Spin-Phonon and Spin-Lattice Couplings

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Magnetic Properties From First Principles, TUBITAK, Nov. 2021

Outline

1. Phonons from first principles
2. Symmery & Magnetism
3. Spin-Phonon & Spin-Lattice Couplings

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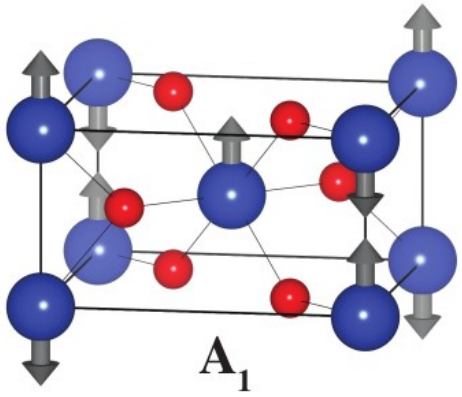
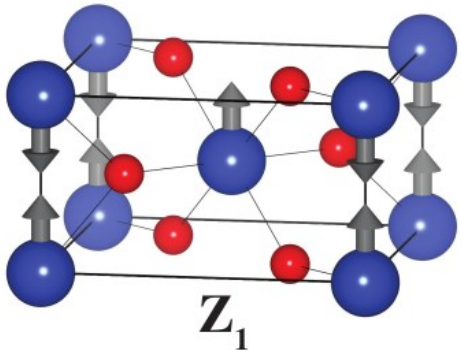
Phonons



Collective oscillations of atoms in solids
(Normal Modes)

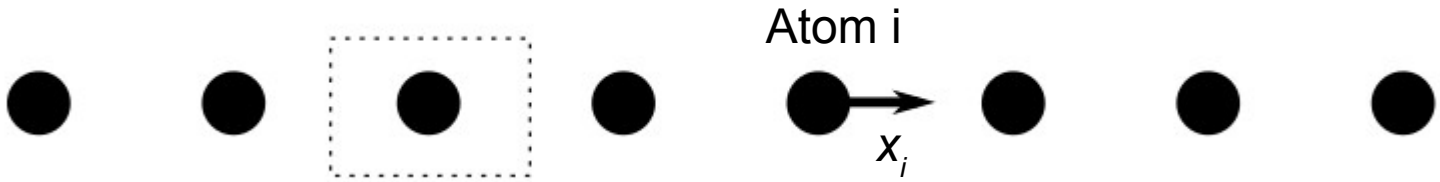
(Partially) responsible of thermal, dielectric, etc. behavior

Frequencies and representations (symmetry)
carry information on crystal structure & bonding



Phonons can be experimentally measured by:
IR absorption
Raman scattering
Neutron scattering

Phonons – Monoatomic chain



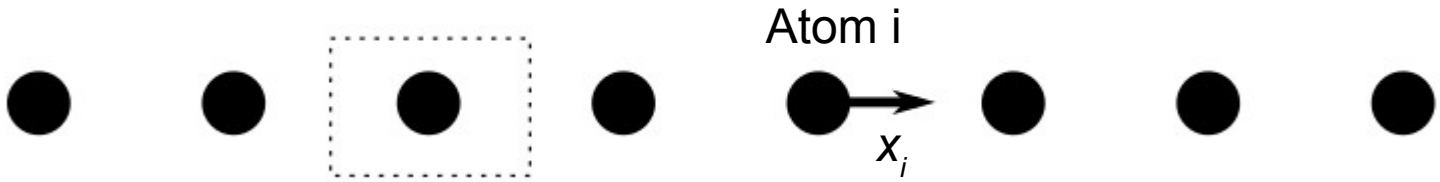
Force on atom i: $F_i = -\frac{\partial E}{\partial x_i}$ $F_i = -\sum_j C_{ij} x_j$

Force constant: $C_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$

Phonon with wavevector k: $x_i = x_o \exp\left(i[ki - \omega t]\right)$ $k = \frac{2\pi}{\lambda}$

Plugging into Newton's 2nd...

Phonons – Monoatomic chain



$$x_i = x_o \exp\left(i[ki - \omega t]\right) \qquad F_i = -\sum_j C_{ij} x_j \qquad C_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$

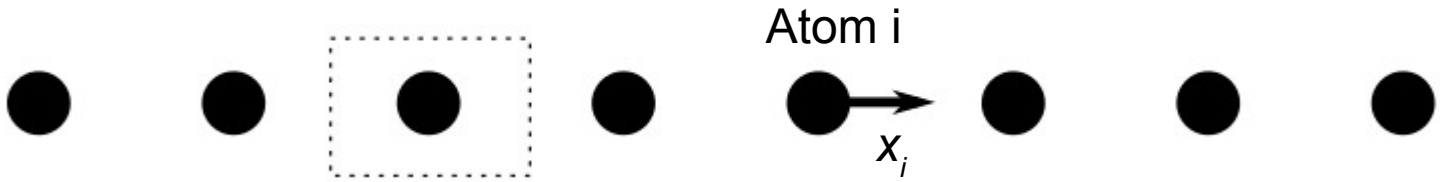
$$F = ma$$

$$-\sum_j C_{ij} x_j = m\ddot{x}_i$$

$$-\sum_j C_{ij} \left(x_o \exp\left(i[kj - \omega t]\right)\right) = -m\omega^2 \left(x_o \exp\left(i[ki - \omega t]\right)\right)$$

$$m\omega^2 = \sum_j C_{0j} \exp\left(i[kj]\right)$$

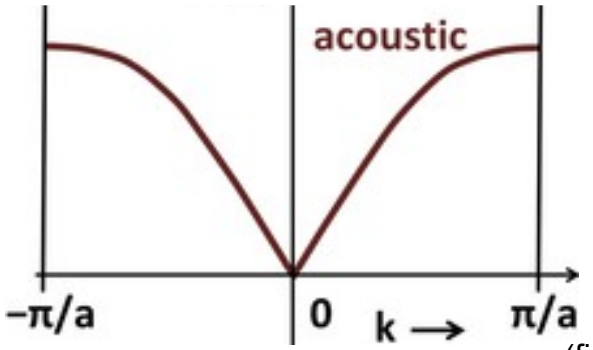
Phonons – Monoatomic chain



$$m\omega^2 = \sum_j C_{0j} \exp\left(i[kj]\right)$$

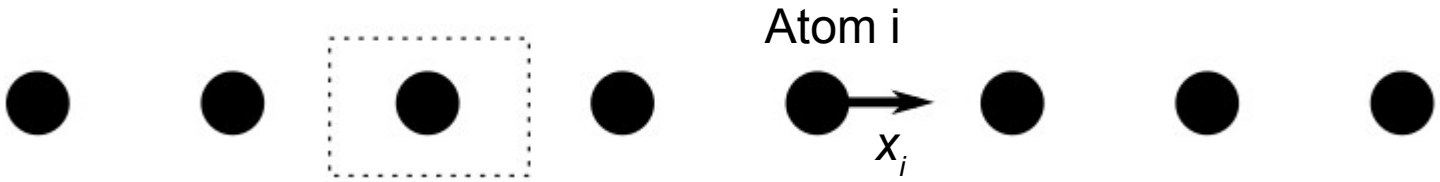
Simplest case: C_{01}=-C and C_{00}=2C

$$\omega = \sqrt{\frac{2C}{m}\left(1 - \cos ka\right)}$$



(figure: wikipedia)

Phonons – Monoatomic chain



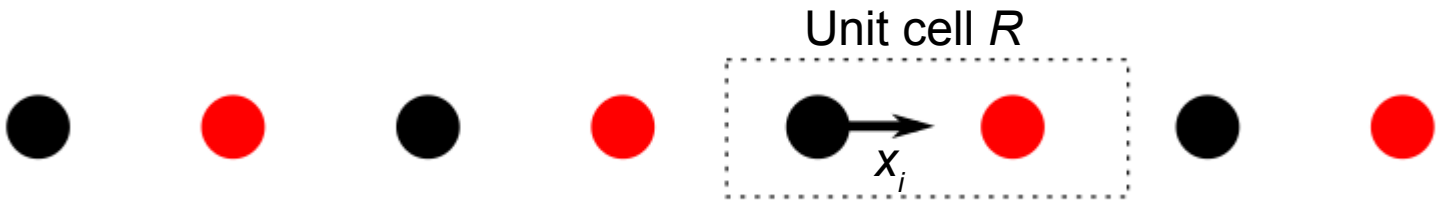
In typical DFT calculations, we work with small unit cells and periodic boundary conditions.

This makes it hard to calculate the *real space* force constants directly.

Instead, it makes more sense to work in the reciprocal space, with phonons of well defined wavelengths.

One can then take the *reciprocal space* force constants' Fourier transform to obtain real space forces, if need be.

Phonons – Diatomic chain

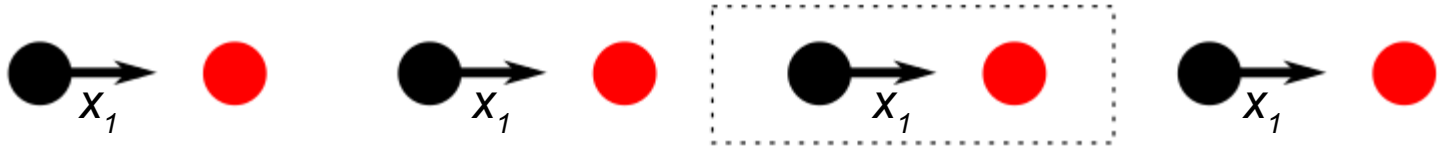


Label atoms with two numbers:

R points to the unit cell

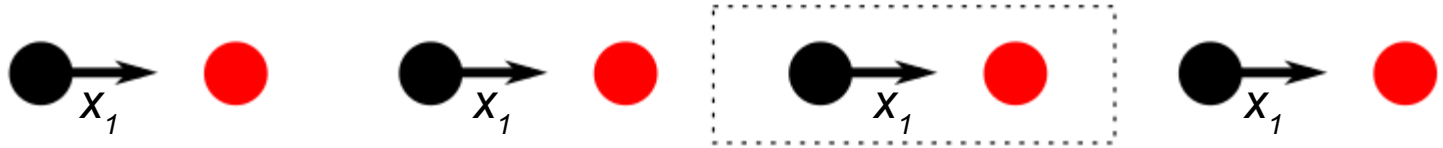
i points to the atom in the cell. (Black or Red)

Consider a 'gamma point' displacement: k=0



(No need to specify *R* any more)

Phonons – Diatomic chain



Write Newton's 2nd for black (1) and red (2) atoms for k=0 displacements:

$$F_i = m_i \ddot{x}_i \qquad F_i = -\sum_j C_{ij} x_j \qquad C_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$

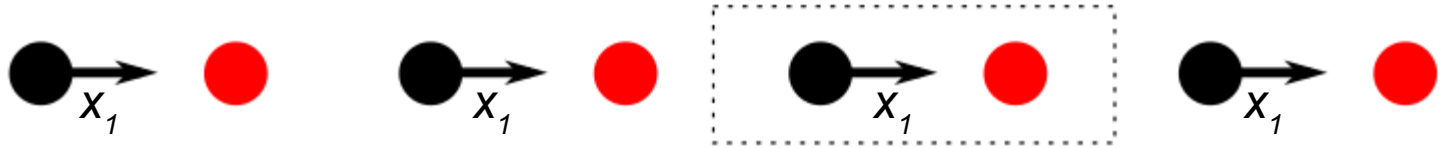
(*C* is now a 2x2 matrix.)

$$x_i = x_{0i} \exp\left(-i\omega t\right)$$

$$m_i \omega^2 x_{0i} = \sum_j C_{ij} x_{0j}$$

Let: $y_i = \sqrt{m_i} x_{0i} \longrightarrow \omega^2 y_i = \sum_j \frac{C_{ij}}{\sqrt{m_i m_j}} y_j$

Phonons – Diatomic chain



$$\omega^2 y_i = \sum_j \frac{C_{ij}}{\sqrt{m_i m_j}} y_j$$

This is an eigenvalue equation for the dynamical matrix: $D_{ij} = \frac{C_{ij}}{\sqrt{m_i m_j}}$

Eigenvalues of the dynamical matrix give the square of the phonon frequencies.

Dynamical Matrix & Phonons from DFT

How to calculate $D_{ij} = \frac{C_{ij}}{\sqrt{m_i m_j}}$ from DFT?

Hellmann-Feynman theorem gives forces on all atoms using the ground state wavefunction.

One can displace each atom in the unit cell one by one, along x, y, z separately, and get all force constants.

Density Functional Perturbation Theory (DFPT) can also give all force constants + more.

For phonons that don't have *k=0*, one needs either a supercell, or DFPT at finite k.

Simple codes like Phonopy help with building supercells, but care is needed.

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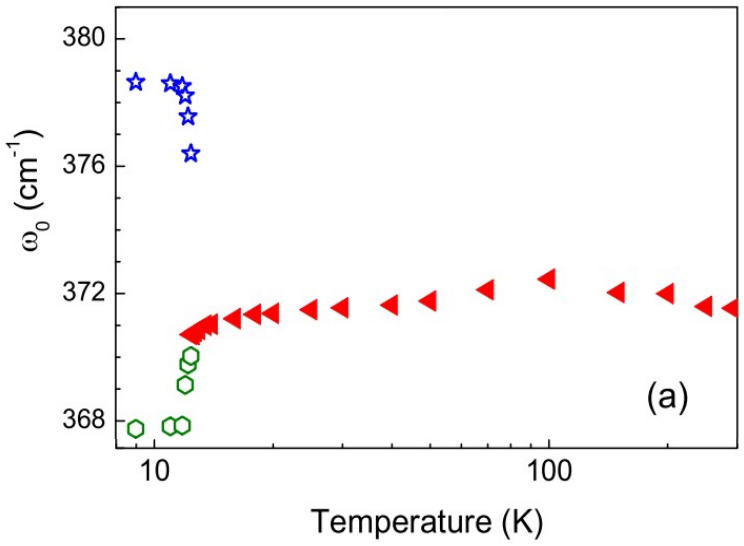
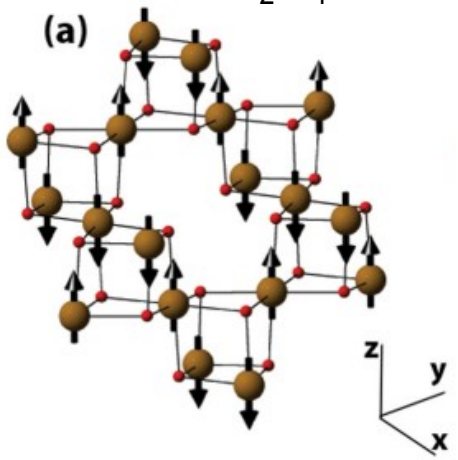
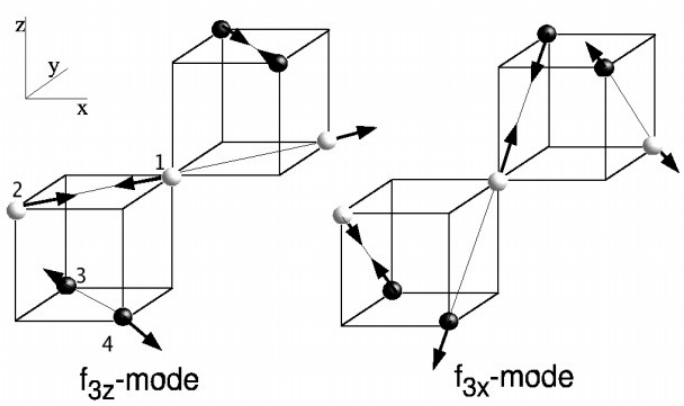
Phonons in magnetic materials

Does magnetism affect phonon frequencies?

Magnetically induced IR active phonon splitting in Spinel $ZnCr_2O_4$





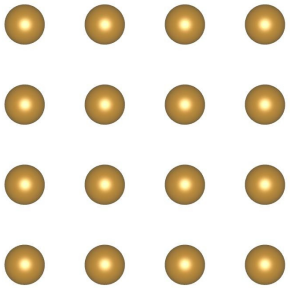


[Sushkov et al. (2005); Fennie & Rabe (2006)]

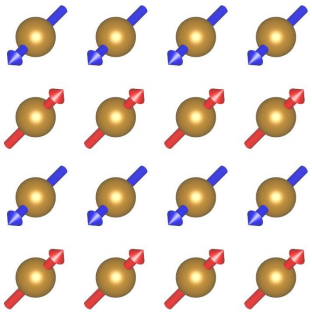
Spin-phonon coupling

Magnetic order can break crystal symmetries, and split phonon frequencies

Paramagnet
C_4



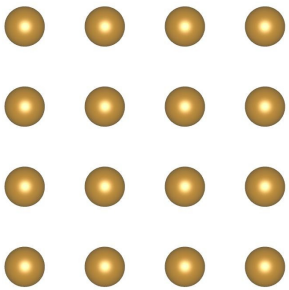
Antiferromagnet
C_2

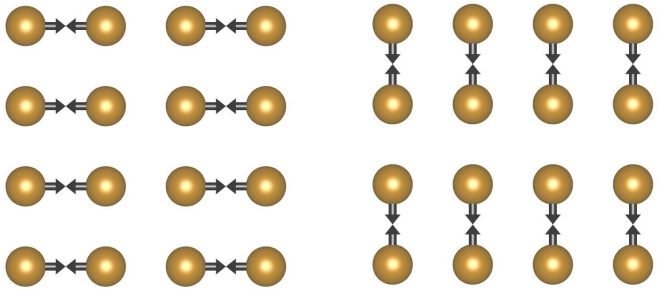


Spin-phonon coupling

Magnetic order can break crystal symmetries, and split phonon frequencies

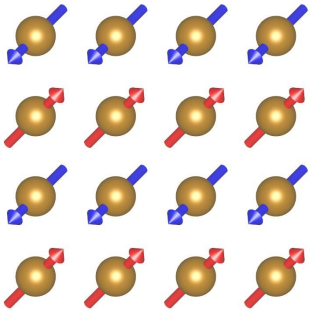
Paramagnet
C_4





$\omega_x = \omega_y$

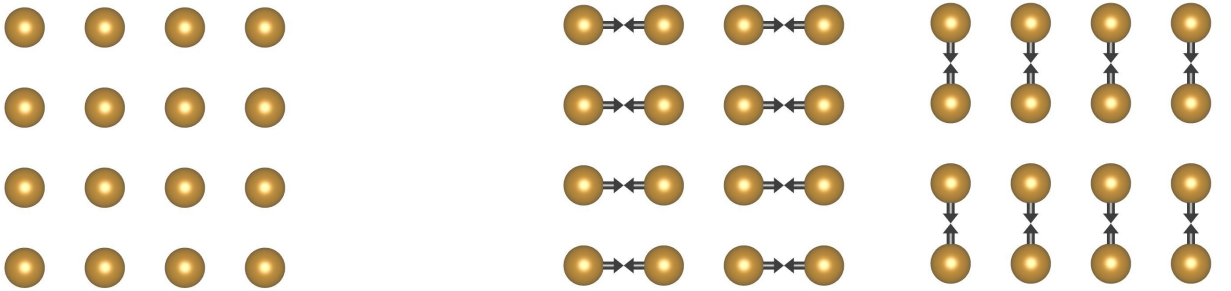
Antiferromagnet
C_2



Spin-phonon coupling

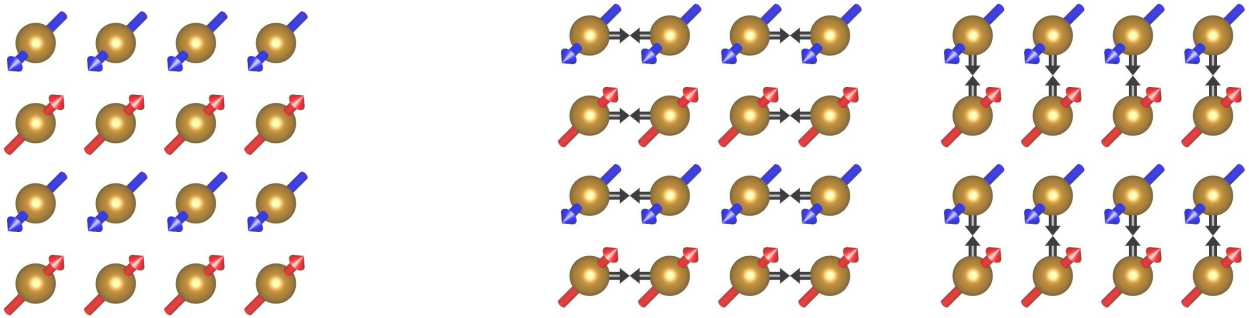
Magnetic order can break crystal symmetries, and split phonon frequencies

Paramagnet
C_4



$\omega_x=\omega_y$

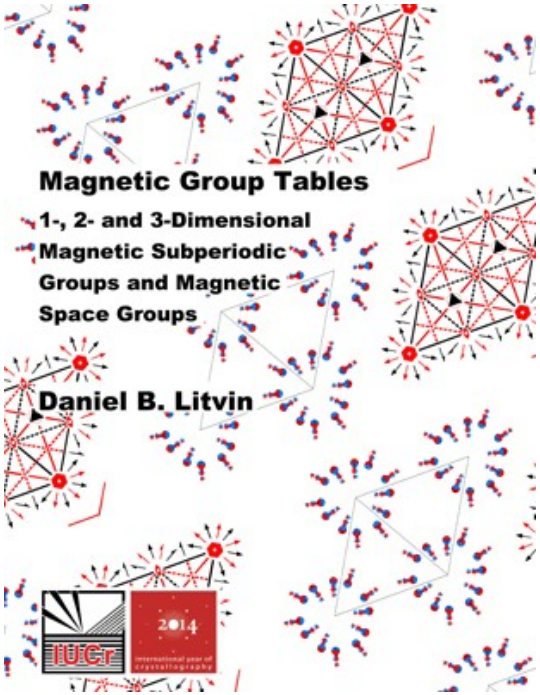
Antiferromagnet
C_2



$\omega_x\neq\omega_y$

Magnetic space groups

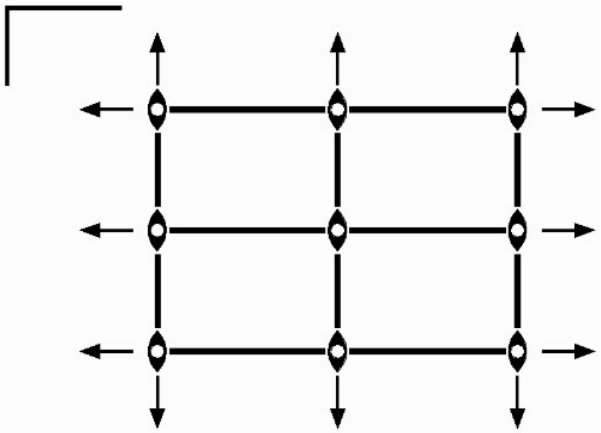
Need to add *time reversal* as a symmetry operation to space groups to understand the symmetries of magnetic materials



1651 magnetic space groups
(vs 230 non-magnetic space groups)

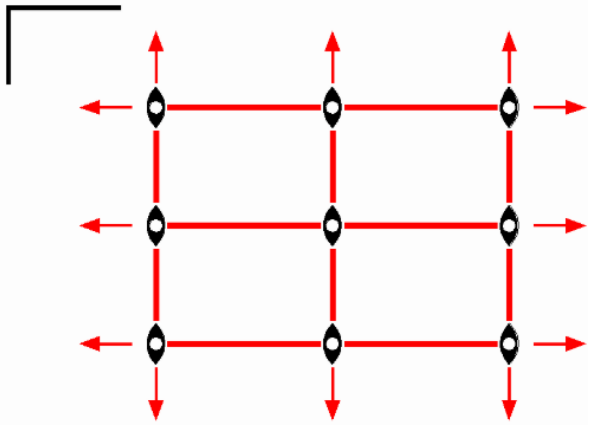
Pmmm

47.1.347



Pm'm'm

47.4.350



Ferromagnetic with
out-of-plane magnetization

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1. Phonons from first principles
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Dynamical matrix of magnetic materials

The same definition for force constants and dynamical matrices should also work for a magnetic material:

force constants matrix

$$C_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$

dynamical matrix

$$D_{ij} = \frac{C_{ij}}{\sqrt{m_i m_j}}$$

But the energy should also have a magnetic part, in addition to the paramagnetic part:

$$E = E_{PM} + J \sum_{m,n} S_m \cdot S_n$$

energy of the paramagnetic phase

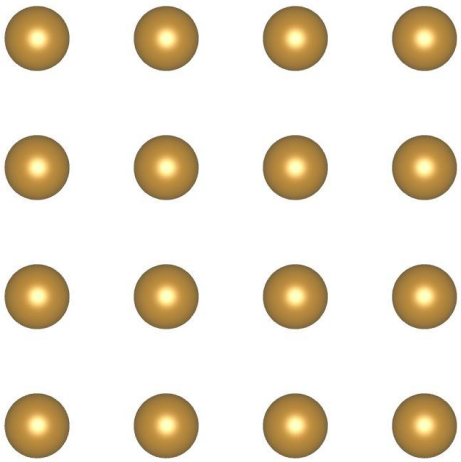
magnetic energy

Paramagnetism in DFT

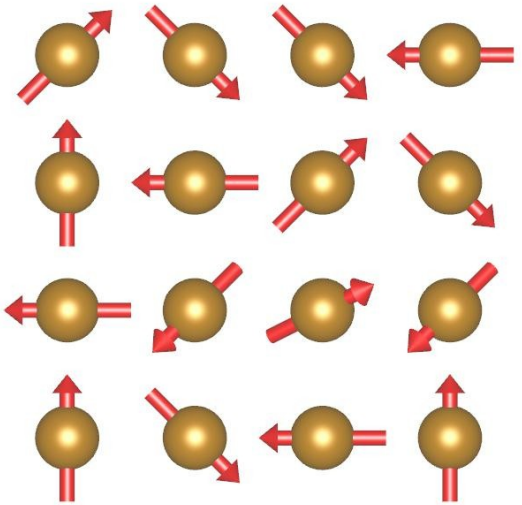
$$E = E_{PM} + J \sum_{m,n} S_m \cdot S_n$$

energy of the paramagnetic phase

magnetic energy



Non-spin polarized DFT
No local moments
Diamagnetic



Paramagnet with local moments
(Curie-Weiss behavior)
Not possible in DFT
(Need dynamical fluctuations)

Dynamical matrix of magnetic materials

$$E = E_{PM} + J \sum_{m,n} S_m \cdot S_n \qquad C_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$

$$C_{ij} = \frac{\partial^2 E_{PM}}{\partial x_i \partial x_j} + \frac{\partial^2 J}{\partial x_i \partial x_j} \sum_{m,n} S_m \cdot S_n$$

(Assumption: Magnetic order does not change when atoms are displaced.)

Mean Field Approximation: $S_m \cdot S_n \rightarrow \langle S_m \cdot S_n \rangle$

$$J \sum_{m,n} S_m \cdot S_n \rightarrow Z \langle S_m \cdot S_n \rangle$$

Z: Number of (nearest) neighbor bonds

$$C_{ij} = C_{ij}^{PM} + \Delta C_{ij} \langle S_m \cdot S_n \rangle$$

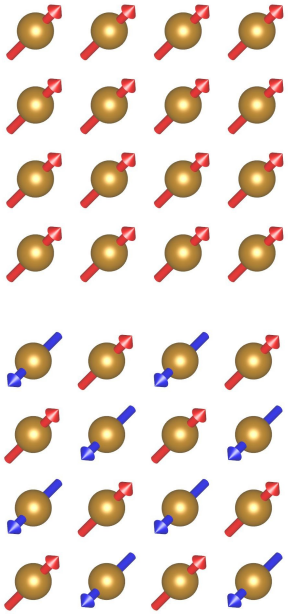
Spin-spin correlations

Dynamical matrix of magnetic materials

$$C_{ij} = C_{ij}^{PM} + \Delta C_{ij} \langle S_m \cdot S_n \rangle$$

Paramagnetic force constants matrix

One can get the phonon frequencies of the paramagnetic phase from DFT using this approach!



Ferromagnetic

$$C_{ij}^{FM} = C_{ij}^{PM} + \Delta C_{ij}$$

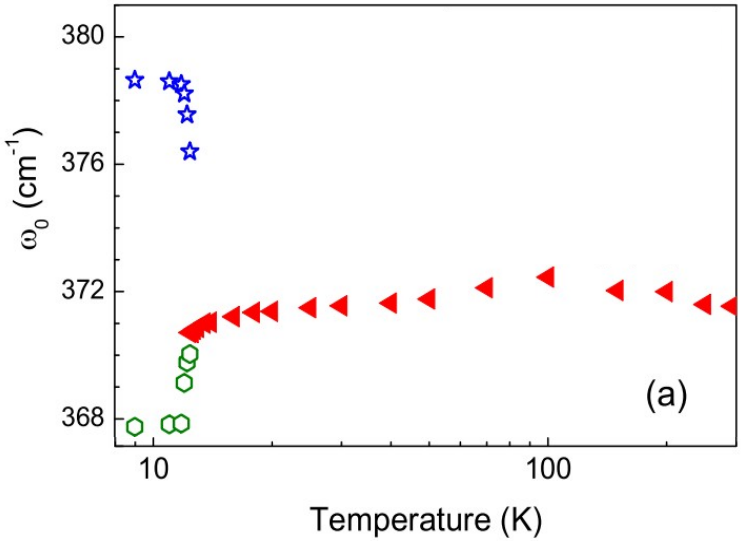
Antiferromagnetic

$$C_{ij}^{AFM} = C_{ij}^{PM} - \Delta C_{ij}$$

Average of the FM and AFM force constants matrices gives the PM one!

Example: Spinel $ZnCr_2O_4$

Magnetically induced phonon splitting in Spinel $ZnCr_2O_4$



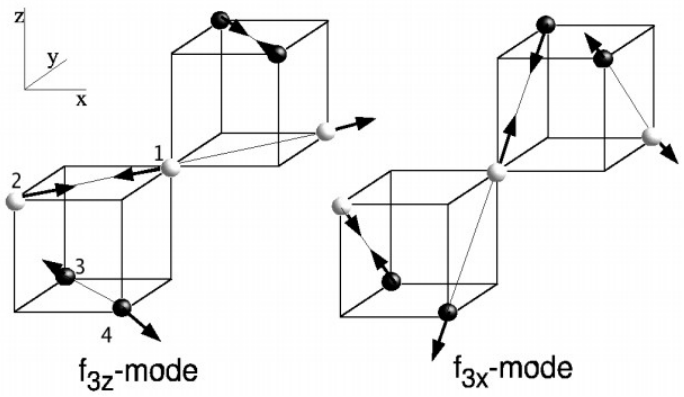


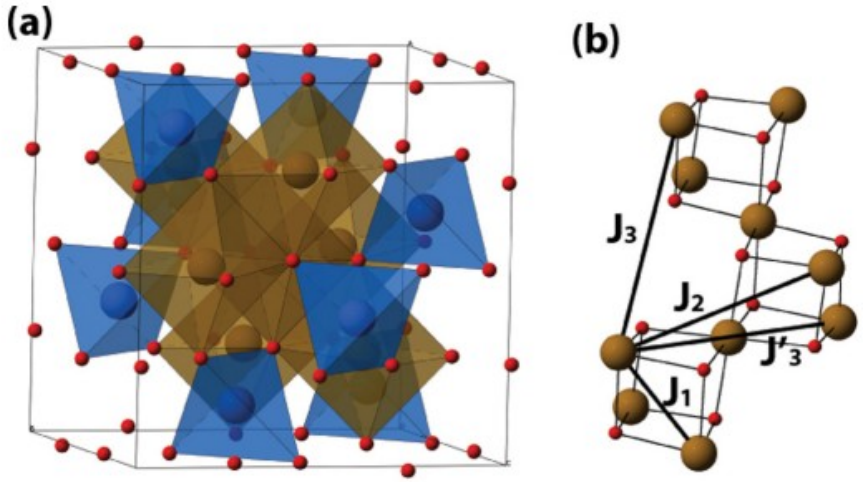
TABLE I. Infrared-active T_{1u} phonons frequencies in cm^{-1}.

	Experiment Ref. [6]		Present Theory						
			Model					LSDA + U	
	13 K	9 K	PM	AFM		$\mathcal{J}''_\perp$	$\mathcal{J}''_\parallel$	AFM	
		$\hat{x}$ $\hat{z}$		$\hat{x}$	$\hat{z}$			$\hat{x}$	$\hat{z}$
(1)	186	186 + δ	189	186	191	−240	0	174	198
(2)	371	368 379	366	361	372	−999	22	342	392
(3)	501	501	514	514	517	−254	225	510	526
(4)	619	619	621	621	623	−66	257	620	630

$$\tilde{C}_{n,n'}(\alpha) = C_{n,n'}(\alpha) - J''_{\perp n,n'} \sum_{\hat{r}_\perp} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle - J''_{\parallel n,n'} \sum_{\hat{r}_\parallel} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$$

[Sushkov et al. (2005); Fennie & Rabe (2006)]

Example: Other ACr_2O_4 Spinels



A	J_1	J_2	J_3	J_3'
Mg	3.8	−0.1	0.1	0.2
Zn	3.8	−0.1	0.1	0.2
Cd	0.3	−0.1	0.1	0.2
Hg	−0.6	−0.0	0.2	0.1

It was claimed that J_2 and J_3 can affect the phonon splitting

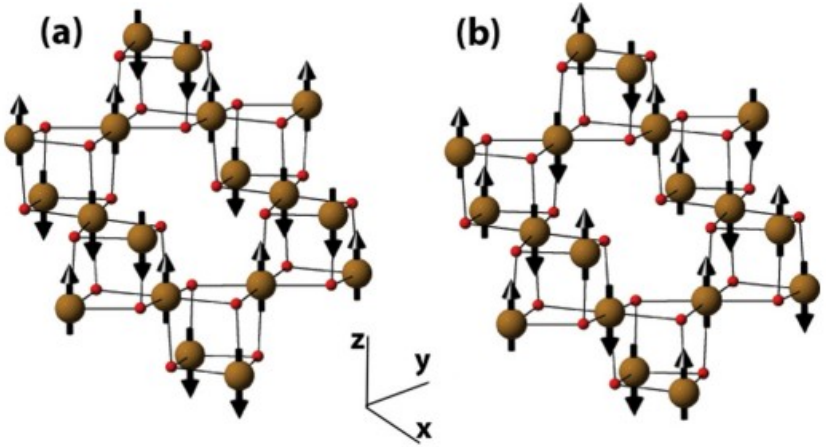
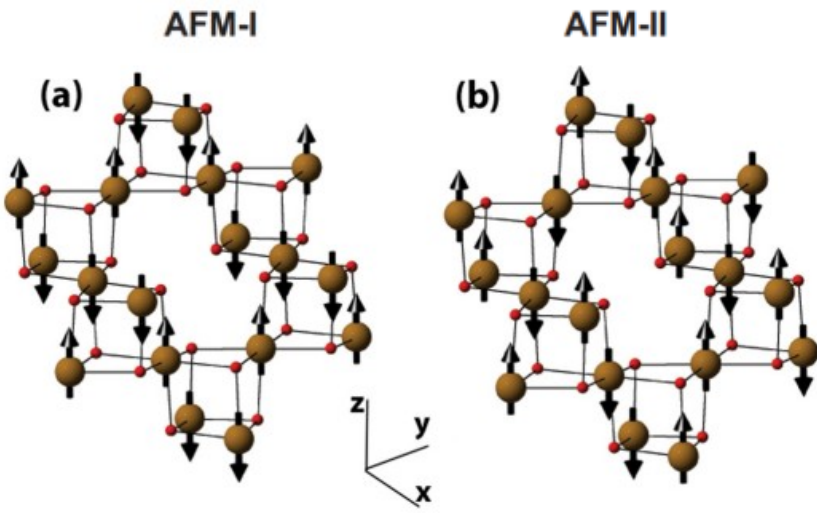
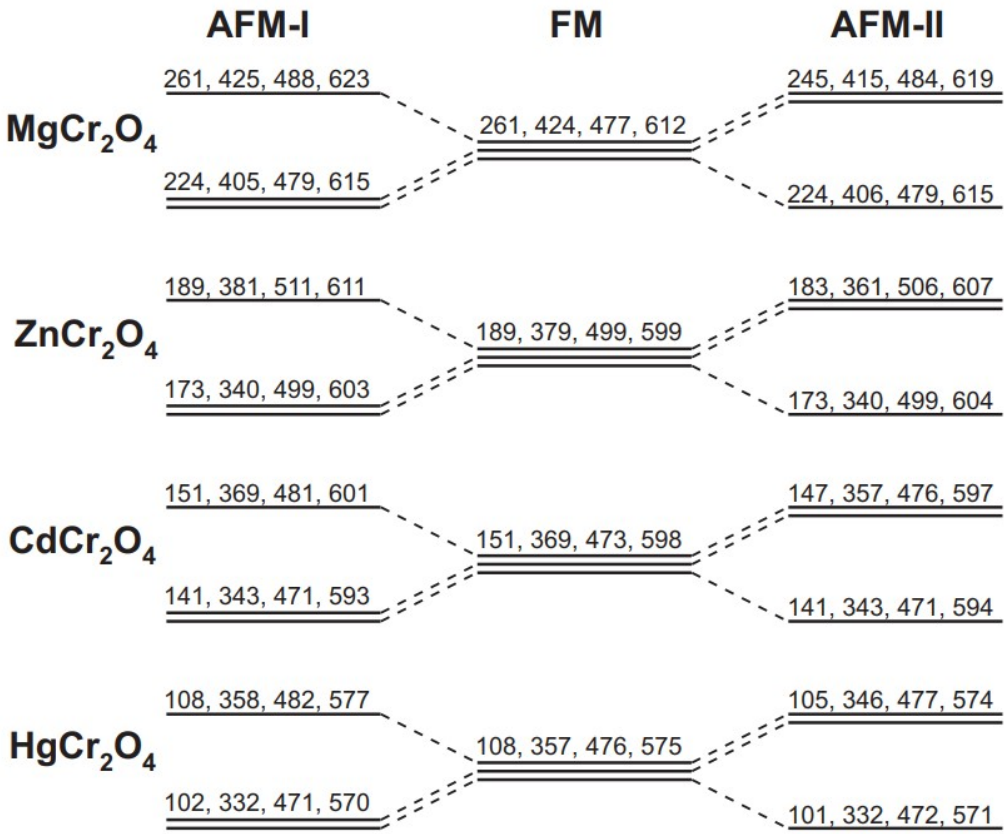


FIG. 3. Two collinear magnetic orderings relevant for ACr_2O_4 spinels. (a) AFM-I order that is similar to the true magnetic ground state in $ZnCr_2O_4$ and $MgCr_2O_4$. (b) AFM-II order that approximates the spin order in $CdCr_2O_4$. Brown and red spheres denote Cr and O atoms, respectively.

[Wysocki, Birol (2016)]

Example: Other ACr_2O_4 Spinels



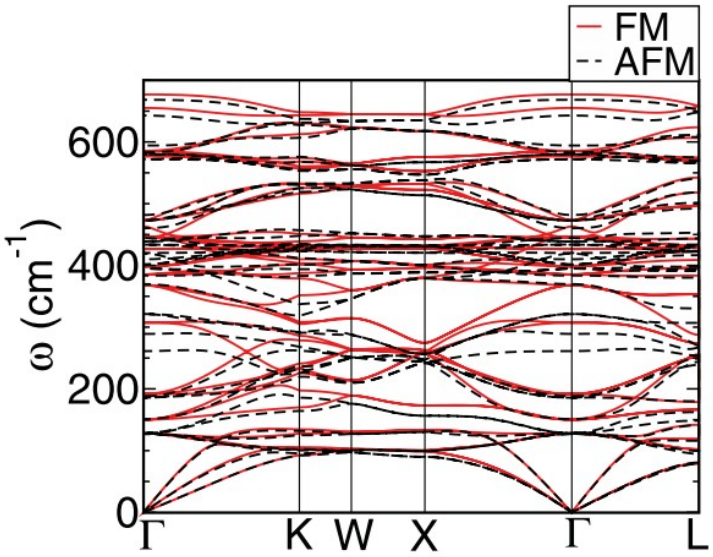


[Wysocki, Birol (2016)]

Example: Phonon band structure of $CdCr_2O_4$

[Kumar, Fennie, Rabe (2012)]

Predicting phonons with different wavevectors is also possible



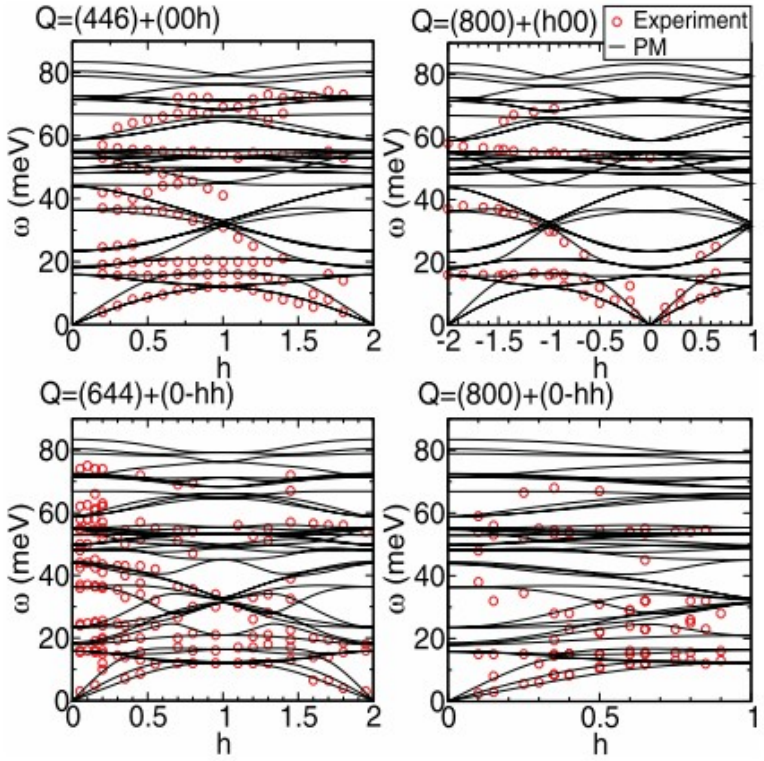
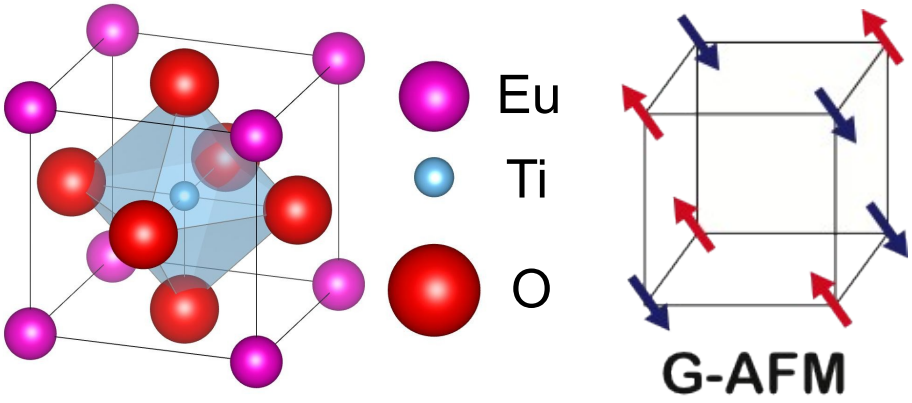


FIG. 5. (Color online) A comparison of the calculated phonon dispersion relation for the cubic PM with the experimental phonon dispersion obtained at 10 K (Ref. 18).

Example: Magnetodielectric effect in $EuTiO_3$

Paraelectric antiferromagnet (T_N = 5.5 K)

Half-filled f-shell of Eu^{2+} (J = 7/2)

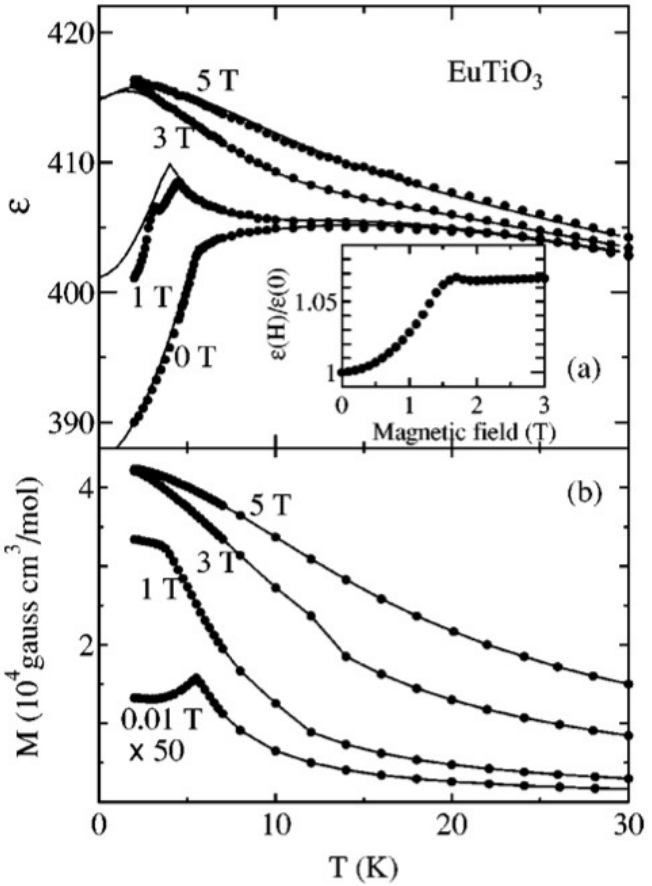


Strong coupling between dielectric and magnetic properties.

[Katsufuji, Takagi, PRB 2001]

$$\tilde{\omega}^2 \approx \omega_{\mathrm{PM}}^2 - \lambda \langle \mathbf{S} \cdot \mathbf{S} \rangle$$

Ionic contribution to permittivity: $\epsilon \propto \sum_m \frac{S_m}{\omega_m^2}$

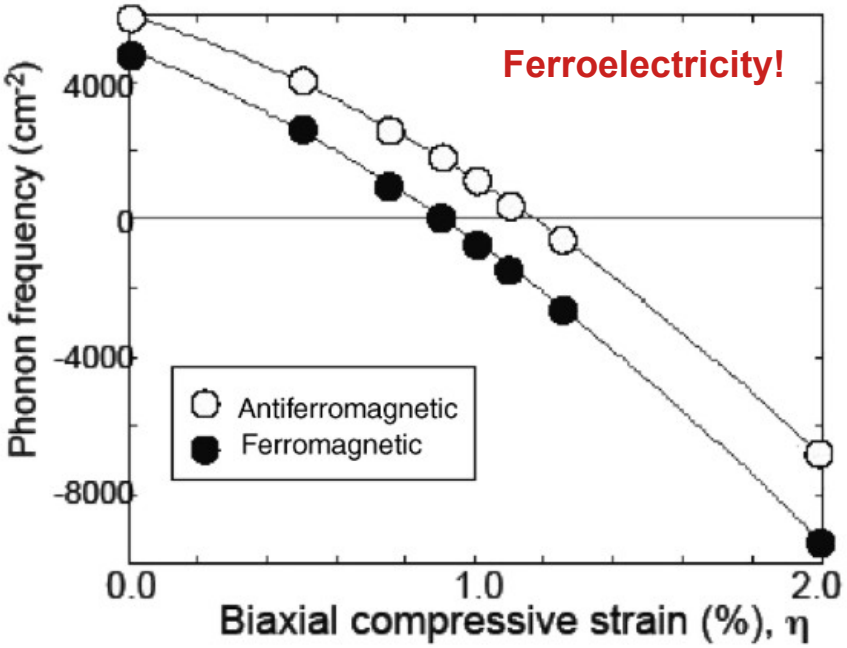


[Katsufuji&Takagi, (2001)]

Example: $EuTiO_3$ under strain

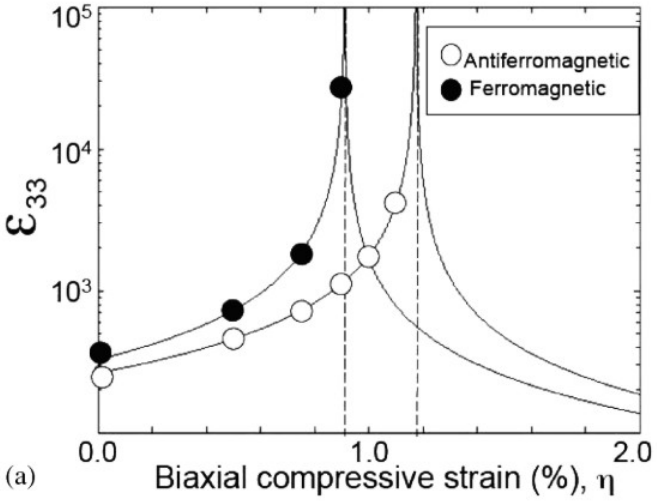
[Fennie & Rabe (2006)]

Idea: grow $EuTiO_3$ thin films on different substrates to change the lattice parameter



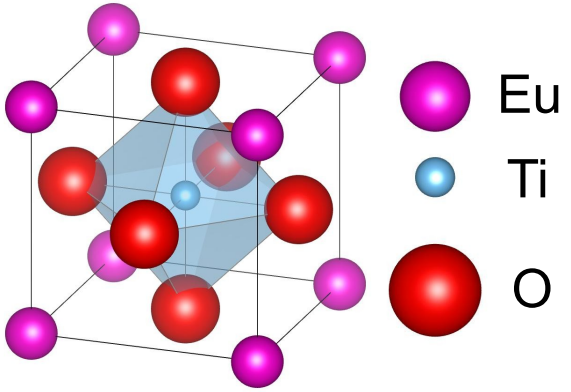
$$\epsilon \propto \sum_m \frac{S_m}{\omega_m^2}$$

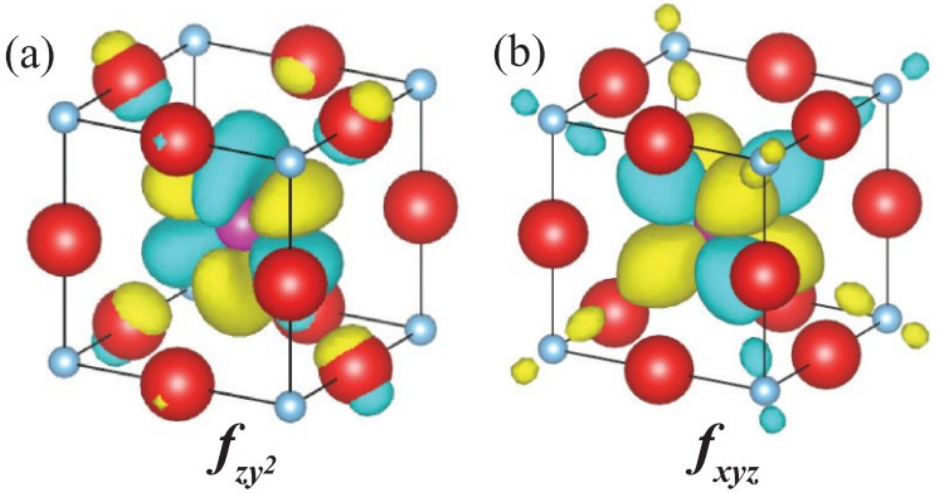
Magnetic field can change the dielectric constant – by a lot (in principle)!

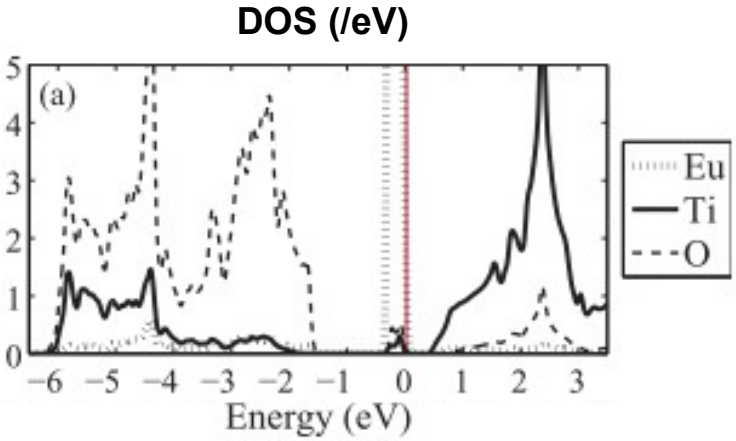


Example: $EuTiO_3$

What's special about $EuTiO_3$?



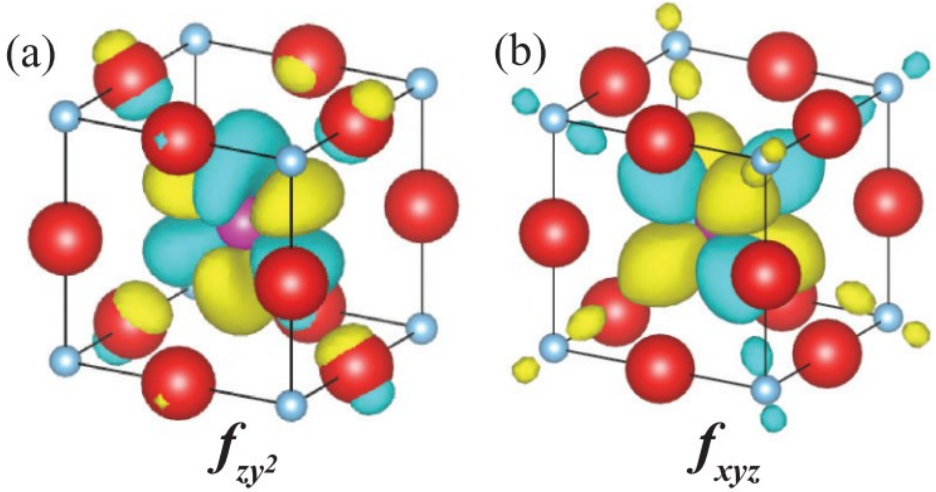




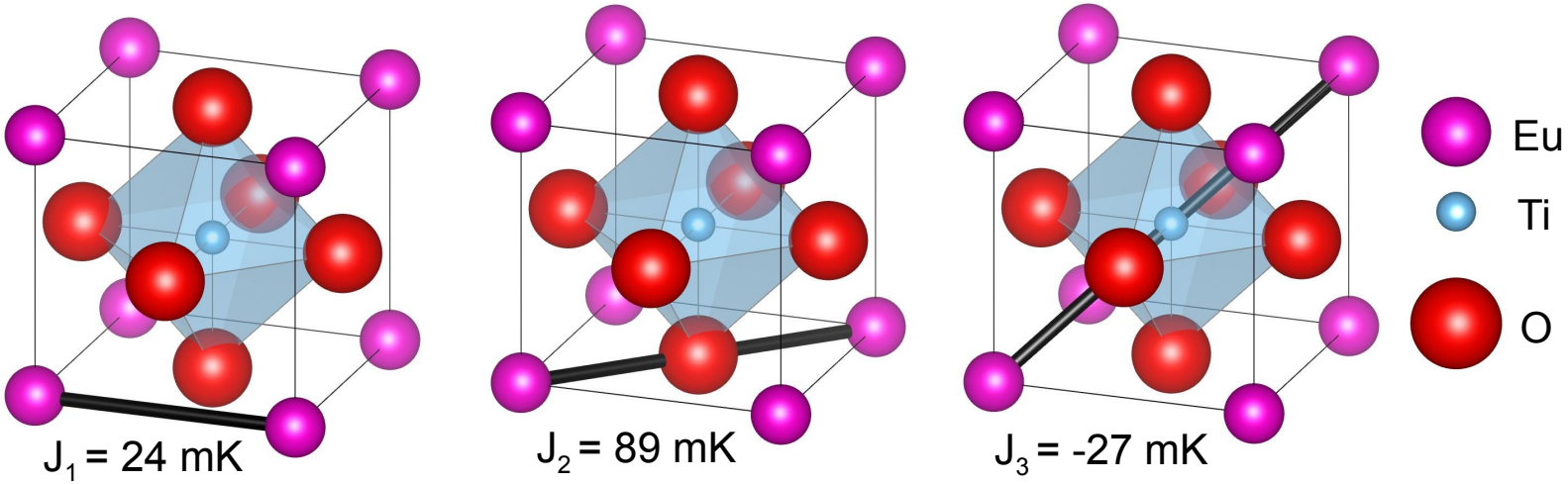
Wannier functions: The f orbitals on Eu hybridize with O and Ti orbitals

[Birol & Fennie (2013)]

Example: $EuTiO_3$



Wannier functions: The f orbitals on Eu hybridize with O and Ti orbitals

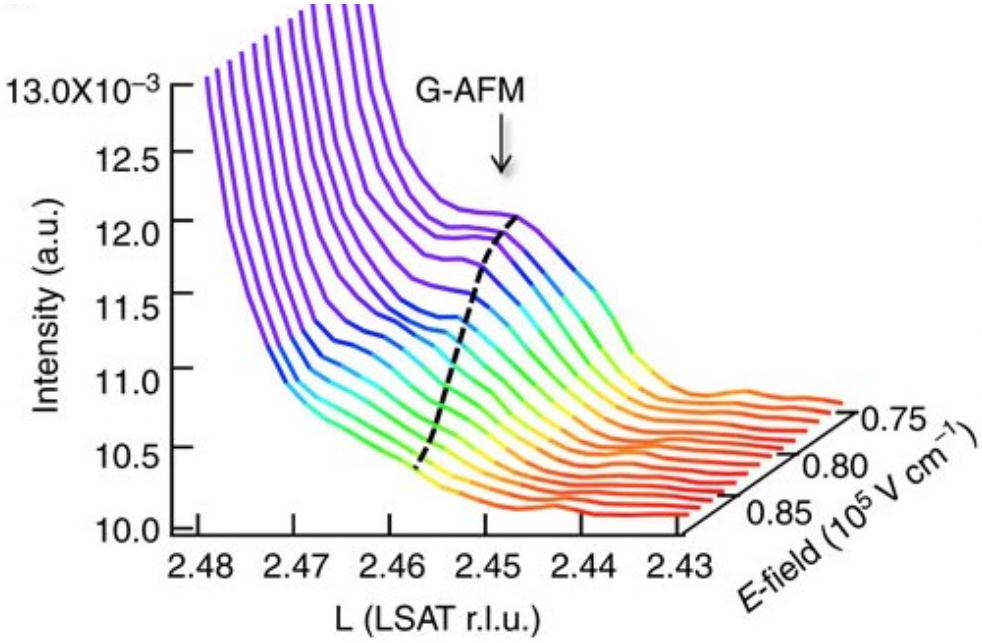


[Birol & Fennie (2013)]

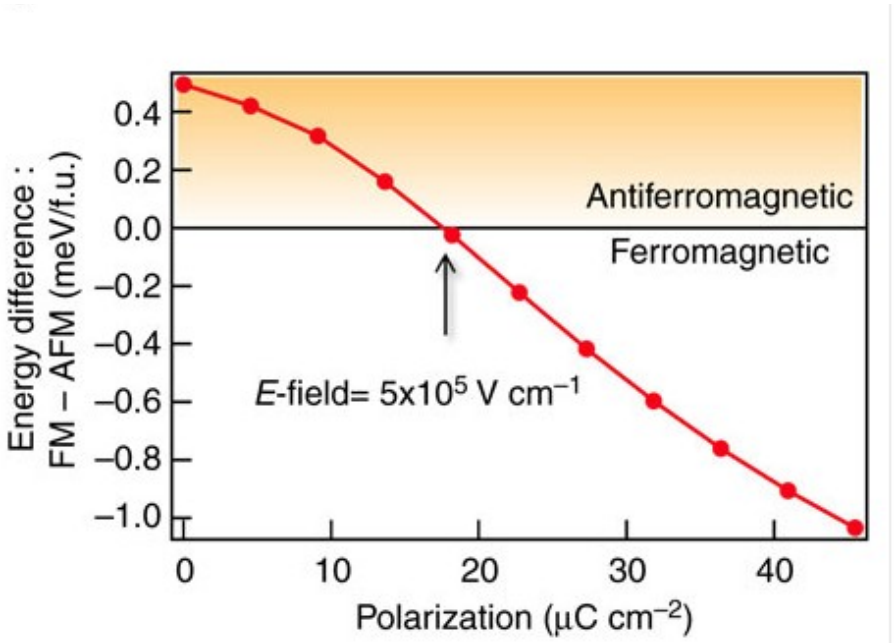
Example: Spin–Lattice Coupling From XRMS

(X-ray Resonant Magnetic Scattering)

Apply E-field, measure the AFM reflection peak



G-AFM scattered $(1/2\ 1/2\ 5/2)_{ETO}$ reflection as a function of electric field

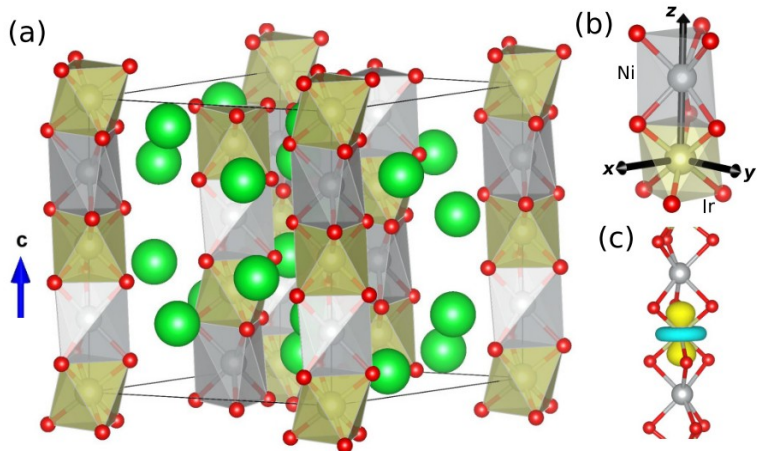


Energy difference between AFM and FM states vs polarization from first principles

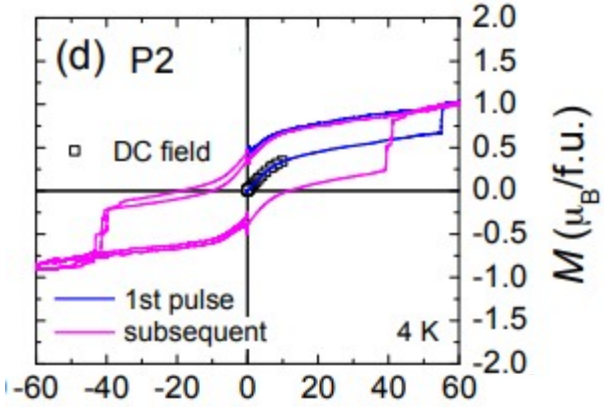
[Ryan, Kim, Birol et al., Nat. Comm. 4, 1334 (2013)]

Example: Sr_3NiIrO_6

Strong spin-orbit coupling



Record breaking coercive field



[Zapf et al. (2014)]

J_{eff}=1/2 states in octahedral environment:

$$|J_{1/2},\uparrow\rangle = \frac{1}{\sqrt{3}}\left(-|xy,\downarrow\rangle - i|xz,\uparrow\rangle + |yz,\uparrow\rangle\right)$$

$$|J_{1/2},\downarrow\rangle = \frac{1}{\sqrt{3}}\left(+|xy,\uparrow\rangle + i|xz,\downarrow\rangle + |yz,\downarrow\rangle\right)$$

Spin-orbital entanglement

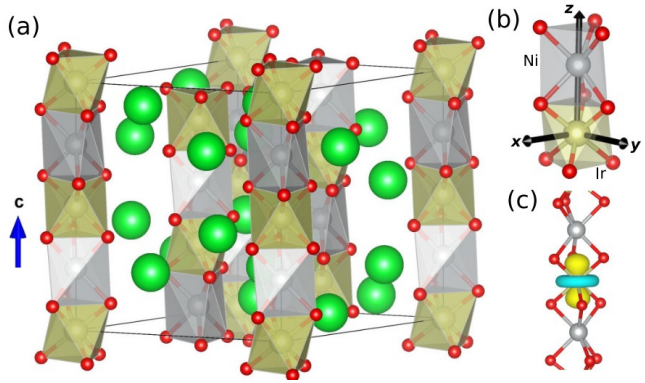
Ir has one hole on a J_{eff}=1/2 → effective spin ½

Ni has two electrons in e_g with minimal SOC (quenched orbital angular momentum)

[Birol, Haule, Vanderbilt (2018)]

Example: Sr_3NiIrO_6

Strong spin-orbit coupling



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$$|J_{1/2},\downarrow\rangle = \frac{1}{\sqrt{3}}\left(+|xy,\uparrow\rangle + i|xz,\downarrow\rangle + |yz,\downarrow\rangle\right)$$

J_{eff}=1/2 states of Ir in -3 point group:

$$|J_{1/2},\uparrow\rangle = \frac{1}{\sqrt{|\gamma|^2+2}}(i\gamma|A,\downarrow\rangle + \sqrt{2}|E^+,\uparrow\rangle)$$

$$|J_{1/2},\downarrow\rangle = \frac{1}{\sqrt{|\gamma|^2+2}}(i\gamma|A,\uparrow\rangle + \sqrt{2}|E^-,\downarrow\rangle)$$

$$|A\rangle = |3z^2 - r^2\rangle$$

$$|E^+\rangle = -\frac{i}{\sqrt{3}}|xy\rangle + \frac{i}{\sqrt{6}}|xz\rangle + \frac{1}{\sqrt{6}}|yz\rangle - \frac{1}{\sqrt{3}}|x^2-y^2\rangle$$

$$|E^-\rangle = +\frac{i}{\sqrt{3}}|xy\rangle - \frac{i}{\sqrt{6}}|xz\rangle + \frac{1}{\sqrt{6}}|yz\rangle - \frac{1}{\sqrt{3}}|x^2-y^2\rangle$$

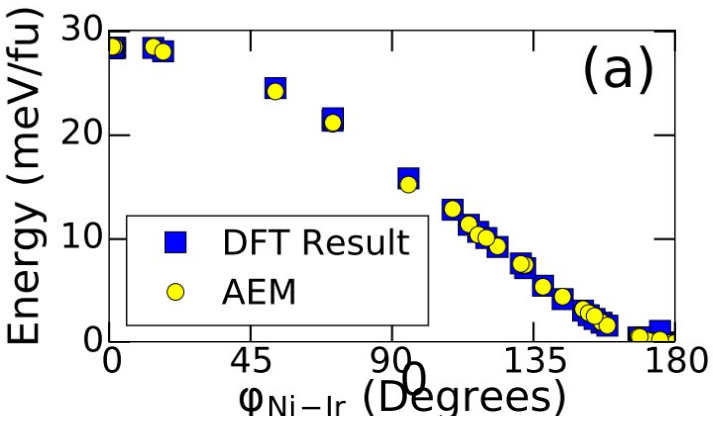
Slightly more complicated, but an effective spin-½ model still works for Ir

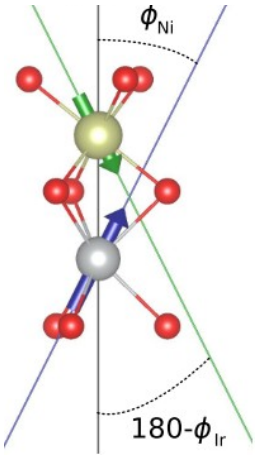
[Birol, Haule, Vanderbilt (2018)]

Example: Sr_3NiIrO_6 – Anisotropic exchange

(Radically) anisotropic exchange model:

$$E = J_{\parallel} M_{i,z} M_{i+1,z} + J_{\perp}(M_{i,x} M_{i+1,x} + M_{i,y} M_{i+1,y})$$





$$J_{\parallel} = 19.0 \text{ meV}/\mu_B^2$$

$$J_{\perp} = -8.4 \text{ meV}/\mu_B^2$$

[Birol, Haule, Vanderbilt (2018)]

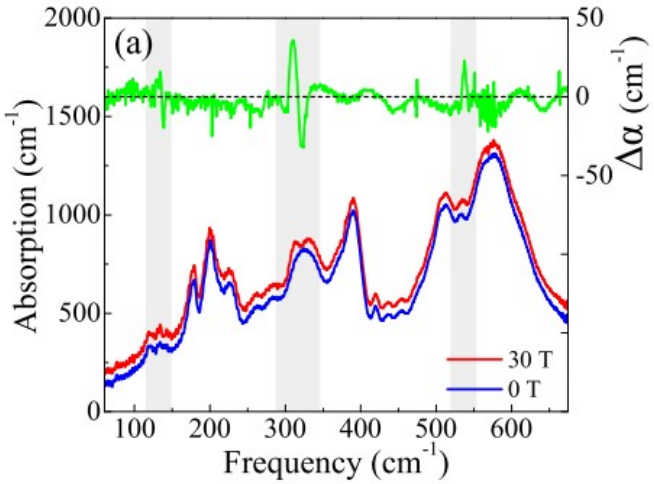
Example: Sr_3NiIrO_6 – Spin-phonon coupling

A complete Hamiltonian needs to include

- Anisotropic exchange
- Single ion anisotropy
- Phonons
- Anti-symmetric (DM) exchange

$$\mathcal{H} = \sum_{i,j,\alpha} J_{i,j,\alpha} S_{i,\alpha} S_{j,\alpha} + \sum_{i} K_i S_{i,z}^2 + \sum_{n} \frac{1}{2} k_n u_n^2 + \sum_{n} u_n \sum_{i,j,\alpha} \lambda_{i,j,\alpha,n} S_{i,\alpha} S_{j,\alpha} + \sum_{n} u_n \sum_{i,j} \vec{\gamma}_n \cdot \left(\vec{S}_i \times \vec{S}_j \right)$$

No way to get as many coefficients from DFT



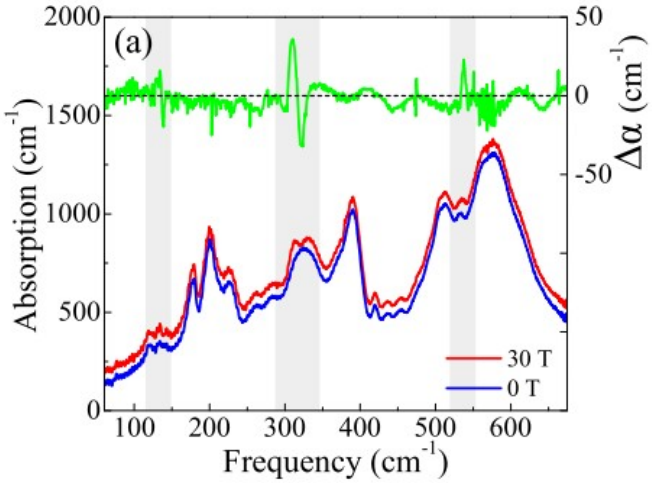
How can we explain the spin-phonon coupling observed in IR absorption spectroscopy?

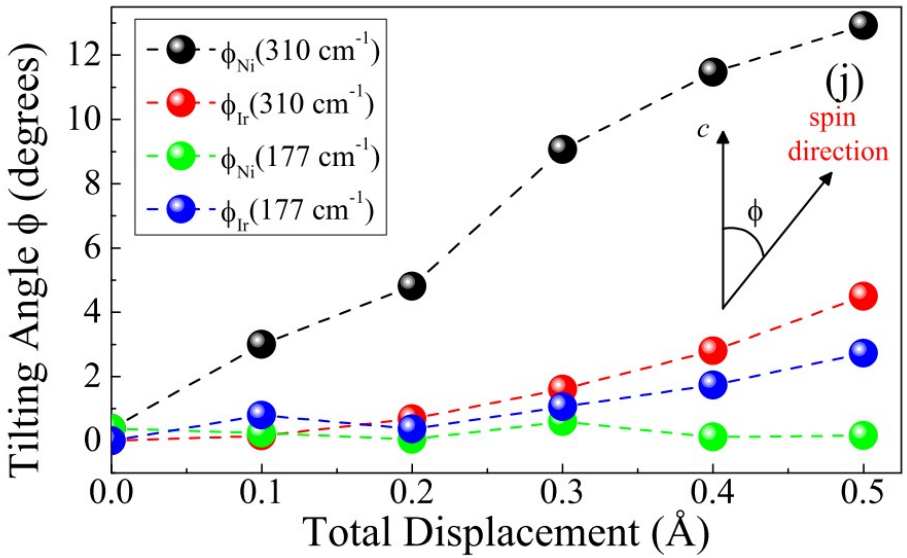
[O'neal, Paul, Birol, Musfeldt, et al. (2019)]

Example: Sr_3NiIrO_6 – Spin-phonon coupling

Trick:

Recalculate DFT electronic structure for different displacements of phonons
The modes with large spin-phonon coupling will lead to more tilting

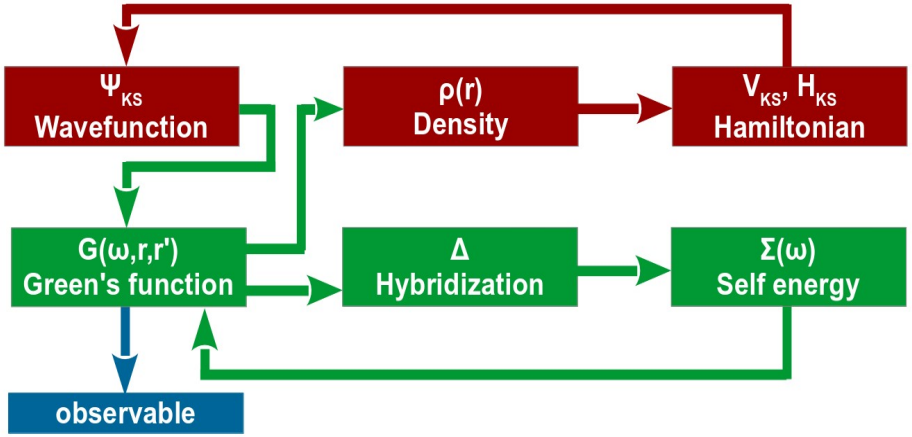


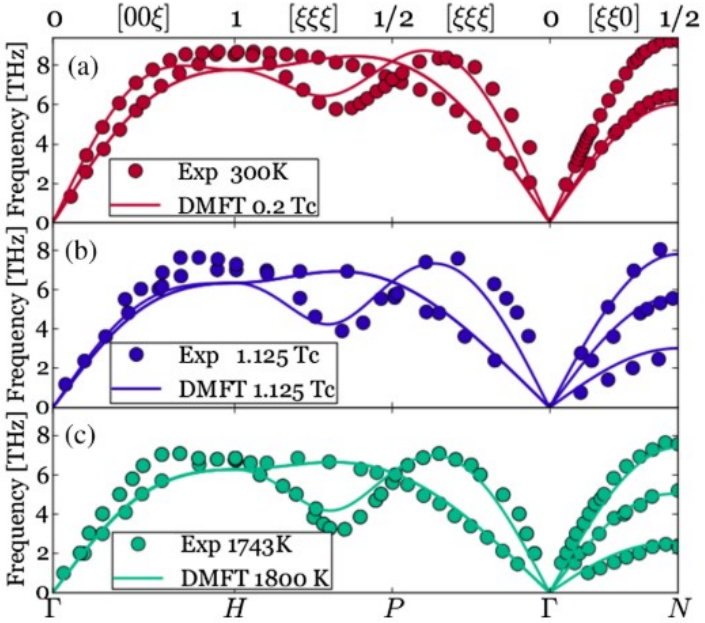


[O'neal, Paul, Birol, Musfeldt, et al. (2019)]

Example: Ferromagnetic vs paramagnetic iron

Dynamical Mean Field Theory (DFT+DMFT) can reproduce dynamic fluctuations and hence predict paramagnetic properties.





Conclusions & Summary

Magnetism, lattice dynamics, and crystal structure are intertwined in different ways in different materials.

First principles methods, e.g. DFT, provide a way to predict and explain the spin-phonon and spin-lattice couplings.

These methods can be supplemented by group and representation theories to extract meaningful and complete models, and simplify calculations.

DMR – 2011401 & DMR – 2046020