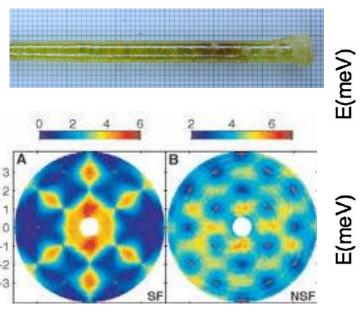


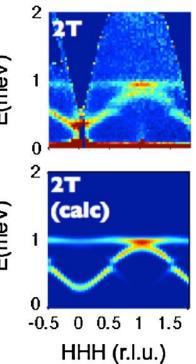
# **Magnetic Scattering**

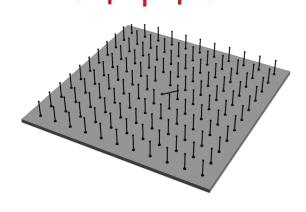














Pat Clancy
Dept. of Physics & Astronomy
McMaster University

**McMaster** 

University

# Introduction to Magnetic Scattering



- Magnetic Scattering with Neutrons
- Essential tool for the study of magnetic materials
- Elastic Scattering (diffraction) magnetic structure, phase transitions
- Inelastic Scattering (spectroscopy) magnetic dynamics, excitations, interactions

- Magnetic Scattering with X-rays
- How does it work?
- When is it a good idea?



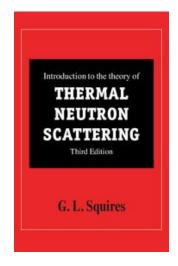


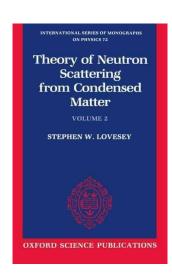
# Suggestions for Further Reading...

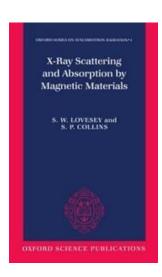
- Magnetic Scattering with Neutrons:
   Introduction to the Theory of Thermal Neutron Scattering, G. L. Squires (2012)

   Theory of Neutron Scattering from Condensed Matter (Vol. 2), S. W. Lovesey (1984)
- Magnetic Scattering with X-rays: X-ray Scattering and Absorption by Magnetic Materials, S. W. Lovesey & S. P. Collins (1996)

"Magnetic Scattering" by J. W. Lynn and B. Keimer in Handbook of Magnetism (arXiv:1910.01218)

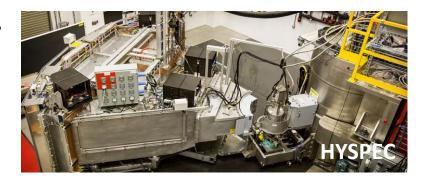






# Magnetic Scattering with Neutrons

- One of the "killer applications" of neutron scattering
- Essential tool for investigating magnetic materials











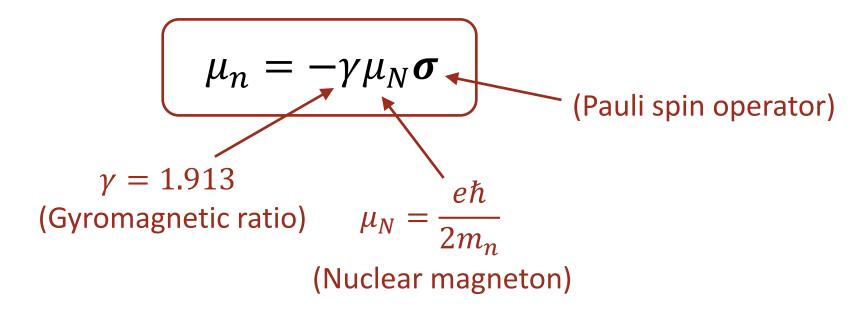






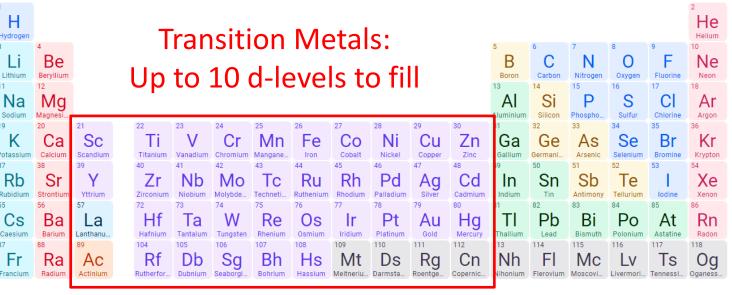
# Magnetic Scattering with Neutrons

- Neutrons are spin ½ particles
- They carry no charge, but do carry a magnetic dipole moment:



- $\bullet$   $\mu_n$  can interact with the electrons in a material via magnetic potentials
- Scattering from these potentials can be comparable in strength to nuclear scattering

# Magnetic Materials



 Magnetic moments arise on atoms which have unpaired electrons in partially filled electronic orbitals

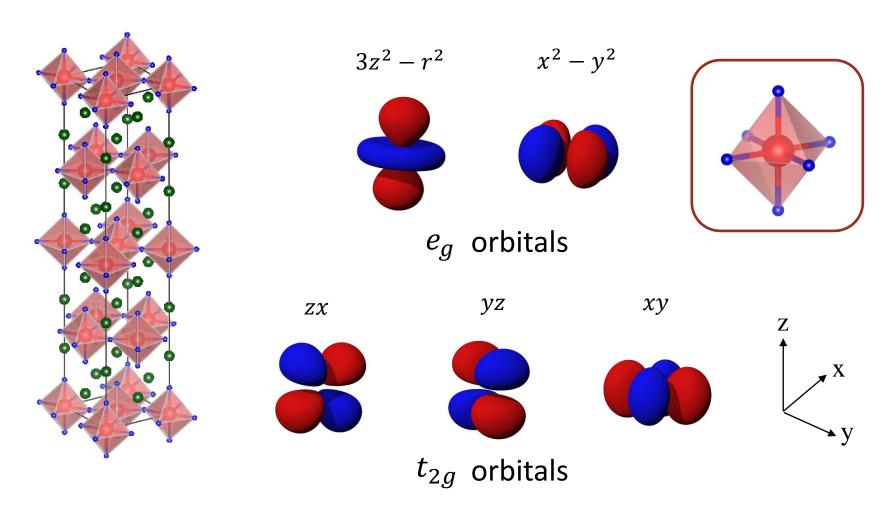


Lanthanides/Rare Earths and Actinides: Up to 14 f-levels to fill

 Most common families of magnetic materials tend to be based on elements with partially filled d- or f-shells (e.g. transition metals or rare earth/lanthanides)

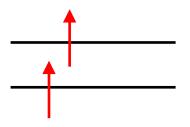
# Magnetic Materials

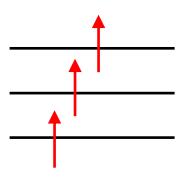
• Size of magnetic moments is determined by Hund's Rules:



e.g. Mn<sup>2+</sup> (3d<sup>5</sup>)

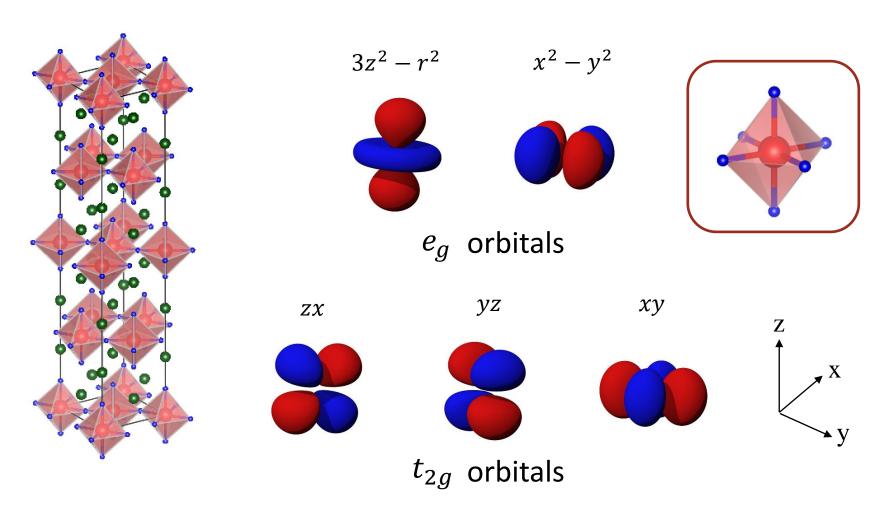
$$\left[S=5/2\right]$$





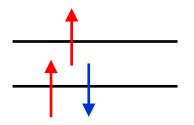
# Magnetic Materials

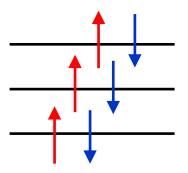
• Size of magnetic moments is determined by Hund's Rules:



e.g. Cu<sup>2+</sup> (3d<sup>9</sup>)

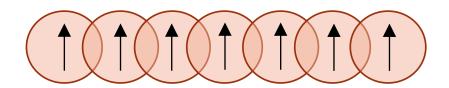
$$S=1/2$$



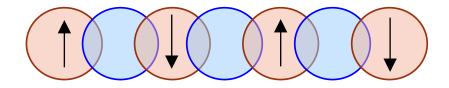


# Magnetic Interactions

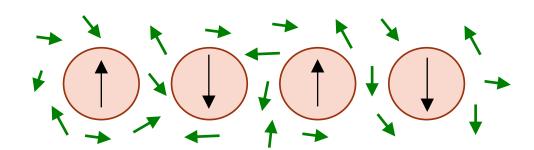
• Direct exchange:



• Superexchange:



• RKKY exchange:

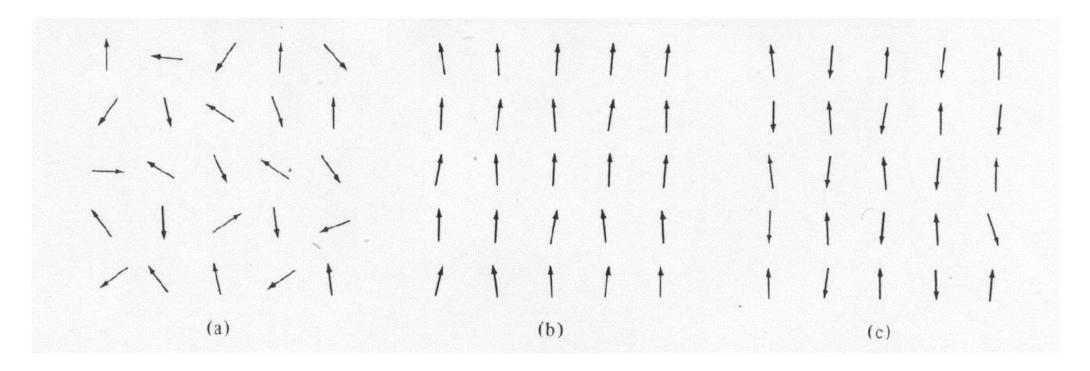


Describe interactions by a magnetic Hamiltonian:

e.g. 
$$H = J \sum_{i,j} S_i \cdot S_j$$

(exchange parameter)

# Magnetic Order



Paramagnet  $(T > T_c)$ 

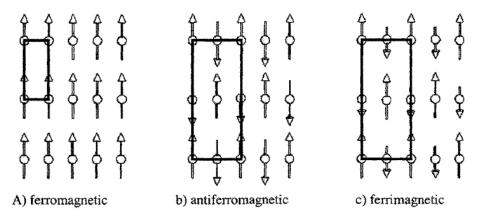
Ferromagnet (T < T<sub>C</sub>)

Antiferromagnet  $(T < T_N)$ 

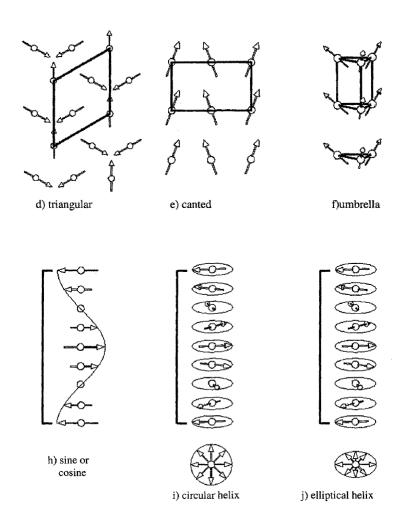
# Magnetic Structures

 Magnetically ordered structure that develops in a material depends on nature of underlying magnetic interactions

Structures can be relatively simple...

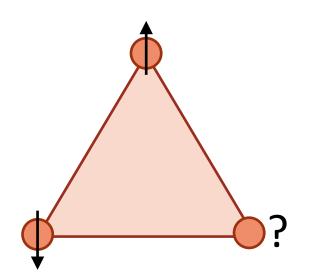


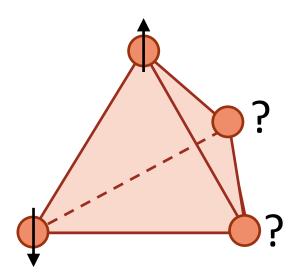
### ... or more complex

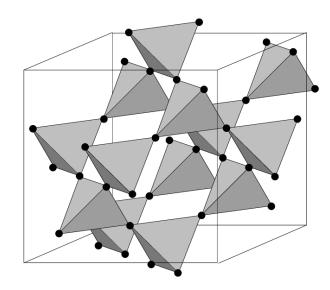


## **Geometric Frustration**

• We can also try to design magnetic materials which don't order at all:







The Pyrochlore Lattice

• Geometrically frustrated magnets can display exotic quantum ground states at low temperatures, e.g. quantum spin liquids, spin ices, spin glasses...

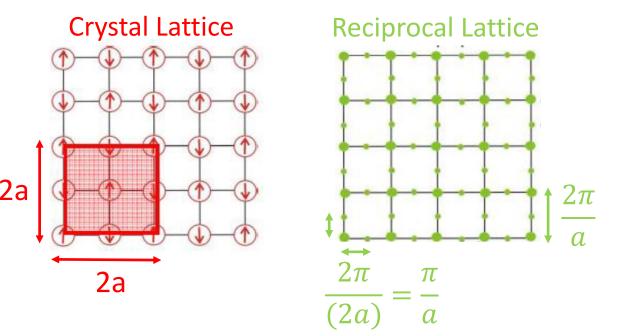
# Scattering from a Magnetically Ordered Crystal

How can we detect magnetic order in a neutron scattering experiment?

### Paramagnetic State $(T > T_N)$

# Crystal Lattice a\*1 a\*1 $a*=\frac{2\pi}{a}$

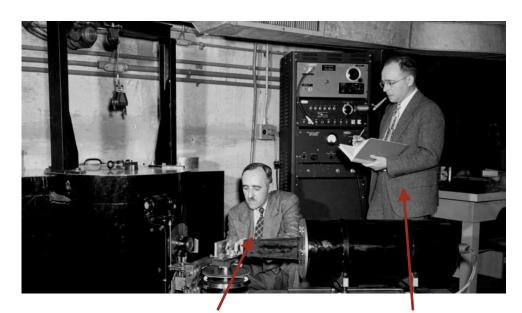
### Antiferromagnetic State $(T < T_N)$



Development of AF order increases size of unit cell → new magnetic Bragg peaks appear

# First Observation: Magnetic Neutron Scattering from MnO

• Early neutron diffraction experiments at the ORNL X-10 Graphite Reactor:



**Ernest Wollan** 

**Clifford Shull** 



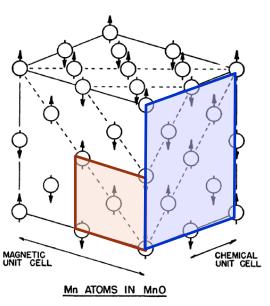


Fig. 5. Antiferromagnetic structure existing in MnO below its Curie temperature of 120°K. The magnetic unit cell has twice the linear dimensions of the chemical unit cell. Only Mn ions are shown in the diagram.

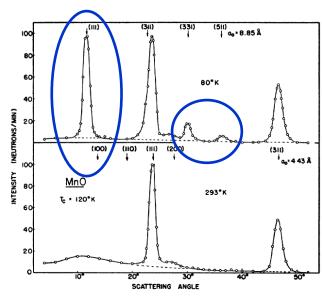


Fig. 4. Neutron diffraction patterns for MnO taken at liquid nitrogen and room temperatures. The patterns have been corrected for the various forms of extraneous, diffuse scattering mentioned in the text. Four extra antiferromagnetic reflections are to be noticed in the low temperature pattern.

### First direct evidence of antiferromagnetism

Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951)

# First Observation: Magnetic Neutron Scattering from MnO

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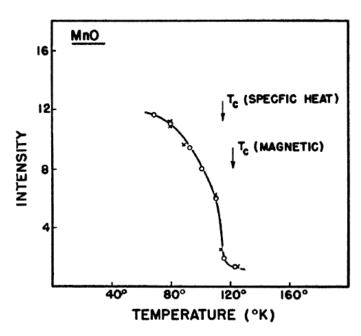


Fig. 7. Temperature dependence of magnetic intensity for MnO. The Curie temperatures suggested by specific heat and magnetic susceptibility data are shown.

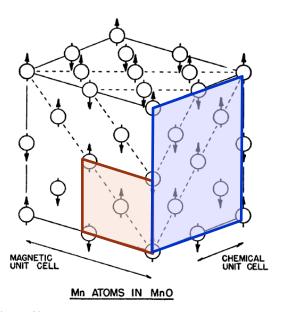


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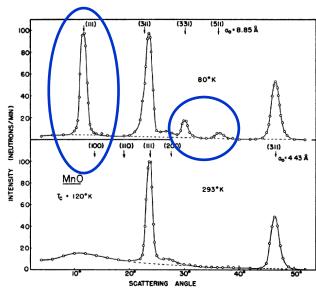


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First direct evidence of antiferromagnetism

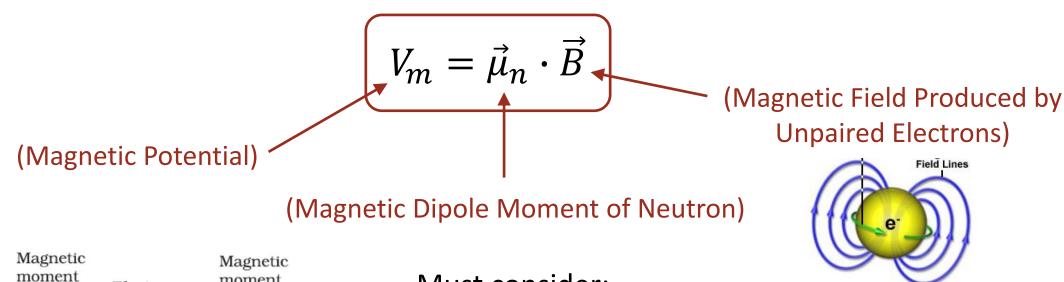
Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951)

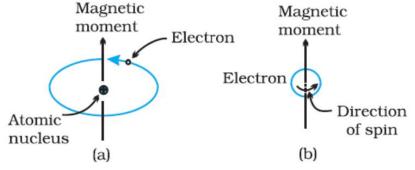
- What fraction of neutrons will scatter off a sample with a particular change in energy and momentum?
- Change in momentum:  $\vec{Q} = \vec{k} \vec{k}'$
- Change in energy:  $\Delta E = \hbar \omega = \frac{\hbar^2 k^2}{2m} \frac{\hbar^2 k'^2}{2m}$
- Apply Fermi's Golden Rule (1st order perturbation theory):

$$\frac{d^{2}\sigma}{d\Omega \ dE'}_{k,\sigma,\lambda \to k',\sigma',\lambda'} = \underbrace{\left(\frac{m}{2\pi\hbar^{2}}\right)^{2} \frac{k'}{k}} \left[ |\langle k' \ \sigma' \ \lambda' | V_{m} | k \ \sigma \ \lambda \rangle|^{2} \right] \delta\left(E_{\lambda} - E_{\lambda'} + \hbar\omega\right)$$
(Kinematics) (Interaction Term) (Energy Conservation)

# The Magnetic Potential

• In order to evaluate the matrix element in the interaction term, we need to determine the magnetic potential produced by all of the unpaired electrons in the material:





Must consider:

 $B_l$  = Magnetic field from **orbital motion** of an electron

 $B_s = \text{Magnetic field from spin of an electron}$ 

- Evaluating the interaction term  $|\langle k' \sigma' \lambda' | V_m | k \sigma \lambda \rangle|^2$  can be quite complicated.
- Jumping to the final result:

$$\frac{d^{2}\sigma}{d\Omega dE'} = \frac{(\gamma r_{0})^{2}}{2\pi\hbar} \frac{k'}{k} N \left[ \frac{1}{2} gF(\vec{Q}) \right]^{2} \sum_{\alpha\beta} \left( \delta_{\alpha\beta} - \hat{Q}_{\alpha} \hat{Q}_{\beta} \right) \\
\times \sum_{l} e^{i\vec{Q}\cdot\vec{l}} \int \left\langle e^{-i\vec{Q}\cdot\vec{u}_{0}(0)} e^{i\vec{Q}\cdot\vec{u}_{l}(t)} \right\rangle \left\langle S_{0}^{\alpha}(0) S_{l}^{\beta}(t) \right\rangle e^{-i\omega t} dt$$

### Key features:

- 1. From constants magnetic scattering comparable in strength to nuclear scattering ( ${}^{\sim}r_0^2$ )
- 2. Proportional to square of **magnetic form factor**,  $F\left(\vec{Q}\right)^2$

- Evaluating the interaction term  $|\langle k' \sigma' \lambda' | V_m | k \sigma \lambda \rangle|^2$  can be quite complicated.
- Jumping to the final result:

$$\frac{d^{2}\sigma}{d\Omega dE'} = \underbrace{\frac{(\gamma r_{0})^{2}}{2\pi\hbar}}^{k'} \frac{k'}{k} N \underbrace{\left[\frac{1}{2}gF\left(\vec{Q}\right)\right]^{2}}_{\alpha\beta} \underbrace{\sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \hat{Q}_{\alpha}\hat{Q}_{\beta}\right)}_{\alpha\beta} \\
\times \sum_{l} e^{i\vec{Q}\cdot\vec{l}} \int \left\langle e^{-i\vec{Q}\cdot\vec{u}_{0}(0)}e^{i\vec{Q}\cdot\vec{u}_{l}(t)}\right\rangle \left\langle S_{0}^{\alpha}(0) S_{l}^{\beta}(t)\right\rangle e^{-i\omega t} dt$$

### Key features:

3. **Polarization factor** – describes dependence on spin direction. Term vanishes if components of spin are parallel to scattering vector  $\vec{Q} \to$  only sensitive to  $S \perp \vec{Q}$ 

- Evaluating the interaction term  $|\langle k' \sigma' \lambda' | V_m | k \sigma \lambda \rangle|^2$  can be quite complicated.
- Jumping to the final result:

$$\frac{d^{2}\sigma}{d\Omega dE'} = \underbrace{\frac{(\gamma r_{0})^{2}}{2\pi\hbar} \frac{k'}{k} N \left[\frac{1}{2}gF\left(\vec{Q}\right)\right]^{2}}_{\chi} \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \hat{Q}_{\alpha}\hat{Q}_{\beta}\right) \times \sum_{l} e^{i\vec{Q}\cdot\vec{l}} \int \left\langle e^{-i\vec{Q}\cdot\vec{u}_{0}(0)}e^{i\vec{Q}\cdot\vec{u}_{l}(t)} \right\rangle \left\langle S_{0}^{\alpha}(0) S_{l}^{\beta}(t) \right\rangle e^{-i\omega t} dt$$

### Key features:

4. **Dynamic spin pair correlation function** – measures correlation between spin  $\alpha$  at origin and t=0 and spin  $\beta$  at position l and time t. The Fourier transform of this term is the **dynamic structure factor**,  $S(\overrightarrow{Q}, \omega)$ 

# Magnetic Form Factor

•  $F(\vec{Q})$  = Fourier transform of the spin distribution in real space

$$F(\vec{Q}) = \int S(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d^3r$$

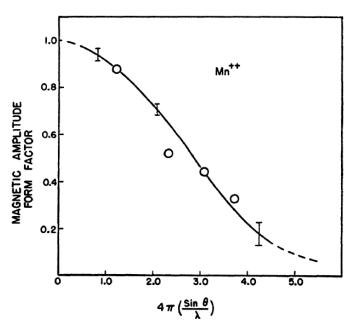
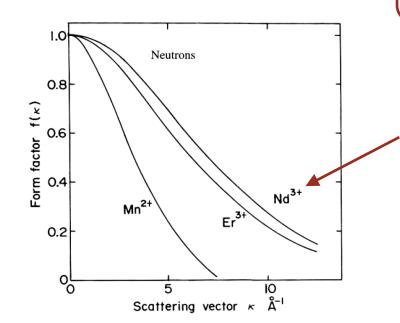


Fig. 2. Magnetic amplitude form factor for Mn<sup>++</sup> ions. The curve is that obtained from paramagnetic diffuse scattering with estimated error as shown. The points represent values of the form factor obtained from the low temperature antiferromagnetic reflections of MnO.



 $F\left( \overrightarrow{Q}\right)$  decreases faster as wavefunctions become more spatially extended

- Analogous to chemical form factor for x-ray scattering
- Typically drops off monotonically as  $\vec{Q}$  increases

Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951)

# **Elastic Magnetic Scattering**

- For elastic scattering (i.e. diffraction), we have:  $\Delta E = \hbar \omega = \frac{\hbar^2 k^2}{2m} \frac{\hbar^2 k'^2}{2m} = 0$
- What we measure is the **time-independent** structure factor,  $S(\vec{Q})$

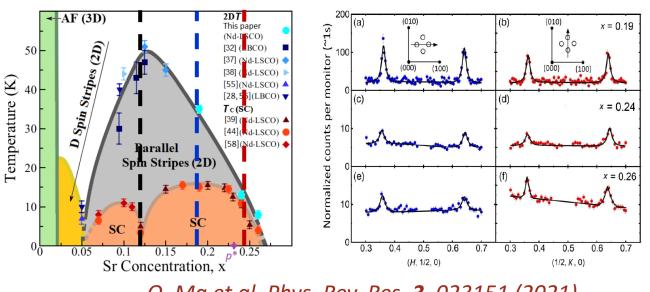
$$\frac{d\sigma}{d\Omega} = (\gamma r_0)^2 \frac{k'}{k} N \left[ \frac{1}{2} g F\left(\vec{Q}\right) \right]^2 e^{-2W} \sum_{\alpha\beta} \left( \delta_{\alpha\beta} - \hat{Q}_{\alpha} \hat{Q}_{\beta} \right) \times \sum_{l} e^{i\vec{Q}\cdot\vec{l}} \int \langle S_0^{\alpha} \rangle \left\langle S_l^{\beta} \right\rangle$$
Debye-Waller Effect

Add up spins with a phase factor of  $e^{i\vec{Q}\cdot\vec{l}}$ 

Polarization Factor: Only sensitive to  $S \perp \vec{Q}$ 

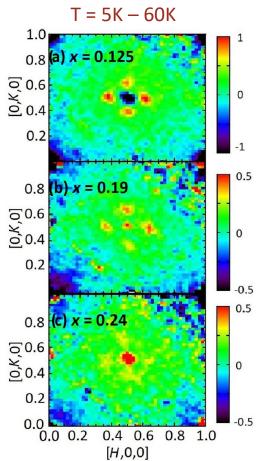
# Elastic Magnetic Scattering: Examples

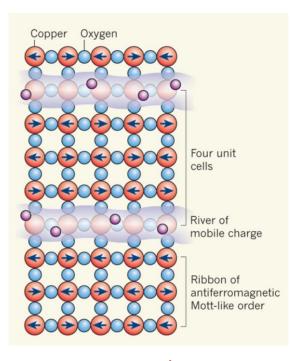
- High temperature superconductors
- e.g. Nd<sub>0.4</sub>La<sub>1.6-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> Single Crystal
- Measured on SEQUOIA at SNS, and HB3 at HFIR



Q. Ma et al, Phys. Rev. Res. 3, 023151 (2021)

• Magnetic scattering is **incommensurate**, arising at  $(0.5 \pm \delta, 0.5, L)$  and  $(0.5, 0.5 \pm \delta, L)$  due to stripe order

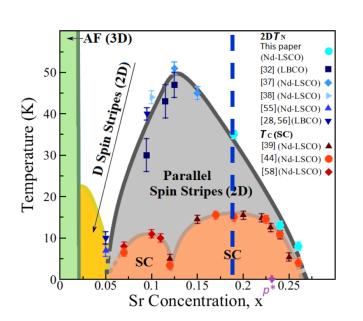


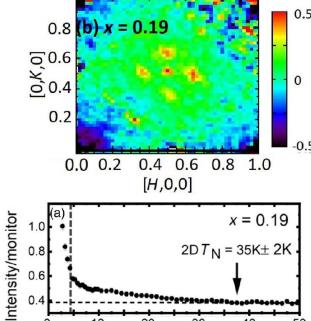


K. A. Moler, Nature **468**, 643 (2010)

# Elastic Magnetic Scattering: Examples

- High temperature superconductors
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- Measured on SEQUOIA at SNS, and HB3 at HFIR





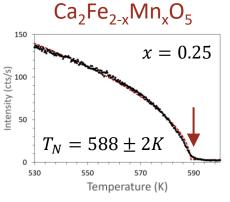
Temperature (K)

- Above T = 5K: Rods of diffuse scattering along the L-direction, indicates shorterrange quasi-2D magnetic correlations
- <u>Below T = 5K</u>: Well-defined **Bragg peaks**, indicates **3D long-range** magnetic order

$$\xi \propto \frac{1}{Q} = \text{correlation length}$$

More conventionally:

$$I \propto M^2 = {M_0}^2 \left(1 - \frac{T}{T_C}\right)^{2\beta}$$



Q. Ma et al, Phys. Rev. Res. 3, 023151 (2021)

J. Greedan et al (2023)

# Inelastic Magnetic Scattering

- For inelastic scattering (i.e. spectroscopy), we have:  $\Delta E = \hbar \omega = \frac{\hbar^2 k^2}{2m} \frac{\hbar^2 k'^2}{2m} \neq 0$
- This implies that  $\left| \overrightarrow{k} \right| \neq \left| \overrightarrow{k'} \right| \to \text{change in both } \overrightarrow{Q} \text{ and } \omega$
- What we measure is the **dynamical structure factor**  $S\left(\vec{Q},\omega\right)$
- Key points:
- Study dynamic magnetic moments (on time scales of 10<sup>-9</sup> to 10<sup>-12</sup> sec)

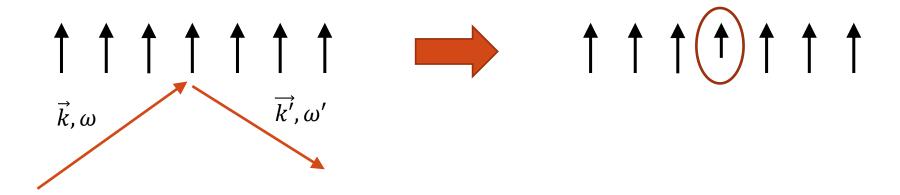
• 
$$S\left(\vec{Q},\omega\right) = \frac{1}{1-e^{-\beta\hbar\omega}} \frac{\chi''(\vec{Q},\omega)}{\pi(g\mu_B)^2} = n(\omega) \chi''(\vec{Q},\omega)$$
 (Fluctuation-Dissipation Theorem)

• Intensity integrated over all  $\vec{Q}$ ,  $\omega$  is constant:  $\int d\omega \int_{BZ} d\vec{Q} \, S\left(\vec{Q},\omega\right) \sim S(S+1)$ 

(Total Moment Sum Rule)

# Inelastic Magnetic Scattering: Spin Waves

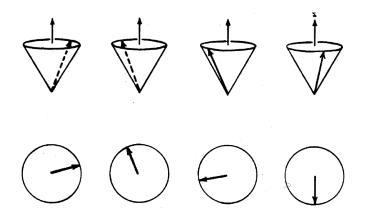
- When a neutron scatters off a sample it can create or destroy an excitation
- If sample is magnetically ordered (e.g. a FM spin chain), the incident neutron can create a spin "defect" which is distributed over all possible sites
- We call this collective excitation a spin wave or magnon

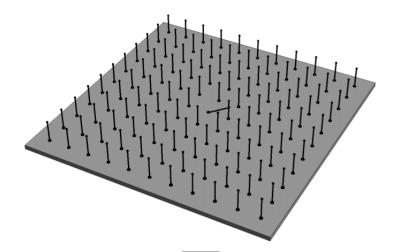


Spins are coupled through magnetic Hamiltonian:  $H = J \sum_{i,j} S_i \cdot S_j$ 

# Inelastic Magnetic Scattering: Spin Waves

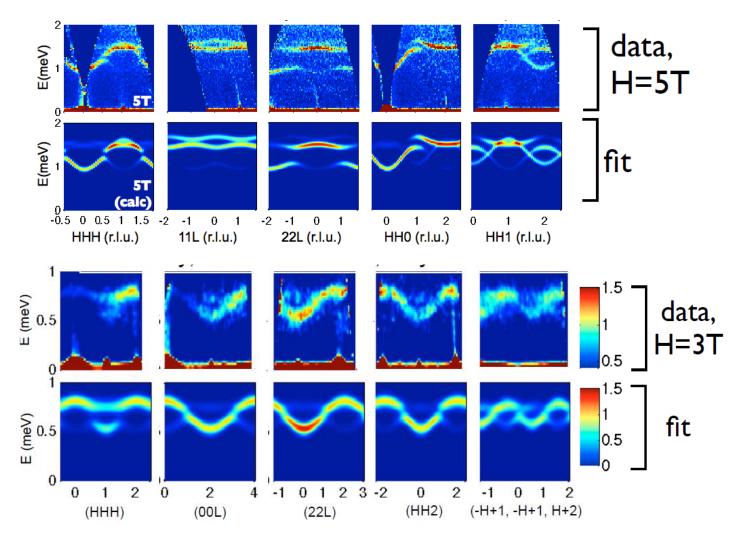
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# Inelastic Magnetic Scattering: Examples



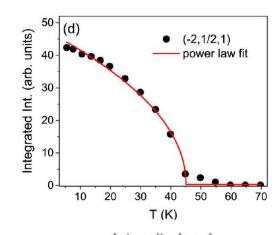
- Frustrated magnetism in pyrochlores
- Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (top) and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (bottom) Single Crystals
- Measured on DCS at NIST
- Fit spin wave dispersion to theoretical model and extract detailed exchange parameters (J<sub>1</sub>, J<sub>2</sub>, J<sub>3</sub>, J<sub>4</sub>)
- Magnetic interactions explain low temperature magnetic ground states

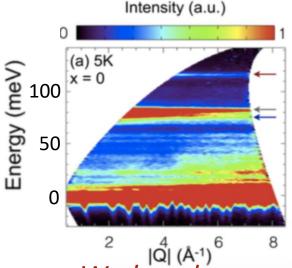
K. A. Ross et al, Phys. Rev. X 1, 021002 (2011)

L. Savary et al, Phys. Rev. Lett. 109, 167201 (2012)

# How can we distinguish magnetic scattering?

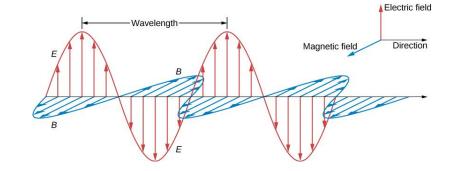
- (1) Temperature dependence:
- Magnetic scattering decreases with increasing T (disappears at  $T > T_C$ )
- Phonon scattering increases with increasing T (∝ thermal population)
- (2) Momentum dependence:
- Magnetic scattering decreases with increasing  $|Q| (\propto |F(Q)|^2)$
- Phonon scattering increases with increasing  $|Q| (\propto |e \cdot Q|^2)$
- (3) Polarization dependence (with polarized beam):
- Magnetic scattering mostly spin flip
- Nuclear scattering mostly non-spin flip



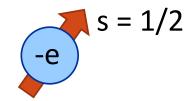


More on polarized neutrons from Barry Winn, Dean Myles & Josh Pierce on Wednesday

# Magnetic Scattering with X-rays



- X-rays carry no magnetic moment
- Primary interaction with matter: E-field of x-ray + charge of electrons
- Also interacts through: **B-field** of x-ray + **spin** of electrons



- Unlike neutrons:
- 1. Magnetic scattering is MUCH weaker than charge scattering

Amplitude ratio: 
$$\frac{A(magnetic)}{A(charge)} = \frac{\hbar\omega}{mc^2}$$
 (for **single** electron)

At Ei ~5 keV: Amplitude ratio ~10<sup>-2</sup> Intensity ratio ~10<sup>-4</sup>

2. X-ray photon energies (~0.5 to 50 keV) are orders of magnitude larger than typical energy scales for magnetic excitations (~0.5 to 500 meV)

# First Observation: Magnetic X-ray Scattering from NiO

### NiO: Antiferromagnet ( $T_N \sim 250 \, ^{\circ}$ C)

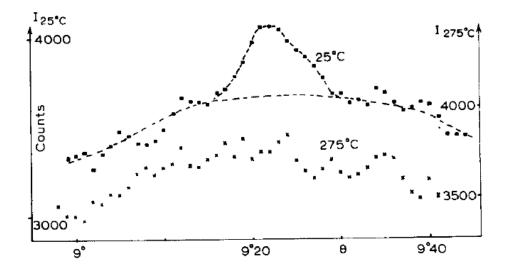


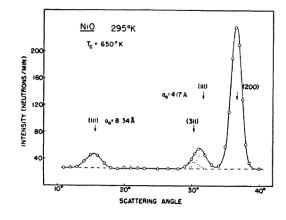
Fig. 1. Intensity  $I_t(\theta)$  near the  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  position at  $t = 25^{\circ}$  C and 275° C in counts/225 min. The hump which cover the interval could be due to some impurity.

De Bergevin and Brunel, Phys. Lett. **39A**, 141 (1972)

- NON-RESONANT magnetic x-ray scattering
- Lab-based experiment carried out using x-ray tube source (Cu K $\alpha$ ,  $\lambda$  = 1.54 Å)
- Hard!
- Counting time: 3 days/scan
   (~2 cts/min signal on ~18 cts/min bkgd)

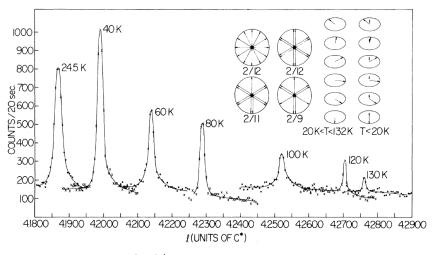
 Compare to magnetic neutron scattering:

Shull et al, Phys. Rev. **83**, 333 (1951)



# To the Synchrotron: Magnetic X-ray Scattering from Ho

Ho: Incommensurate spiral antiferromagnet ( $T_N \sim 131 \text{ K}$ )

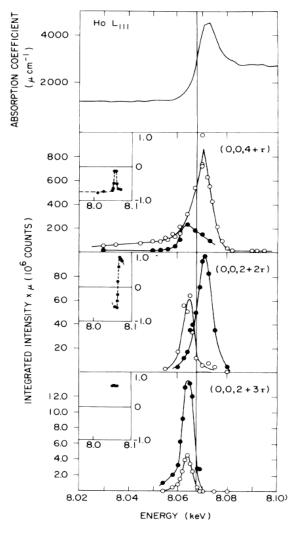


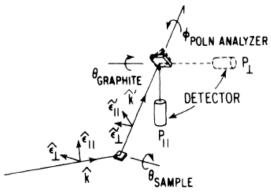
- NON-RESONANT magnetic x-ray scattering
- Synchrotron-based experiment (SSRL)
- Higher flux and higher momentum resolution
- Compare to magnetic neutron scattering:
- X-ray: 25 cts/s on 10 cts/s, FWHM =  $0.001 \, \text{Å}^{-1}$
- Neutron: 50 cts/s on 0.1 cts/s, FWHM =  $0.005 \text{ Å}^{-1}$

FIG. 1. Temperature dependence of the Ho(004)<sup>+</sup> magnetic satellite taken with synchrotron radiation (lines drawn to guide the eye). Inset: Right, schematic representation of the magnetic structure of Ho (after Koehler<sup>9</sup>). Left, projections of the magnetic unit cell for different spin-slip structures. For simplicity the doublet has been drawn as two parallel spins.

D. Gibbs et al, Phys. Rev. Lett. **55**, 234 (1985)

# On Resonance: Magnetic X-ray Scattering from Ho





Gibbs et al, Phys. Rev. Lett. **61**, 1241 (1988)

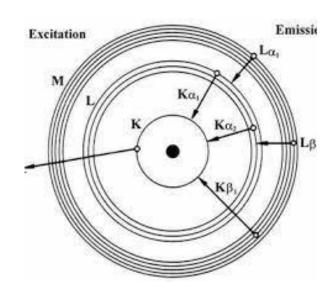
- RESONANT MAGNETIC X-RAY SCATTERING
- First predicted by M. Blume (1985)
- Synchrotron-based experiment (NSLS, CHESS)
- Tune incident energy to Ho  $L_3$ -edge ( $E_i = 8.067 \text{ keV}$ ,  $\lambda = 1.54 \text{ Å}$ )
- Take advantage of polarized beam and resonant enhancement at absorption edge
- Magnetic peak intensity enhanced by ~50x!

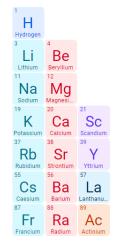
More on resonant scattering at APS tutorials next week

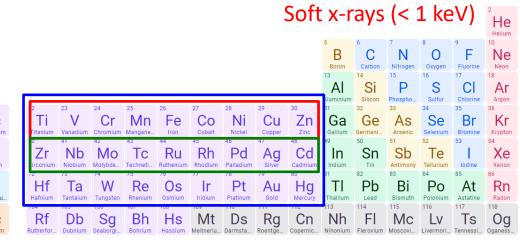
# Resonant Magnetic X-ray Scattering

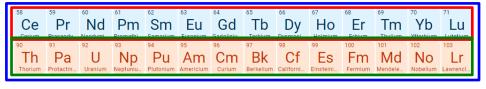
Hard x-rays (> 5 keV)

Tender x-rays (1-5 keV)







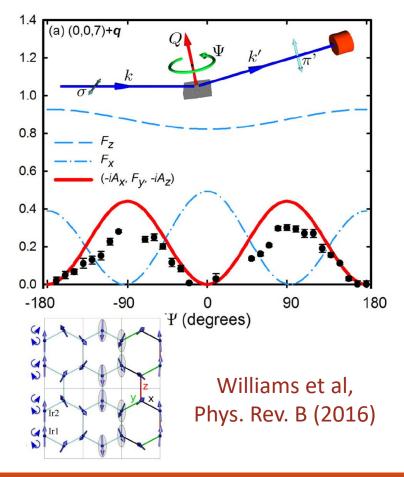


Scattering tensor for magnetic x-ray scattering:

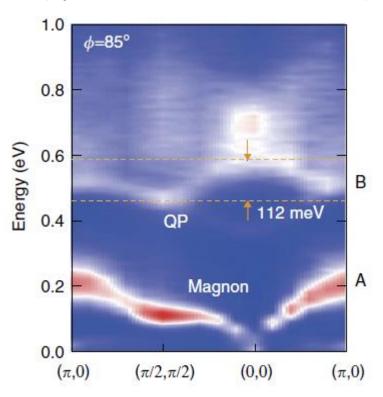
$$F_{j}(E) = \sigma^{(0)}(E)\varepsilon_{i} \cdot \varepsilon_{0}^{*} + \sigma^{(1)}(E) \varepsilon_{i} \times \varepsilon_{0}^{*} \cdot M_{j} + \sigma^{(2)}(E) \left[ \left( \varepsilon_{i} \cdot M_{j} \right) \left( \varepsilon_{0}^{*} \cdot M_{j} \right) - \frac{1}{3}\varepsilon_{i} \cdot \varepsilon_{0}^{*} \right]$$
• Intensity of magnetic Bragg peaks: 
$$I = \left| \sum_{i} e^{ig \cdot r_{j}} \sigma_{j}^{(1)}(E) \varepsilon_{i} \times \varepsilon_{0}^{*} \cdot M_{j} \right|^{2}$$

# Resonant Magnetic X-ray Scattering: Examples

α-Li<sub>2</sub>IrO<sub>3</sub> single crystal (Kitaev model candidate)

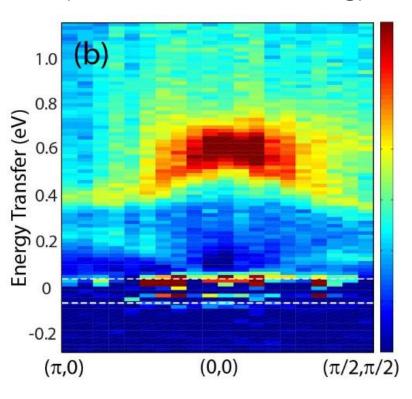


**Sr<sub>2</sub>IrO<sub>4</sub>** single crystal (spin-orbital Mott insulator)



Kim et al, Nat. Comm. (2014)

 $Ba_2IrO_4$  thin film (13 nm thickness = 10 ng)



Clancy et al, Phys. Rev. B (2023)

# Magnetic X-ray Scattering

### **Advantages:**

- Element (and even orbital) specificity
- Smaller samples (ideal for thin films, high pressure diamond anvil cell experiments)
- Better resolution in momentum

### **Disadvantages:**

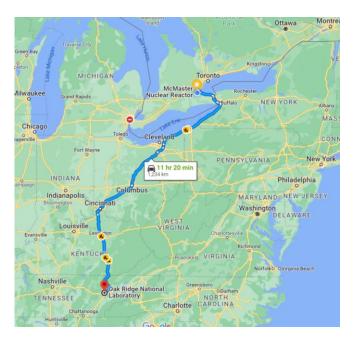
- More complicated theory/modeling
- Magnetic scattering much weaker than charge scattering
- Worse resolution in energy
- Restricted momentum transfer (soft x-ray)

X-ray and neutron scattering are highly complementary techniques for the study of magnetic materials

# Neutron Scattering at McMaster



Home to McMaster Nuclear Reactor — Canada's most powerful neutron source







- 5 MW open-pool reactor used for **neutron scattering**, medical isotopes, neutron radiography, neutron activation/irradiation studies, positron beams...
- Currently 2 neutron scattering beamlines: MAD (triple-axis) and MacSANS (more coming soon)

# Lecture Feedback



https://forms.office.com/g/CyZq6VzCqv

# **Any Questions?**



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