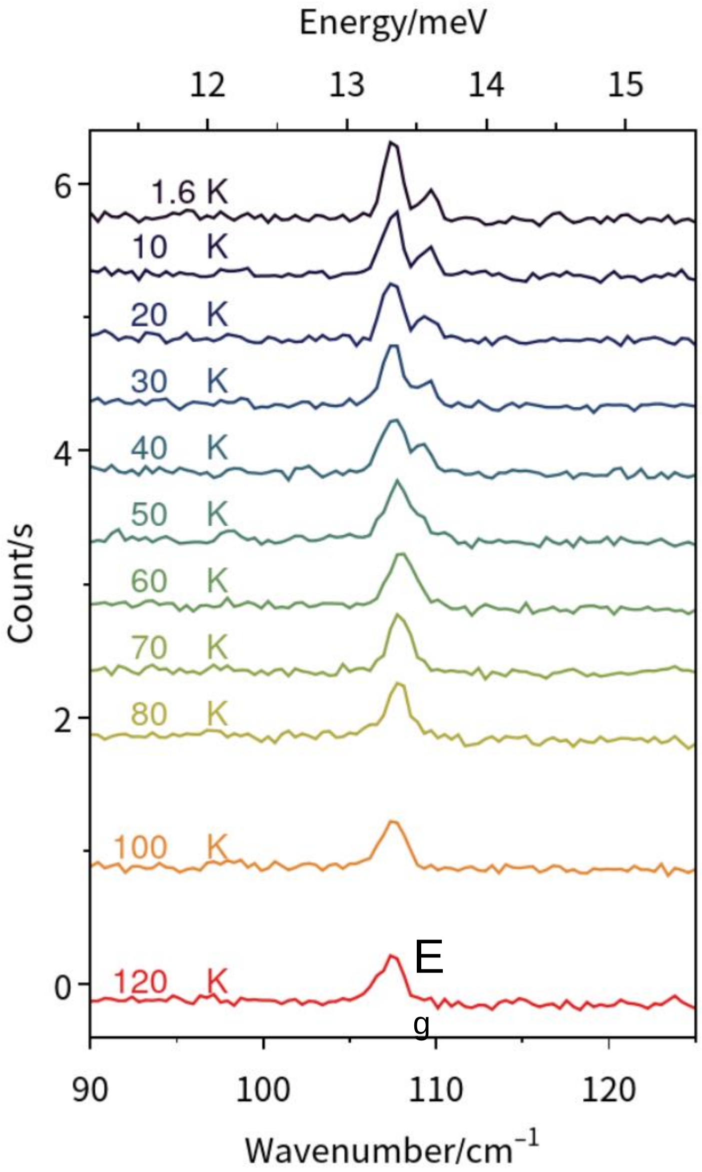



15 count/s
10
5
0
M1
M2
1.6 K
A
B
C
D
120 K
10
50
100
150
200 cm^{-1}
Frequency


30
25
20
15
10
5
0
Wavenumber (cm^{-1})
M2
M1
A
3
2
1
0
Energy (meV)
0
10
20
30
40
50
60
70
Temperature (K)



A	98 cm^{-1}	T_g
B	107 cm^{-1}	E_g
C	179 cm^{-1}	A_g
D	183 cm^{-1}	T_g



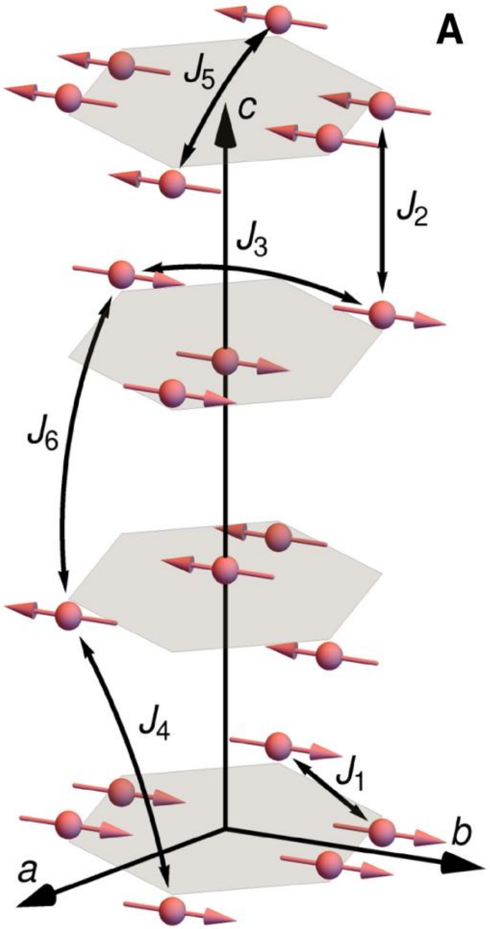
Eg phonon splits.

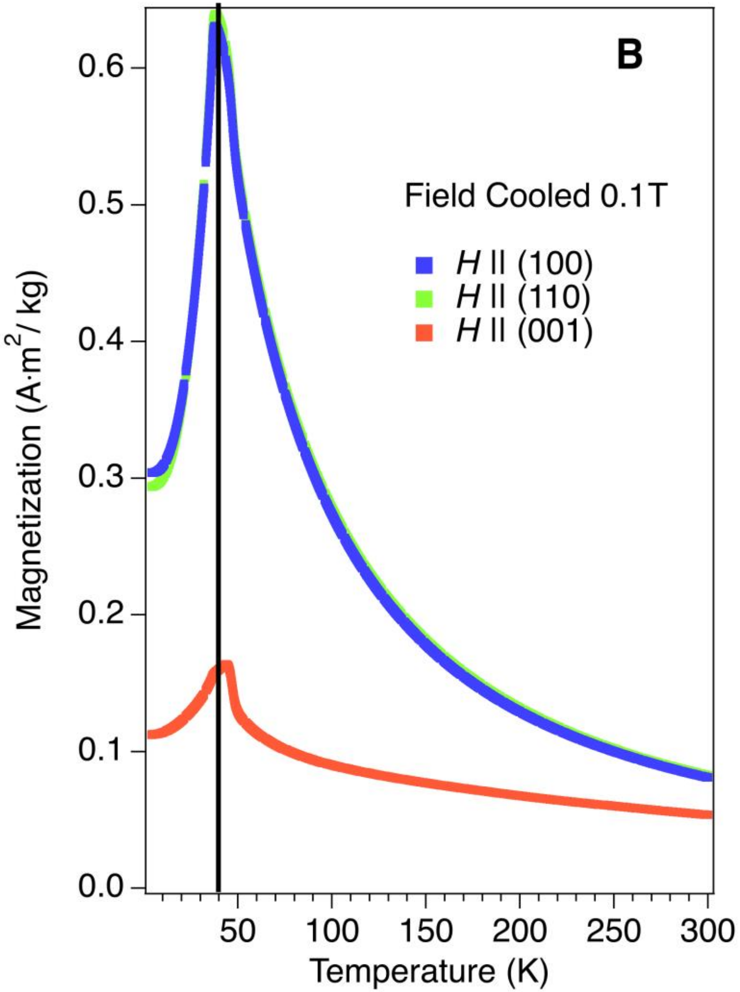
Loss of symmetry?

Yes! Time reversal, upon magnetic order.

$CoTiO_3$

Basic Properties of $CoTiO_3$





$CoTiO_3$ is antiferromagnet.

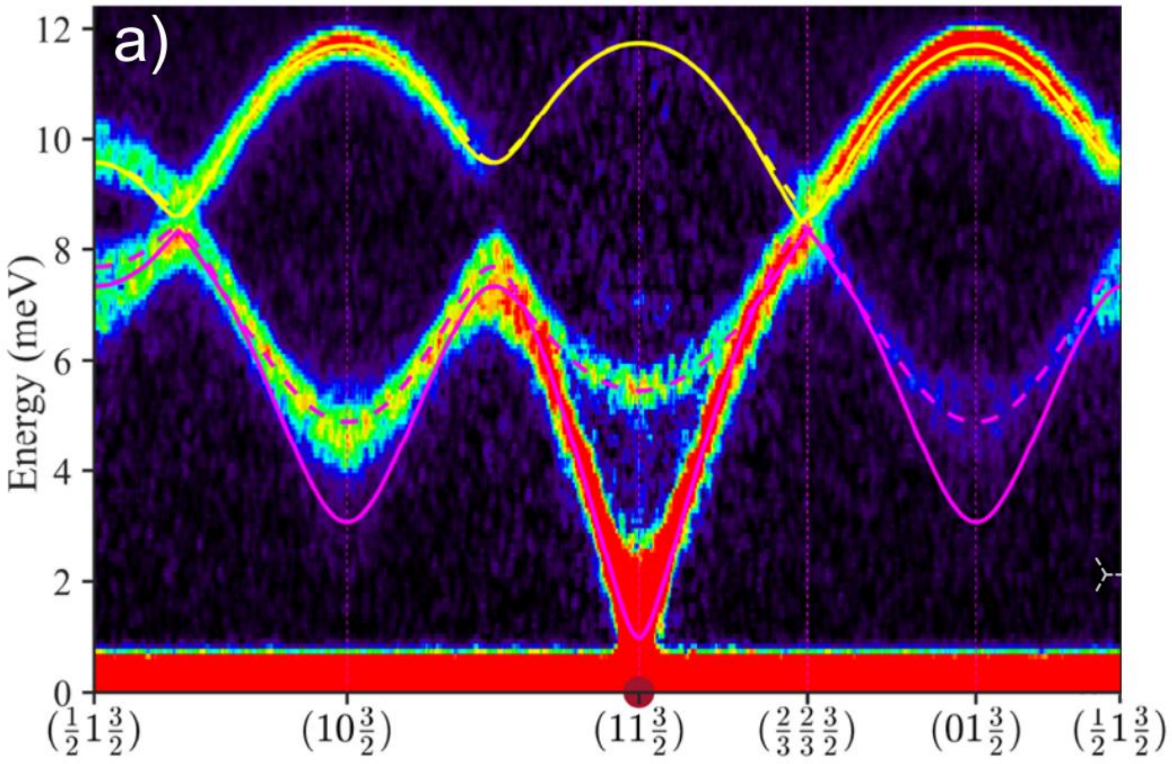
Ordering T is 38 K.

Honeycomb lattice of Co2+ atoms.

Magnetic unit is twice the crystal unit along the c-axis.

Phys. Rev. B **109**, 184436 (2024)

Basic Properties of $CoTiO_3$

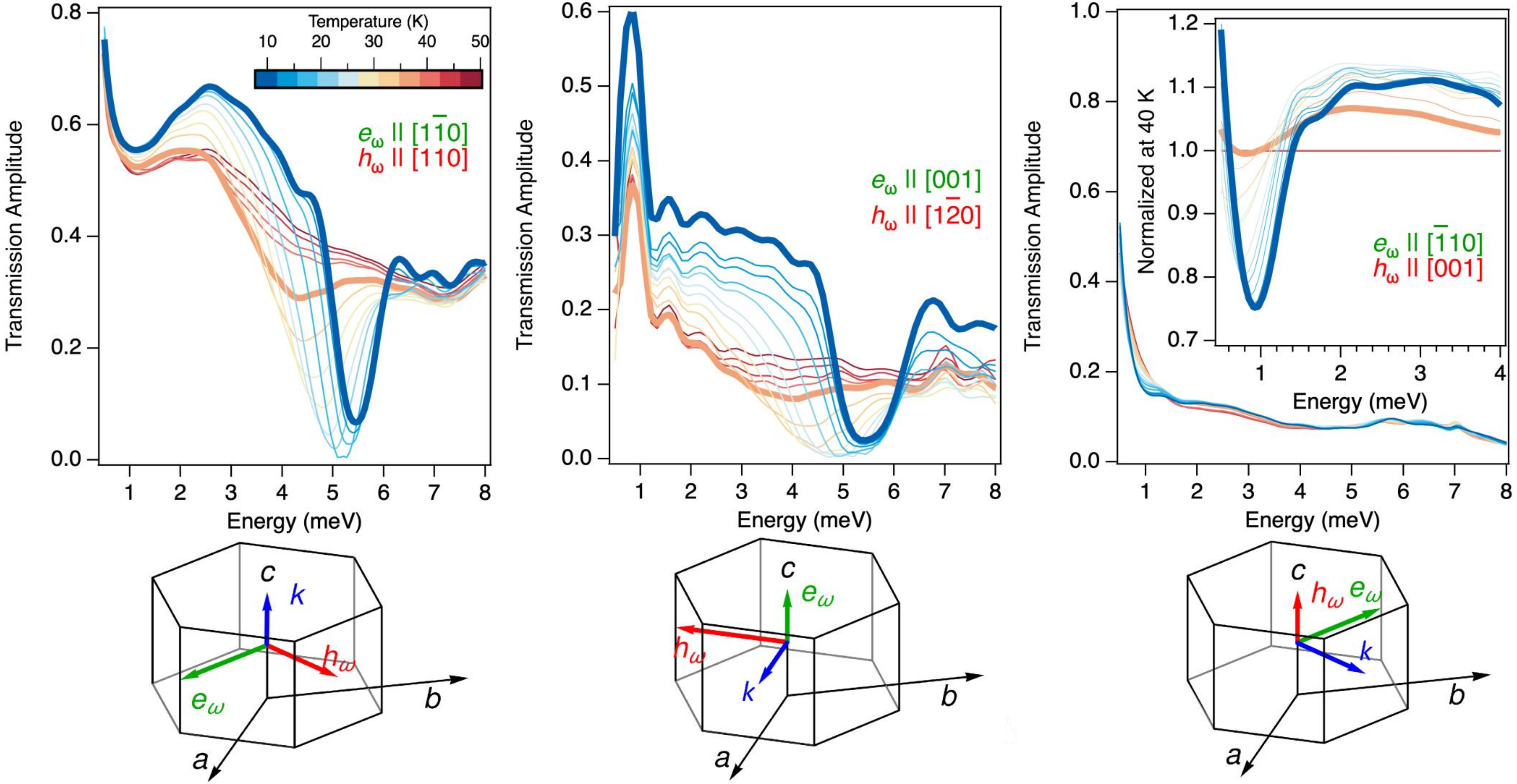


Dirac crossing of magnon bands.

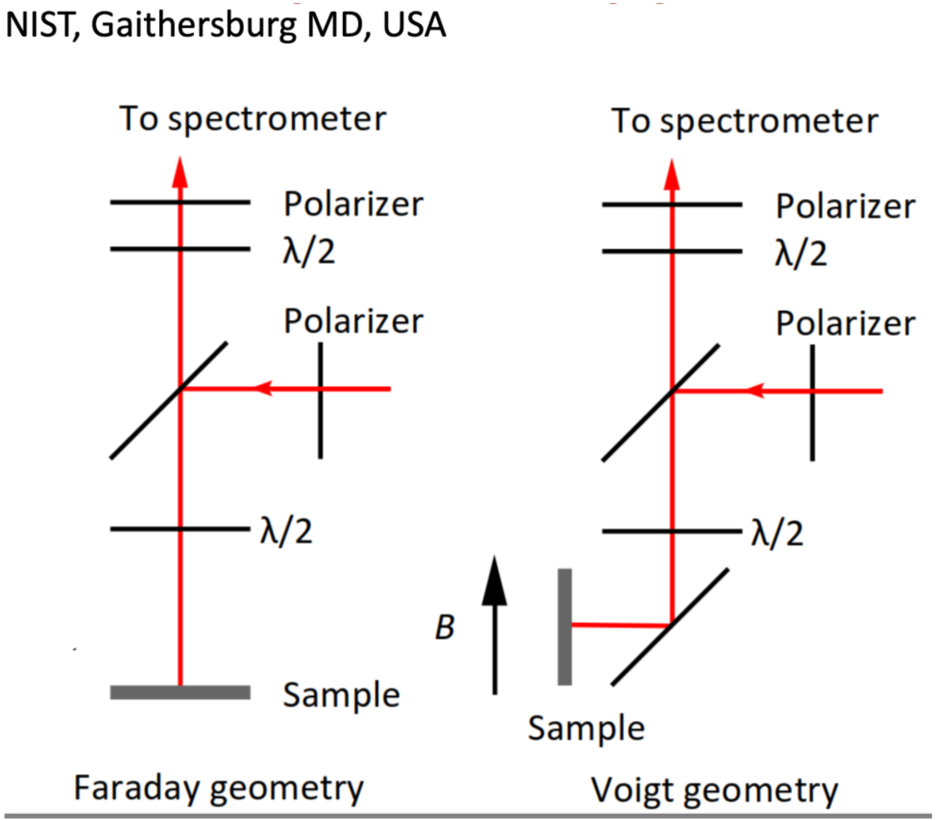
Within LSWT, spectrum must be gapless at zone center.

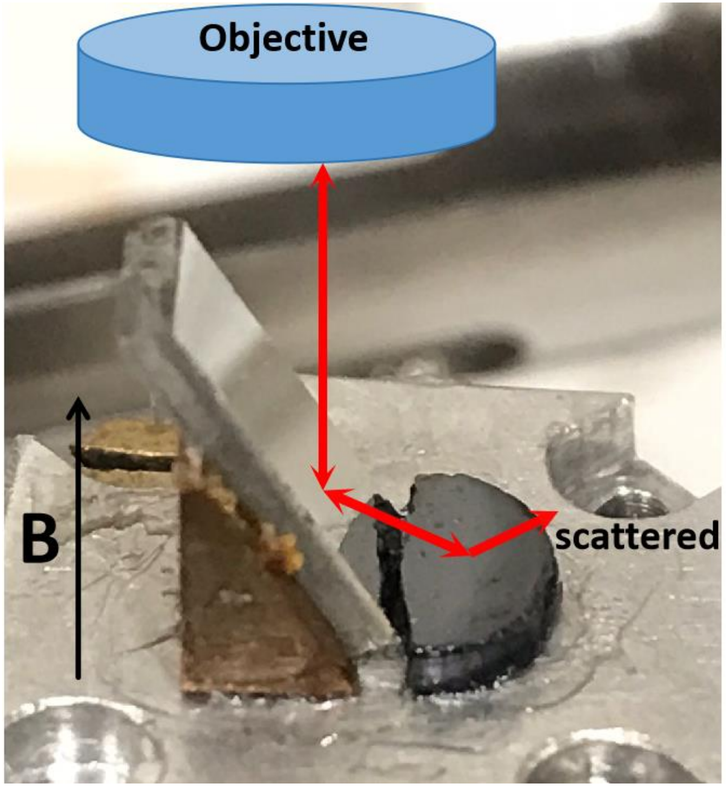
Nat Commun **12**, 3936 (2021)

THz transmission Results

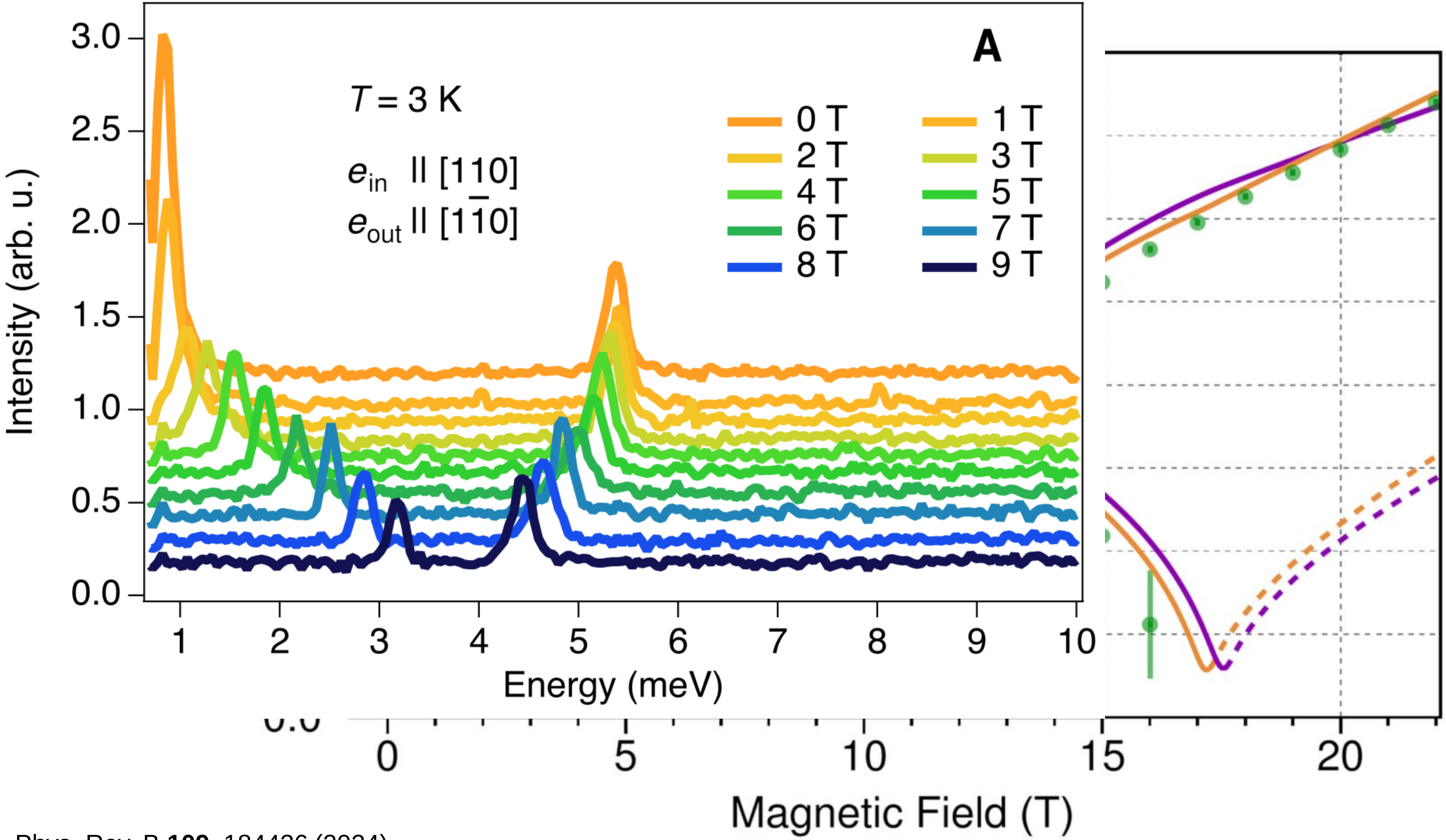


Raman Experiment



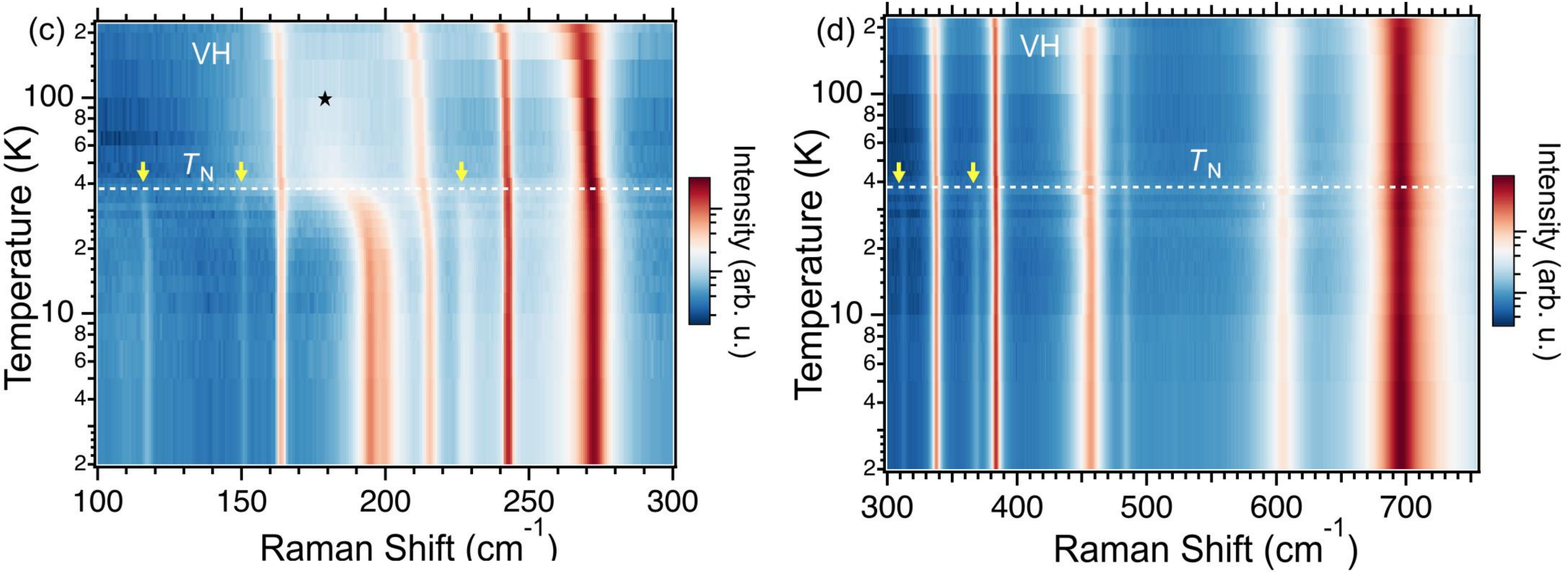


Raman magnetic field dependence

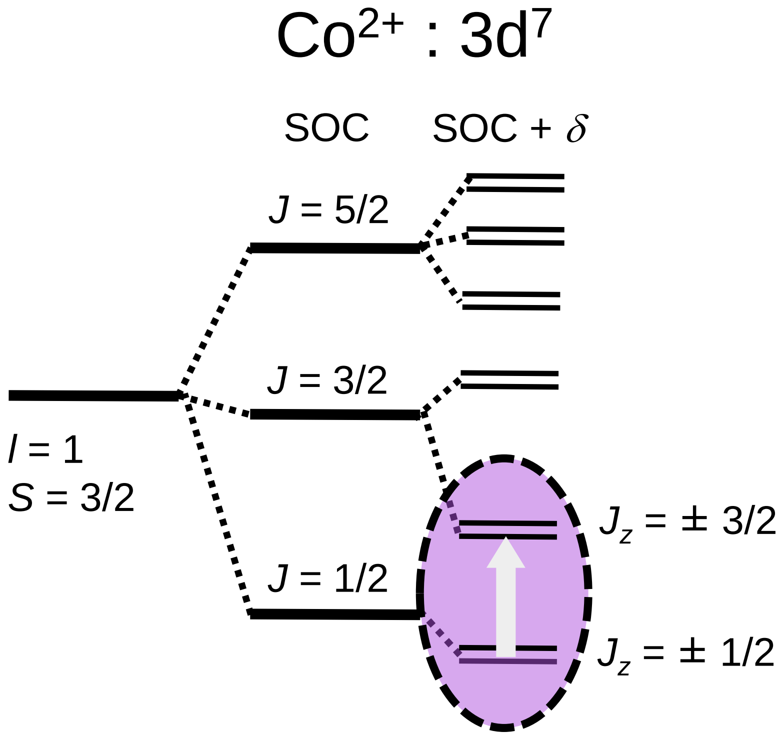


Phys. Rev. B **109**, 184436 (2024)

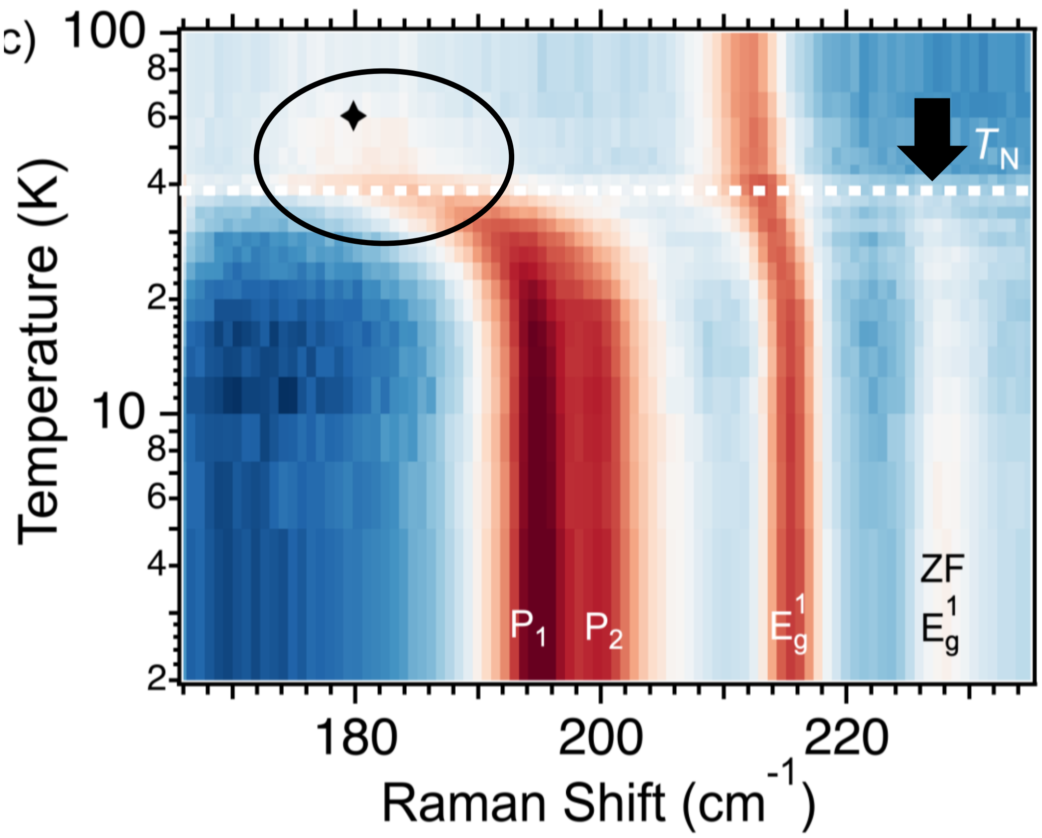
Raman Temperature Dependence

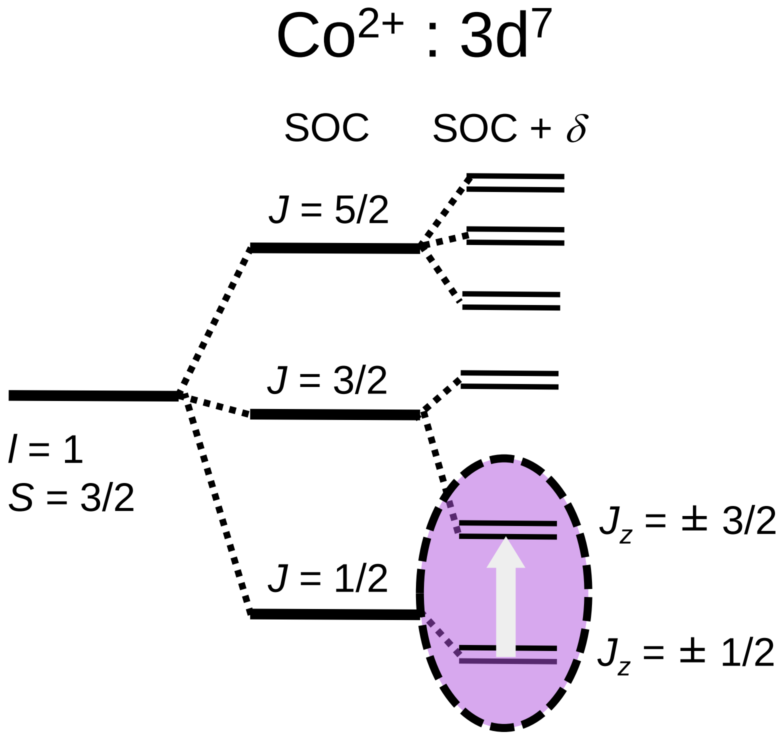


Spin-Orbital Excitations

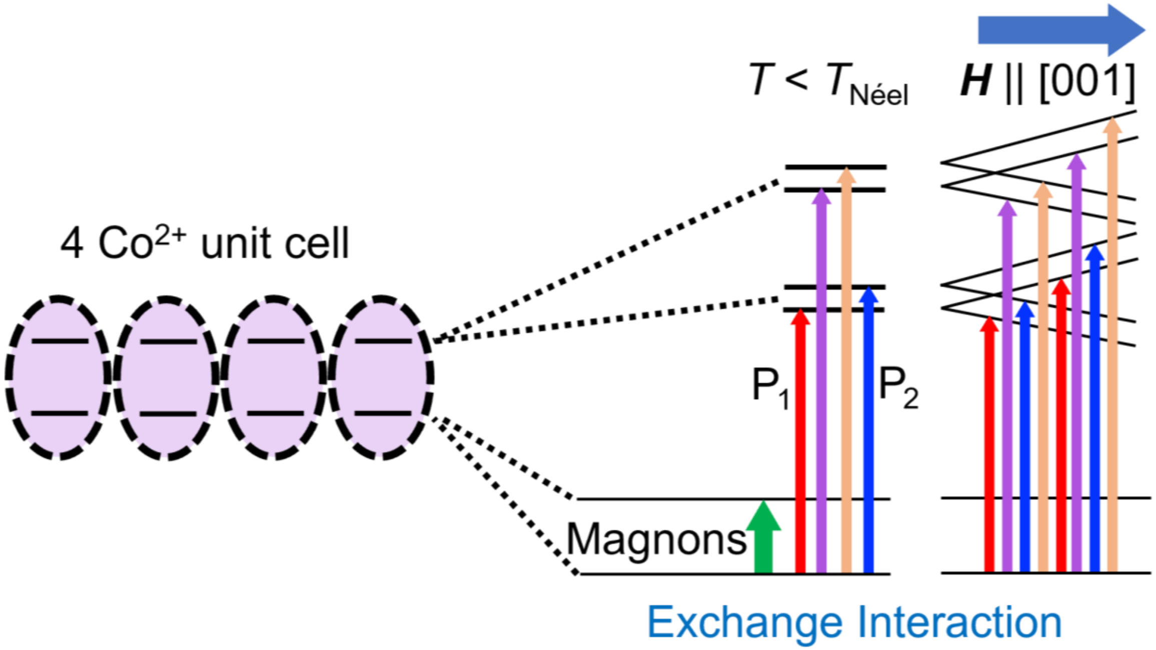


Spin-Orbital Excitations

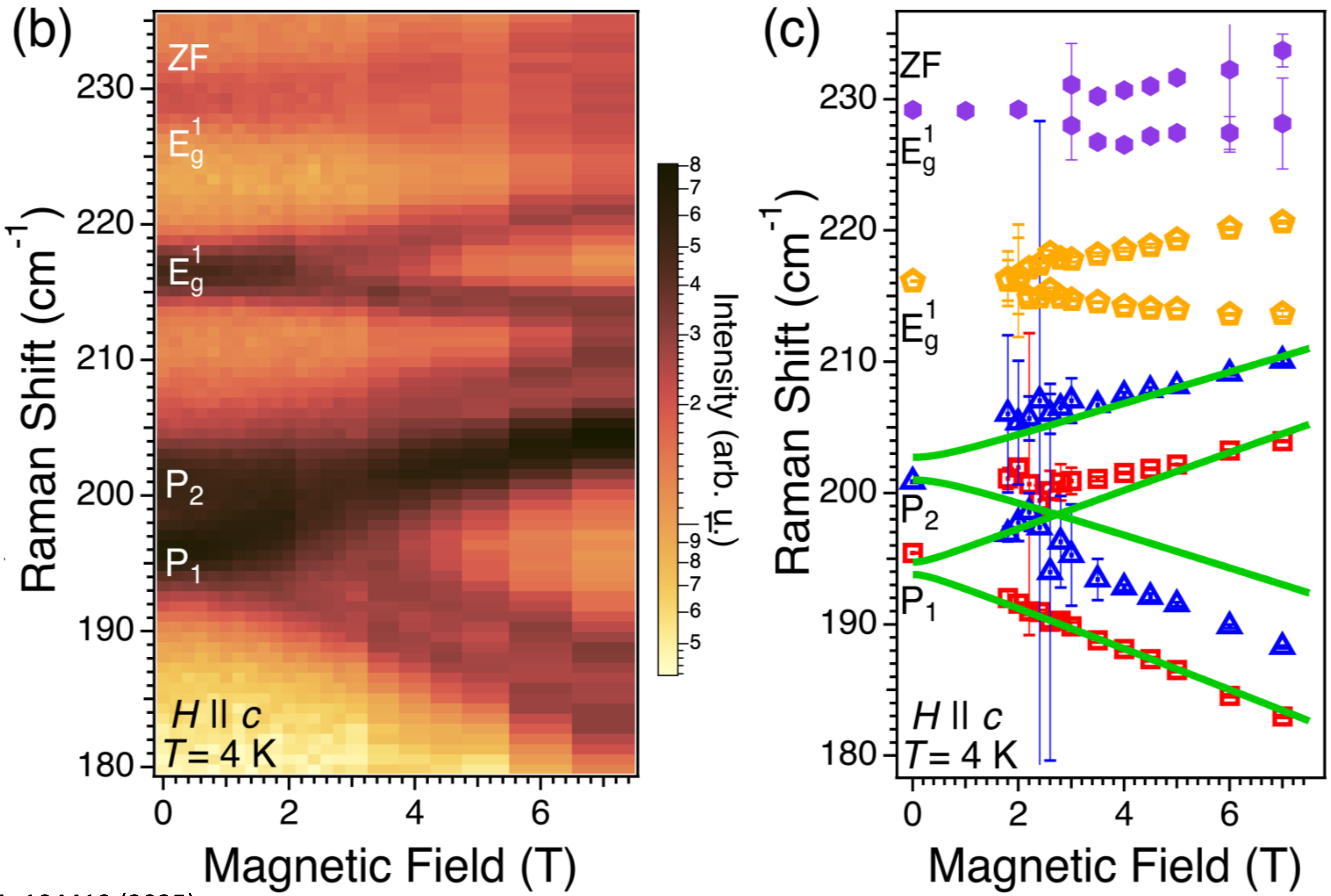




Spin-Orbital Excitations



Spin-Orbital Excitations



PHYS. REV. B **111**, 104419 (2025)

Hamiltonian

Effective $\tilde{S}=1/2$ Model	Flavor Wave Model
$\tilde{H}=\tilde{H}_{\text{bl}}+\tilde{H}_6+\tilde{H}_{\text{Z}}$	$H=H_0+H_{\text{bl}}+H_6+H_{\text{bq}}+H_{\text{Z}}$
	$H_0=\sum_{\boldsymbol{r},i}(3\lambda/2)\boldsymbol{S}_{\boldsymbol{r},i}\cdot\boldsymbol{l}_{\boldsymbol{r},i}+\delta\left(\left(l^z_{\boldsymbol{r},i}\right)^2-2/3\right)$
$\tilde{H}_{\text{bl}}=\frac{1}{2}\sum_{\boldsymbol{r},\delta\boldsymbol{r}}\sum_{i,j}\tilde{\boldsymbol{S}}^{\mathsf{T}}_{\boldsymbol{r},i}\tilde{\boldsymbol{J}}^{ij}_{\delta\boldsymbol{r}}\tilde{\boldsymbol{S}}_{\boldsymbol{r}+\delta\boldsymbol{r},j}$	$H_{\text{bl}}=\frac{1}{2}\sum_{\boldsymbol{r},\delta\boldsymbol{r}}\sum_{i,j}\boldsymbol{S}^{\mathsf{T}}_{\boldsymbol{r},i}\boldsymbol{J}^{ij}_{\delta\boldsymbol{r}}\boldsymbol{S}_{\boldsymbol{r}+\delta\boldsymbol{r},j}$
$\tilde{H}_6=\tilde{\alpha}_6\left(\mathrm{e}^{-\mathrm{i}\tilde{\phi}_6}\sum_{\boldsymbol{r}}\prod_{i=1}^{6}\tilde{S}^+_{\boldsymbol{r}+\boldsymbol{\delta}_i^{\text{ring}}}+\text{h.c.}\right)$	$H_6=\alpha_6\left(\mathrm{e}^{-\mathrm{i}\phi_6}\sum_{\boldsymbol{r}}\prod_{i=1}^{6}S^+_{\boldsymbol{r}+\boldsymbol{\delta}_i^{\text{ring}}}+\text{h.c.}\right)$
	$H_{\text{bq}}=\frac{1}{2}\sum_{<\boldsymbol{r}i,\boldsymbol{r}'j>}q\left((S^+_{\boldsymbol{r}i})^2(S^-_{\boldsymbol{r}'j})^2+q^*(S^-_{\boldsymbol{r}i})^2(S^+_{\boldsymbol{r}'j})^2\right)$
$\tilde{H}_{\text{Z}}=\mu_{\text{B}}\sum_{\boldsymbol{r},i}\tilde{g}_{\parallel}\left(B^x\tilde{S}^x_{\boldsymbol{r},i}+B^y\tilde{S}^y_{\boldsymbol{r},i}\right)$	$H_{\text{Z}}=\mu_{\text{B}}\sum_{\boldsymbol{r},i}\boldsymbol{B}\cdot(2\boldsymbol{S}_{\boldsymbol{r},i}-3\boldsymbol{l}_{\boldsymbol{r},i}/2)$
$\tilde{J}^{xx}_1=\tilde{J}^{yy}_1=-6.36$ meV $\tilde{J}^{zz}_1=1.97$ meV	$J_1=-0.90(2)$ meV
$\tilde{J}^{xx}_2=\tilde{J}^{yy}_2=-0.33$ meV, $\tilde{J}^{zz}_2=0.30$ meV	
$\tilde{J}^{xx}_3=\tilde{J}^{yy}_3=0.78$ meV, $\tilde{J}^{zz}_3=0.15$ meV	
$\tilde{J}^{xx}_4=\tilde{J}^{yy}_4=0.11$ meV, $\tilde{J}^{zz}_4=0.32$ meV	$J_4=0.189(8)$ meV
$\tilde{J}^{xx}_5=\tilde{J}^{yy}_5=-0.39$ meV, $\tilde{J}^{zz}_5=0.20$ meV	
$\tilde{J}^{xx}_6=\tilde{J}^{yy}_6=0.79$ meV, $\tilde{J}^{zz}_6=0.68$ meV	
$\tilde{g}_{\parallel}=2.73(3)$	
	$\delta=52(2)$ meV
	$\lambda=16.4(2)$ meV
$\tilde{\alpha}_6=46(6)$ μeV	$\alpha_6=0.62(7)$ μeV
	$q=-0.15(1)$ meV

SUMMARY

- Introduced how THz and Raman can be used to study quantum magnets.
- Crucial to consider time-reversal to understand symmetry of excitations.
- $CoTiO_3$ can be topological, only if inversion symmetry is broken.
- We developed, through extensive THz and Raman measurements, a model Hamiltonian that explains a wide range of properties.
  - Phys. Rev. B **109**, 184436 (2024)
  - Phys. Rev. B **111**, 104419 (2025)
- A slew of excitations detected below 38 K.
  - Some of them are due to spin-orbit interactions