Introduction to Neutron (and X-ray) Scattering Techniques

Jeffrey Lynn
NIST Center for Neutron Research

University of Texas—Dallas, Arlington
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Outline

- Scattering Basics
  - Cross sections, form factors, x-rays vs. neutrons
- Powder Diffraction (crystal and magnetic diffraction)
  - Profile refinement, subtraction technique, polarized neutrons
- Single Crystal Diffraction (structure and magnetic)
- Small Angle Neutron Scattering (SANS)
  - Nanoparticles, Vortex lattice, ferromagnetic superconductor, skyrmions, domains, … polymers, biological systems,
- Reflectometry (thin films and multilayers)
  - Structural and Magnetic Depth Profile
- Inelastic Scattering
  - Phonons, Magnons, Crystal Field Levels, Spin Liquids,

- Reference Materials

Neutron (and X-ray) scattering

Neutron scattering experiments measure the flux of neutrons scattered by a sample into a detector as a function of the change in neutron wave vector ($\vec{Q}$) and energy ($\hbar\omega$).

$\Phi(Q,\hbar\omega) = \dfrac{\text{neutrons}}{\text{sec–cm}^2}$

Momentum

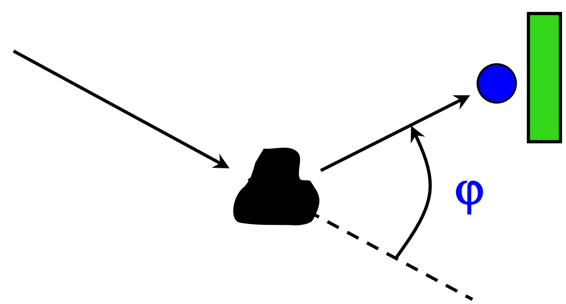
$\hbar k_n = \hbar(2\pi/\lambda_n)$

$\hbar\vec{Q} = \hbar\vec{k}_i - \hbar\vec{k}_f$

Energy

$E = \hbar^2 k_n{}^2/2m$

$E = E_i - E_f$



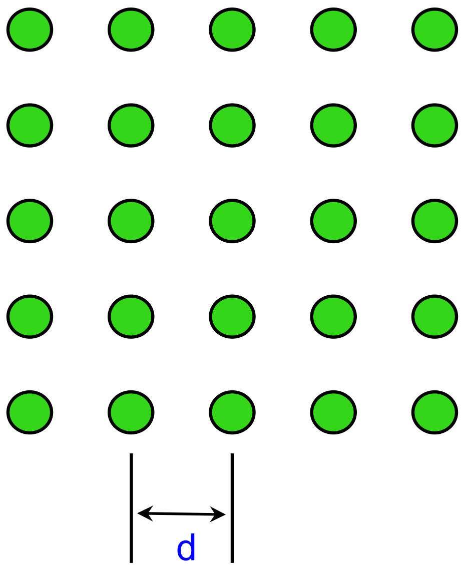
The expressions for the scattered neutron flux Φ depend on the positions and motions of atomic nuclei or unpaired electron spins.

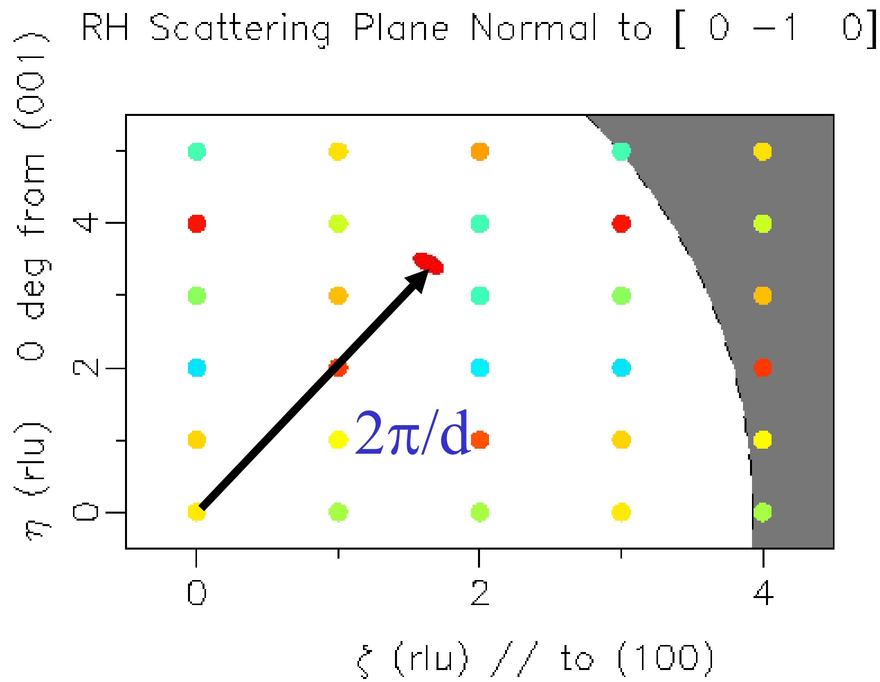
$$\boxed{\Phi = \mathbb{F}\{\vec{r}_i(t), \vec{r}_j(t), \vec{S}_i(t), \vec{S}_j(t)\}}$$

Φ provides information about all of these quantities!

Reciprocal (Scattering) Space

Periodic array of atoms in Real Space





Real space ↔ Reciprocal (Fourier) Space

Other Probes

$$E_{neutron}(meV) = 2.0719k^2 = 81.7968/\lambda^2$$

$$E_{photon}(keV) = 2.0k = 12.4/\lambda$$

$$E_{electron}(eV) = 3.8k^2 = 150/\lambda^2$$

λ = 1 Å: E_n=82 meV; E_p=12,400,000 meV; E_e=150,000 meV

$$1\,meV = 11.6\,K \quad (k_B T)$$

300 K → 25 meV

$$1\,meV = 8.06\,cm^{-1} \quad (E/hc)$$

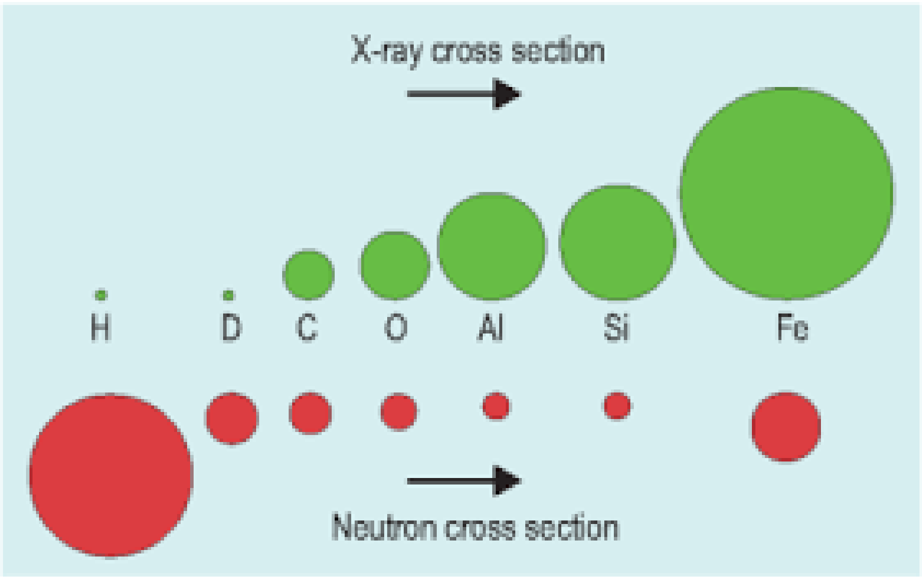
$$1\,meV = 0.2418\,THz \quad (E/h)$$

$$1\,meV/\mu_B = 17.3\,T \quad (E/\mu_B)$$

Neutron and X-ray Scattering

- Both techniques collect data as functions of the energy and the momentum transferred from the system to the neutron or photon beam. The resulting five-dimensional data sets serve as powerful probes of materials. Elastic scattering elucidates the crystal structure, magnetic configuration, direction of the spins, symmetry of the magnetic state, spatial distribution of the magnetization density, and dependence of the order(s) parameter on thermodynamic fields such as temperature, pressure, magnetic and electric fields. Inelastic scattering determines the energies of the fundamental excitations which can be used to elucidate the nature, strength, and range of the interactions.
- Both techniques can measure crystal and magnetic structures and their dynamics.
- Neutron advantages:
  - Magnetic and structural scattering are comparable in strength; Elastic scattering yields quantitative information; energy resolution is orders-of-magnitude better than x-rays; simplicity of sample environment; low T accessible. Theory has solid theoretical basis.
- X-ray advantages:
  - High Flux → small samples; individual domains, topography; pump probe capability; resonant x-ray scattering →element specific; magnetic resonant x-ray scattering; RIXS

Neutrons and X-rays are Complementary



Nucleus looks like a point particle → b is just a constant independent of scattering angle.

Adjacent elements, heavy + light elements, isotope substitution

Neutron Cross Sections

$$I_N(\mathbf{g}) = CM_\tau A(\theta_B)\left|F_N(\mathbf{g})\right|^2$$

$$\left|F_N(\mathbf{g})\right|^2 = \left|\sum_j b_j e^{i\mathbf{g}\cdot\mathbf{r}_j} e^{-W_j}\right|$$

$$I_M(\mathbf{g}_{hkl}) = C\left(\frac{\gamma e^2}{2mc^2}\right)^2 M_{\mathbf{g}} A(\theta_B)\left|F_M(\mathbf{g}_{hkl})\right|^2$$

$$F_M(\mathbf{g}_{hkl}) = \sum_{j=1}^{N} e^{i\mathbf{g}\cdot\mathbf{r}_j}\,\hat{\mathbf{g}}\times\left[\boldsymbol{M}_j(\mathbf{g})\times\hat{\mathbf{g}}\right]e^{-W_j}$$

$$\left|F_M(\mathbf{g})\right|^2 = \left\langle 1-\left(\hat{\mathbf{g}}\cdot\hat{\boldsymbol{\eta}}\right)^2\right\rangle\left\langle\mu^z\right\rangle^2 f^2(\mathbf{g})\left|\sum_j \eta_j e^{i\mathbf{g}\cdot\mathbf{r}_j} e^{-W_j}\right|^2$$

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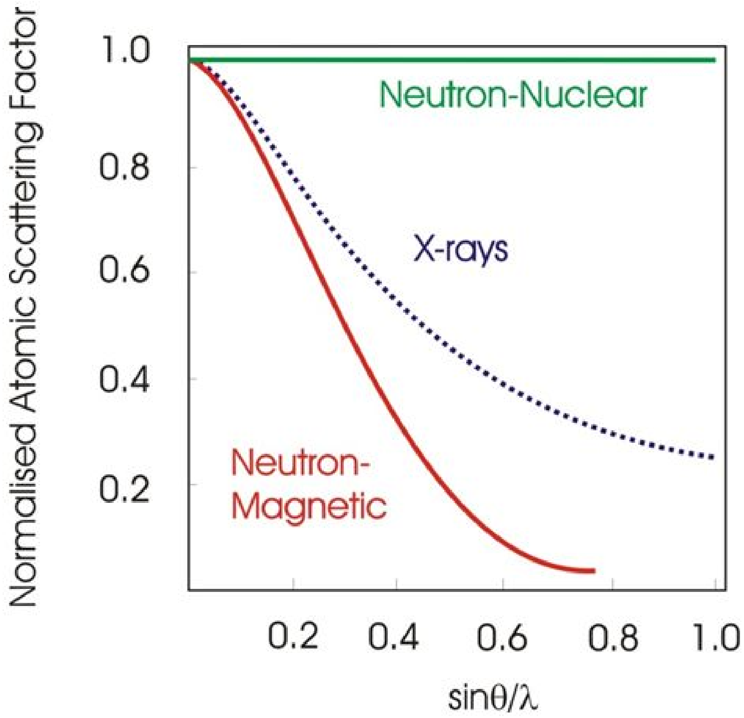
Neutrons and X-rays are Complementary

magnetic scattering amplitude for an ion is related to the Fourier Transform of the total magnetisation density, M(r)::

$$M(q) = \int M(r) \exp\left[i (q \cdot r) \right] d^3 r$$



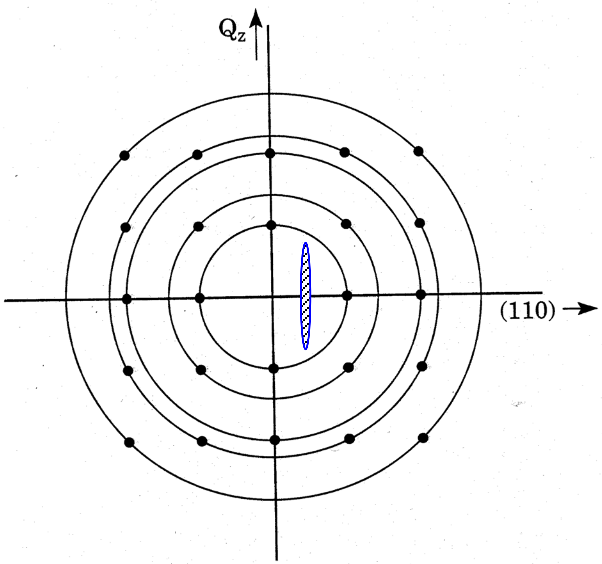
As the magnetism arises from unpaired electrons in *outer shells* and not the nucleus there is a dependence on intensity, similar to the $\sin(\theta) / \lambda$ used for x-rays

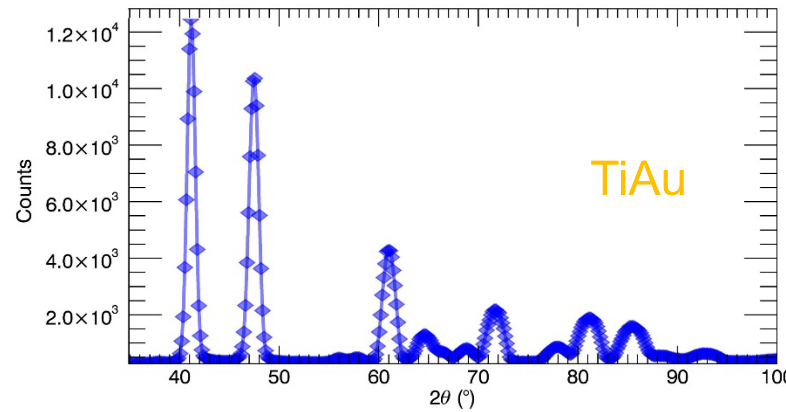
Magnetic X-ray Cross Sections

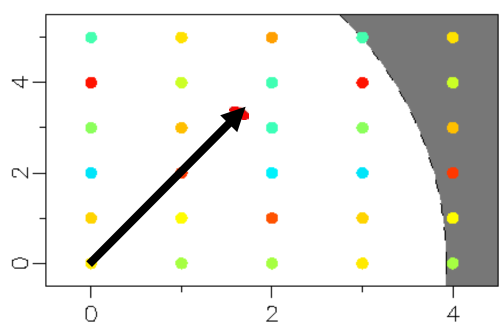
$$F_j(E) = \sigma^{(0)}(E)\,\varepsilon_i \cdot \varepsilon_o^* + \sigma^{(1)}(E)\,\varepsilon_i \times \varepsilon_o^* \cdot M_j + \sigma^{(2)}(E)\left(\left(\varepsilon_i \cdot M_j\right)\left(\varepsilon_o^* \cdot M_j\right) - \frac{1}{3}\varepsilon_i \cdot \varepsilon_o^*\right)$$

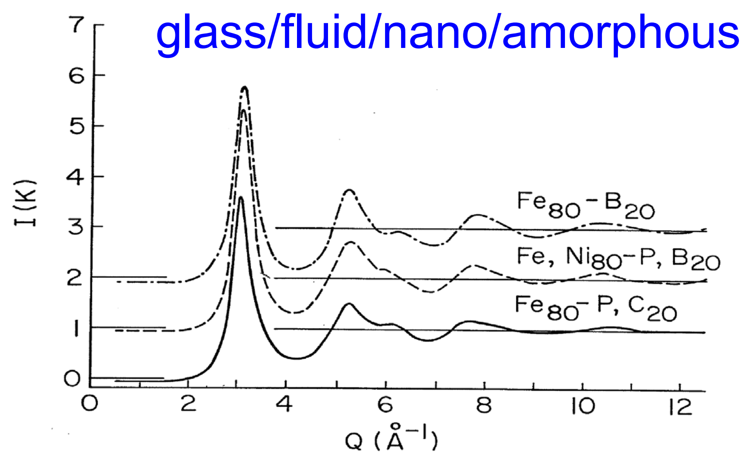
$$I = \left|\sum_j e^{ig\cdot r_j}\sigma_j^{(1)}(E)\,\varepsilon_i \times \varepsilon_o^* \cdot M_j\right|^2$$

Reciprocal Space for Powder





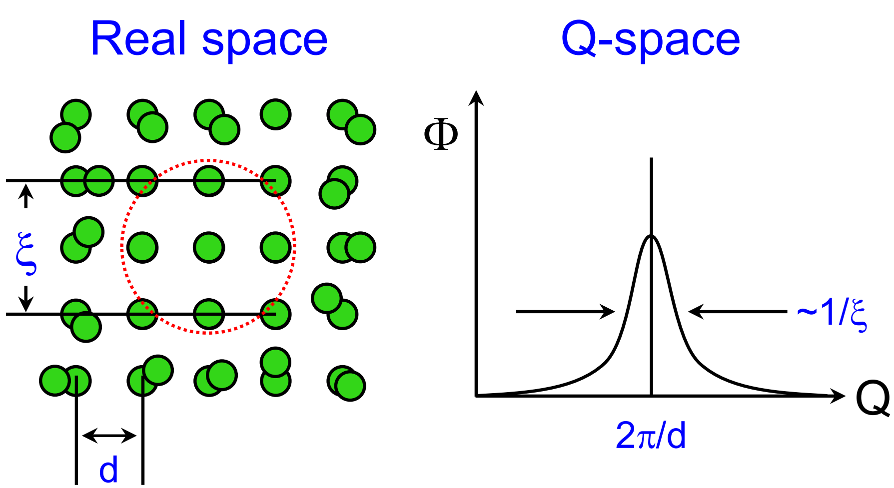


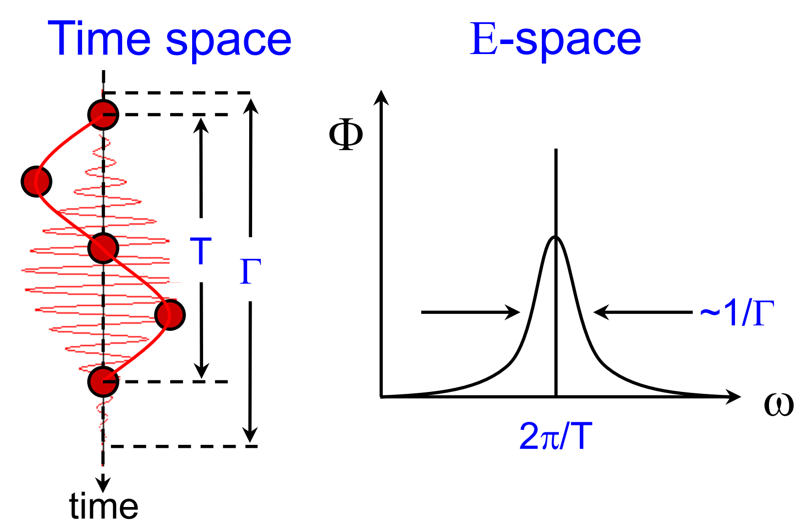


Correlations

The scattered neutron flux $\Phi(\vec{Q},\hbar\omega)$ is proportional to the <u>space</u> ($\vec{r}$) and <u>time</u> (t) Fourier transform of the <u>probability</u> $G(\vec{r},t)$ of finding one or two atoms (*spins*) separated by a particular distance (*angle)* at a particular time.

$$\Phi \propto \frac{\partial^2\sigma}{\partial\Omega\partial\omega} \propto \iint e^{i(\vec{Q}\cdot\vec{r}-\omega t)} G(\vec{r},t)\, d^3\vec{r}\, dt$$





Neutron Scattering Techniques

Diffraction

- **Crystallography**–powder, single crystal
  Atomic positions, site occupancies, lattice parameters, bond distances, mean-square vibrations as a function of T, H, P, E, …
- **Magnetism**
  Magnetic structure, order parameter, spin directions, spin density distribution
  Phase Transitions and Critical Phenomena (Scaling, Universality)
- **Small Angle Neutron Scattering (SANS)**
  Ferromagnetic Correlations, Vortex Structures, Domain Structures, Grain boundaries, twin boundaries, defect structures, nanoparticles, skyrmions, …
- **Thin Film Reflectometry**
  Density profiles, Magnetic structures, Magnetization profiles, Surface and Interface properties (flatness, roughness)

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Inelastic Scattering

Lattice Dynamics

Phonon Dispersion, Density of States
Interatomic Force constants
Mean-square vibrations
Diffusion

Spin Dynamics

Magnon Dispersion, Exchange interactions
Magnetic Anisotropy
Magnetic Fluctuation Behavior
Crystal Field Levels
Magnetic-Structural Coupling

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May 2017

Oak Ridge National Laboratory

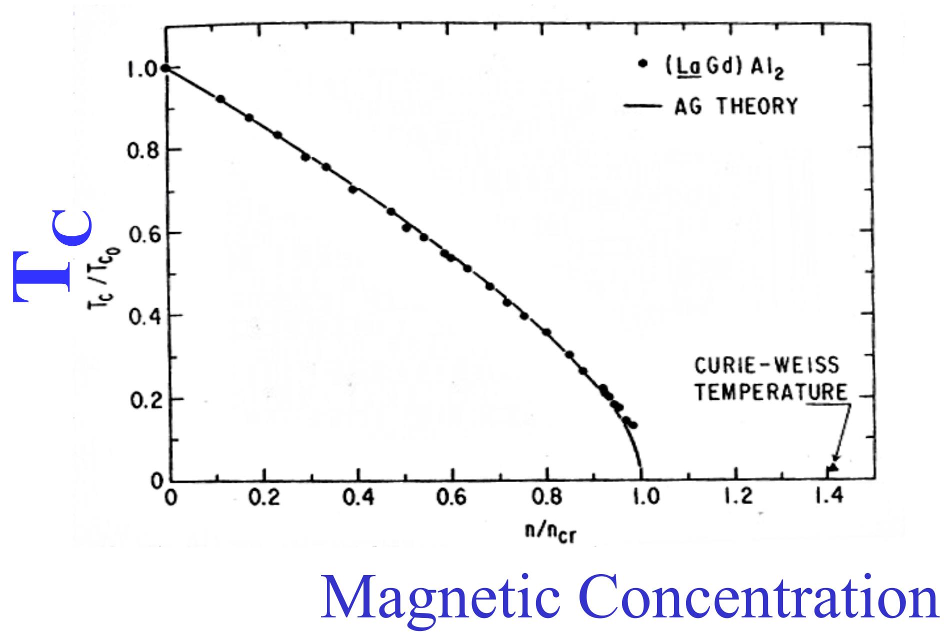
High Flux Isotope Reactor

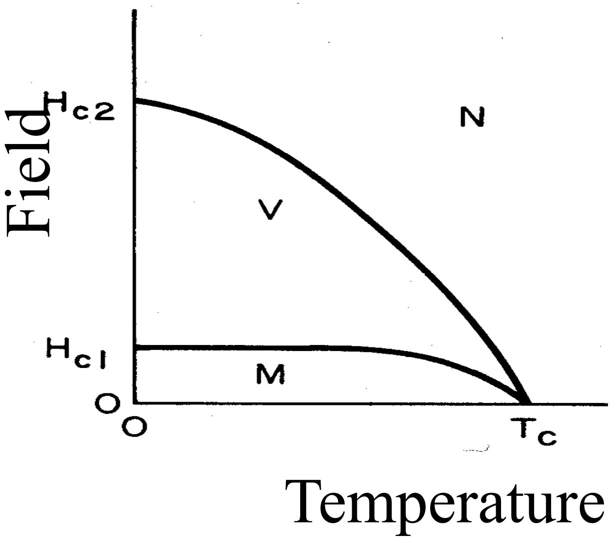
Spallation Neutron Source

Materials that are both Magnetic and Superconducting

Magnetic Impurities Cause Spin depairing

Magnetic Fields and Superconductivity are Antagonists





M. B. Maple, Appl. Phys. **9**,179 (1976)

Magnetic Superconductor History

$(k\uparrow; -k\downarrow)$

- Pure Superconductors (1911→ …)
- **X** Magnetic Impurities **X**
- Concentrated Magnetic Systems (Exceptions to the Rule!)
  - C-15 Cubic Laves phase (Ce-Ho)Ru_2 ('60's-'70's)
- Magnetic Sublattice—Long Range Order
  - Chevrel Phase $DyMo_6S_8$ ('70's)
- Ferromagnets—Competition & Coexistence ⇐
  - Chevrel Phase $HoMo_6(S\text{-}Se)_8$, $ErRh_4B_4$ ('70's – 80's)
- High T_C cuprates—Cu spin order & fluctuations
  - Cuprates $RBa_2Cu_3O_7$ [123], R_2CuO_4 [214] ('80's→…)
- Borocarbides
  - $HoNi_2B_2C$, $ErNi_2B_2C$ ('90's→…)
- New Ferromagnetic Superconductors
  - Ruthenates $RuSr_2GdCu_2O_8$, $RuSr_2(Eu\text{-}Ce)_2Cu_2O_{10}$; $ZrZn_2$, UGe_2 (2000's →…)
- Sodium cobaltates (Magnetic, thermoelectric, and Superconducting) 2000's→…
  - Na_xCoO_2 (+ H_20) [just add water for superconductivity !]
- Iron-based superconductors (2008→…)
  - $R(O_{1-x}F_x)FeAs$; $Sr_{1-x}K_xFe_2As_2$; $LiFeAs$; $Fe(Se_{1-x}Te_x)$
  - 1:1:1:1 1:2:2 1:1:1 1:1

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Ferromagnetic Superconductors

$(Ce\text{-}Ho)Ru_2$

$HoMo_6S_8$, $HoMo_6Se_8$, $ErRh_4B_4$

$ErNi_2B_2C$

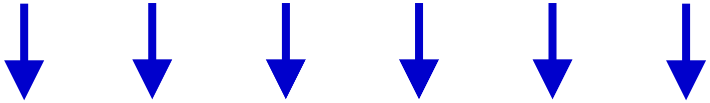
$RuSr_2GdCu_2O_8$ & $RuSr_2Eu_{2-x}Ce_xCu_2O_{10}$

$(Li\text{-}Fe)OHFeSe$

UGe_2, $ZrZn_2$, UCoGe, URhGe, C/S

Magnetic Structures

Ferromagnet

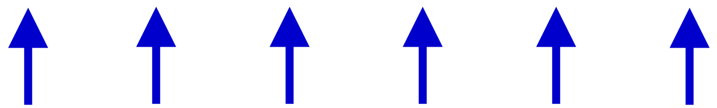


Antiferromagnet

Spin Density Wave

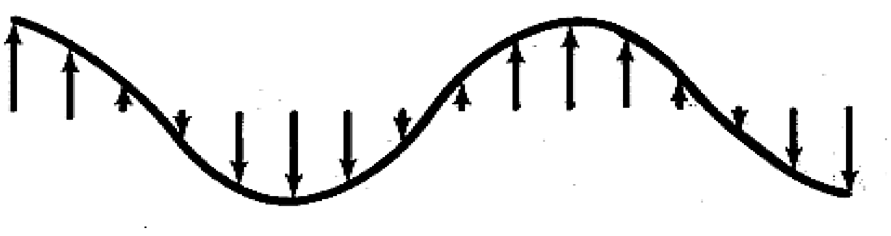
Magnetic Structures

Ferromagnet



Antiferromagnet

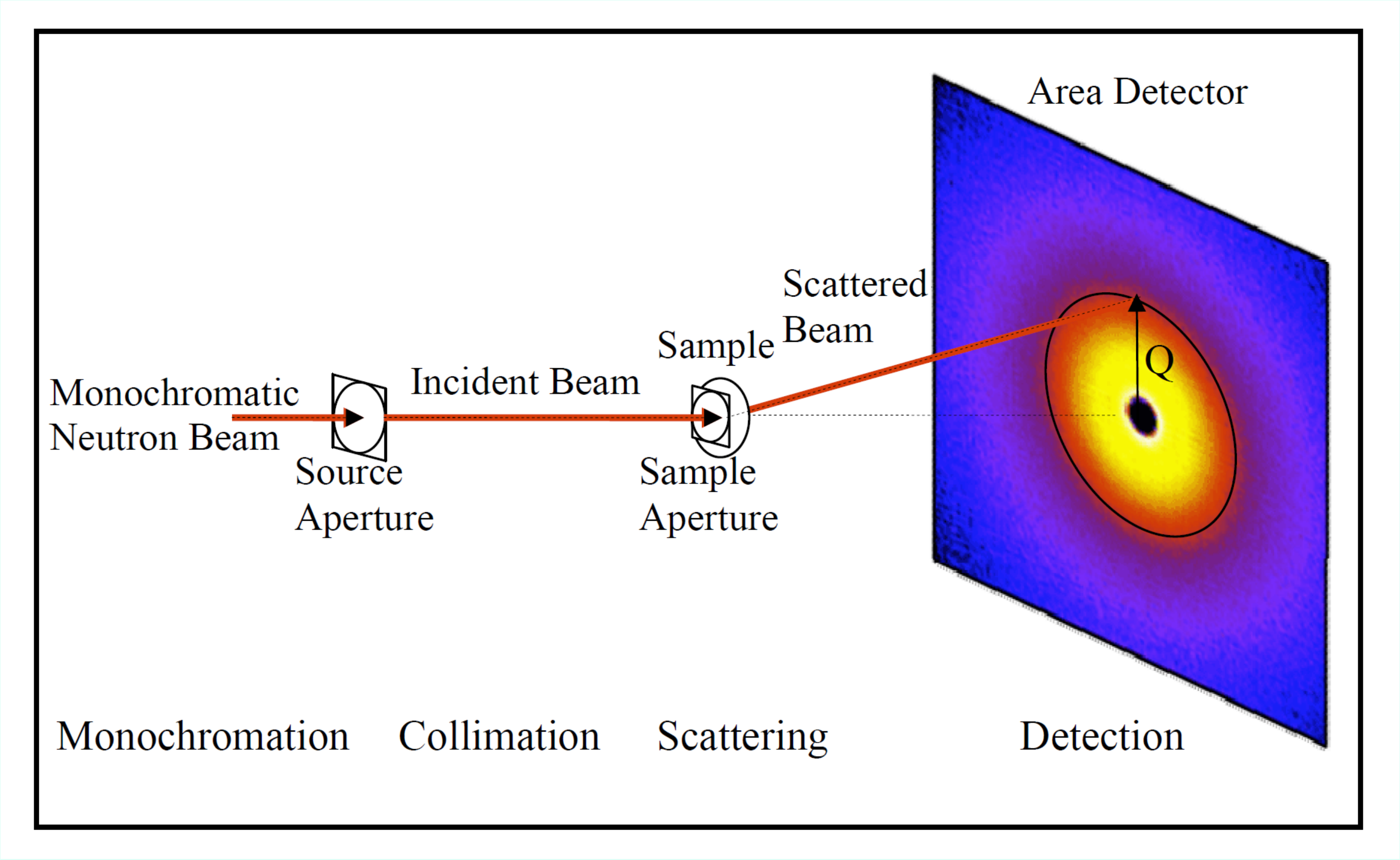
Spin Density Wave



Chevrel Phase Superconductors

	$HoMo_6S_8$,	$HoMo_6Se_8$,	$ErRh_4B_4$
$[(HoS_8)Mo_6$ Magnetic Lattice Isolated]			
T_{super} =	1.8 K	5.6 K	8.6 K
T_{ferro} =	0.7 K	0.5 K	0.9 K
$T_{reentrant}$ =	0.7 K	< 0 K	0.9 K

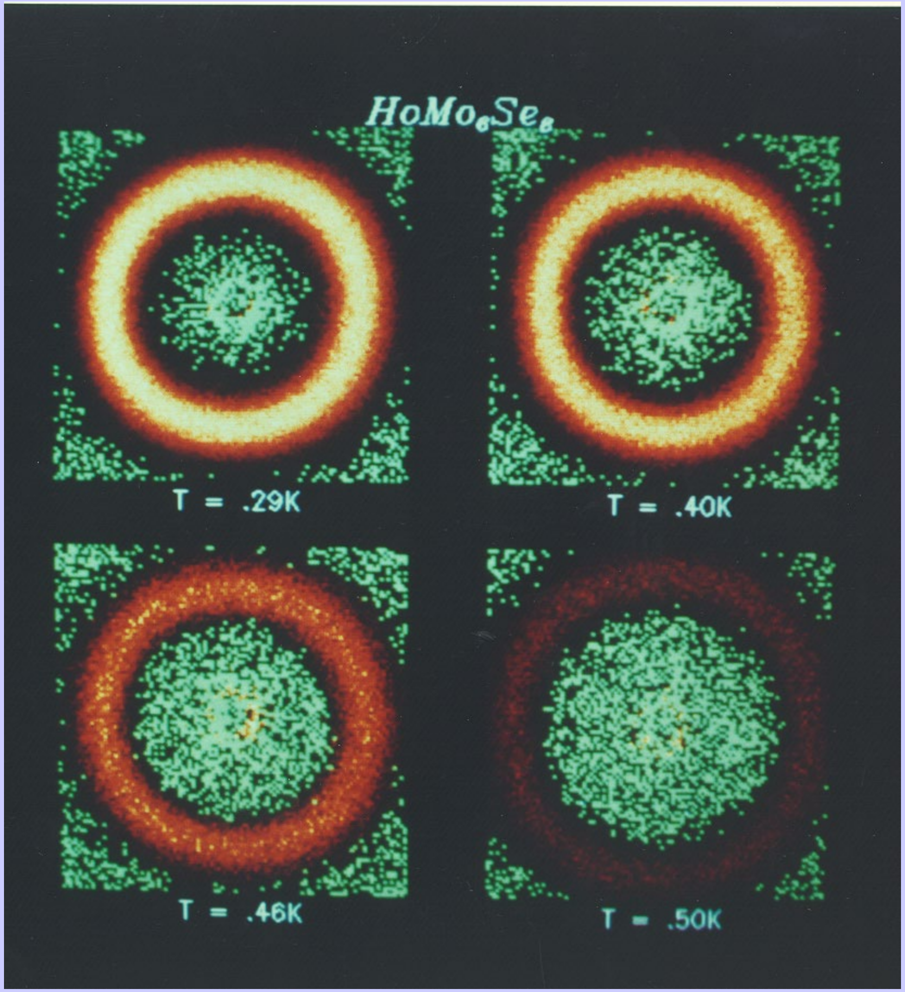
Small Angle Neutron Scattering



$HoMo_6Se_8$

T_S=5.6 K

T_M=0.5K



~100 Å
(10 nm)
periodicity

J. W. Lynn, J. A. Gotaas, R. W. Erwin, R. A. Ferrell, J. K. Bhattacharjee, R. N. Shelton and P. Klavins, Phys. Rev. Lett. **52**, 133 (1984)

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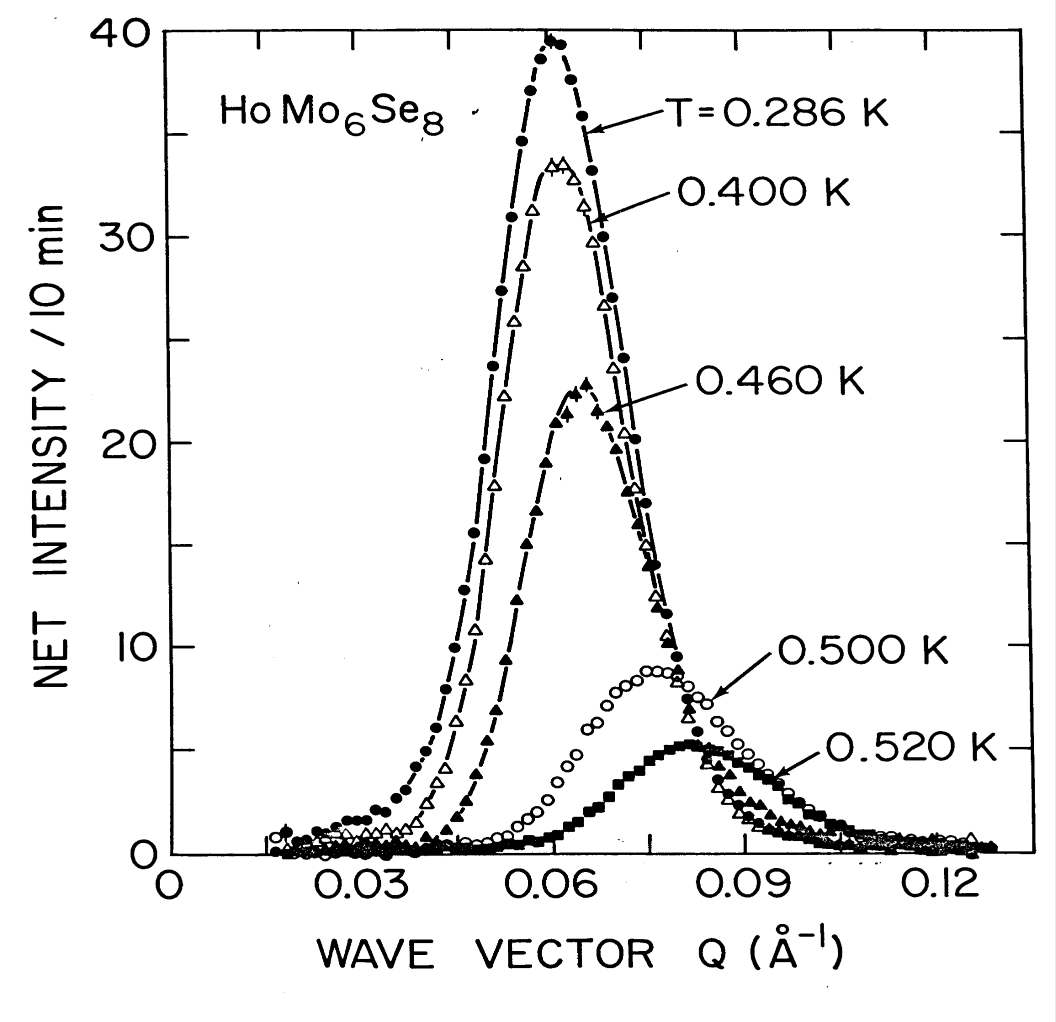
$HoMo_6Se_8$



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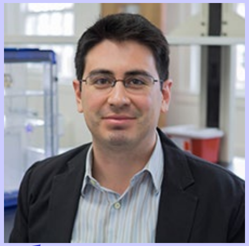
Iron-based High T_C Superconductors

Iron-based superconductors under Investigation at the NCNR

- FeSe, Fe_{1+x}(Se-Te), $K_xFe_{2-y}Se_2$ (1:1)
- LiFeAs (1:1:1)
- $LaO_{1-x}F_xFeAs$ LaOFeAs (1:1:1:1)
- $CeO_{1-x}F_xFe$(As,P) CeOFeAs
- $NdO_{1-x}F_xFeAs$ Nd…
- $PrO_{1-x}F_xFeAs$ Pr…
- $BaFe_2As_2$, $SrFe_2As_2$, $CaFe_2As_2$ (1:2:2)
- $CaFe_2As_2$, Under Pressure; doping
  - https://www.nist.gov/people/jeffrey-w-lynn

$^{7}\mathrm{Li}_{1-x}\mathrm{Fe}_{x}\mathrm{ODFeSe}$



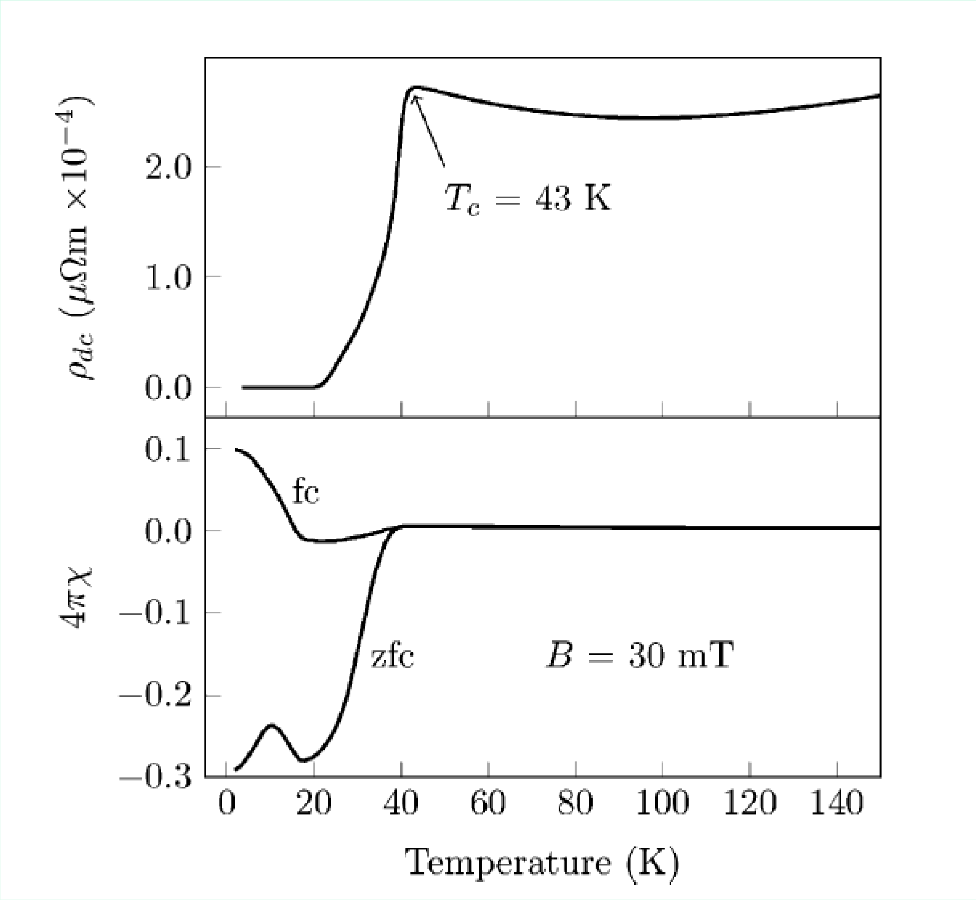
Neutron Investigation of the Magnetic Scattering in an Iron-based Ferromagnetic Superconductor
Jeffrey W. Lynn[1], Xiuquan Zhou[2], Christopher K. H. Borg[2], Shanta R. Saha[3], Johnpierre Paglione[3], and Efrain E. Rodriguez[2]
Phys. Rev. B **92**, 060510(R) (2015).

The Preparation and Phase Diagram of Superconducting ($^{7}Li_{1-x}Fe_{x}OD$)FeSe
Xiuquan Zhou[2], Christopher K. H. Borg[2], Jeffrey W. Lynn[1], Shanta R. Saha[3], Johnpierre Paglione[3], and Efrain E. Rodriguez[2],
J. Mater. Chem. C **4**, 3934 (2016).

Long range magnetic order in Mn-doped (LiOH)FeSe, Brandon Wilfong, Xiuquan Zhou, Huafei Zhang, Navneeth Babra, Craig M. Brown, Jeffery W. Lynn, Simon A. J. Kimber, Keith M. Taddei, Johnpierre Paglione, and Efrain E. Rodriguez, Phys. Rev. Materials **4**, 034803 (2020).

[1]NIST Center for Neutron Research, Gaithersburg, MD (USA)
[2]Department of Chemistry and Biochemistry, University of Maryland, College Park, MD (USA)
[3]Department of Physics, University of Maryland, College Park, MD (USA)

(Li-Fe)OHFeSe Ferromagnetic Superconductor

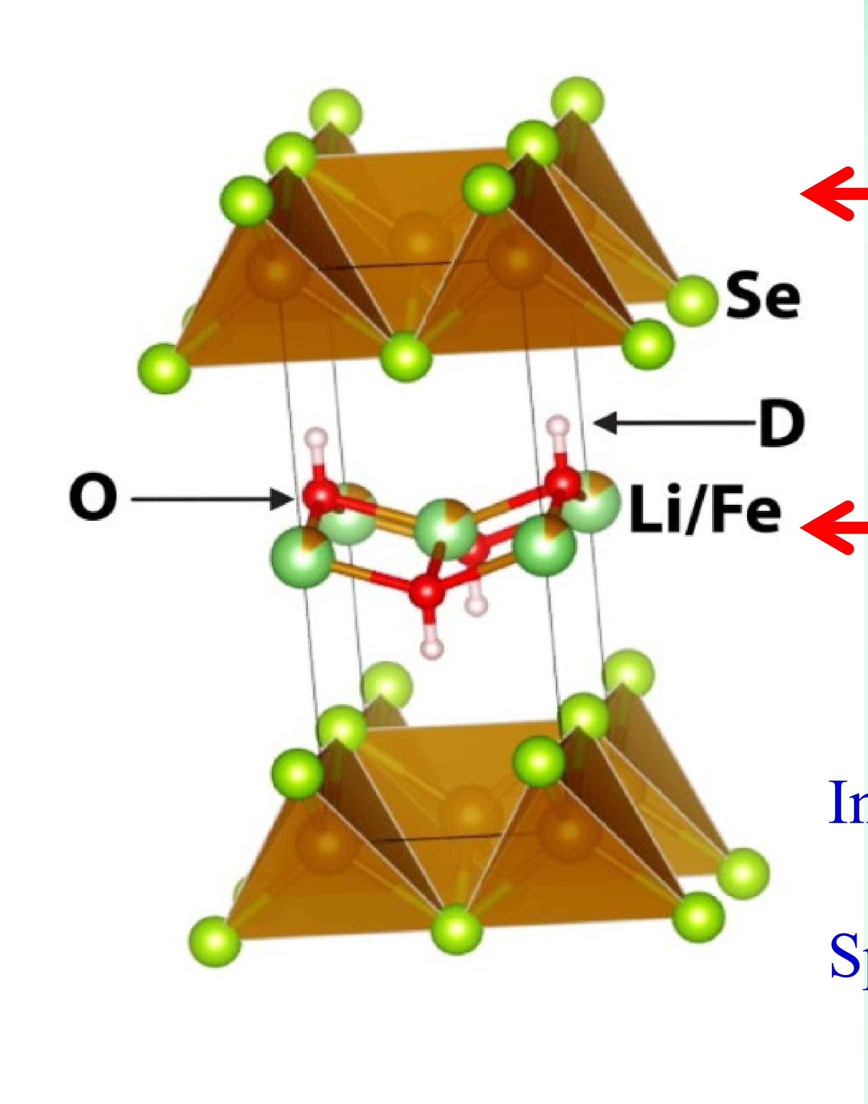


T_S=43 K

T_F=10 K

Coexistence of 3d-ferromagnetism and superconductivity in $[(Li_{1-x}Fe_x)OH](Fe_{1-y}Li_y)Se$, Ursula Pachmayr, Fabian Nitsche, Hubertus Luetkens, Sirko Kamusella, Felix Bruckner, Rajib Sarkar, Hans-Hennig Klauss, and Dirk Johrendt, Angew. Chem. Int. Ed. **54**, 293 (2015)

Crystal Structure



FeSe Superconducting Layer

Magnetic Layer

Incommensurate Long wavelength
Ordered state?
Spontaneous Vortex Lattice?

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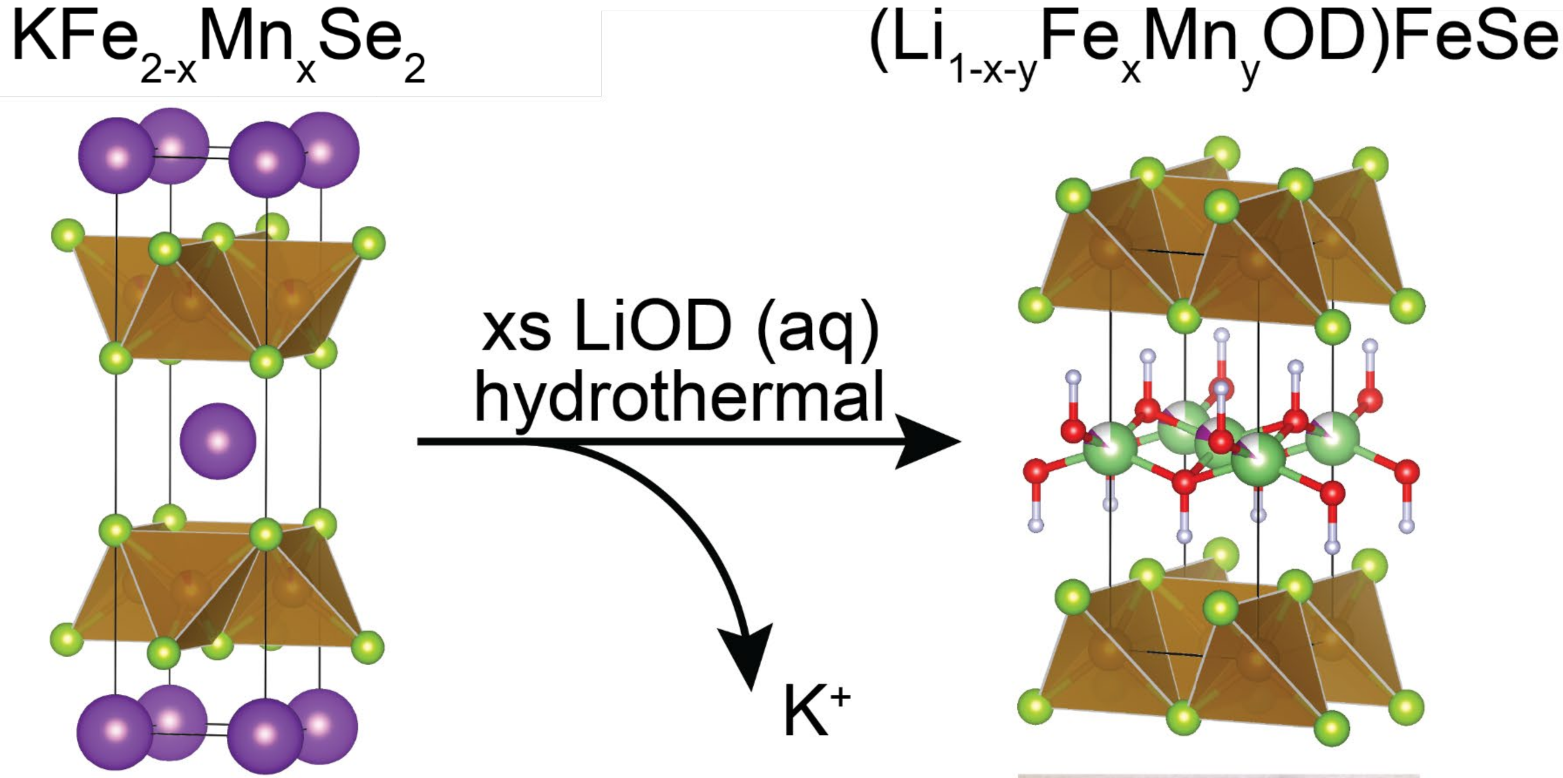
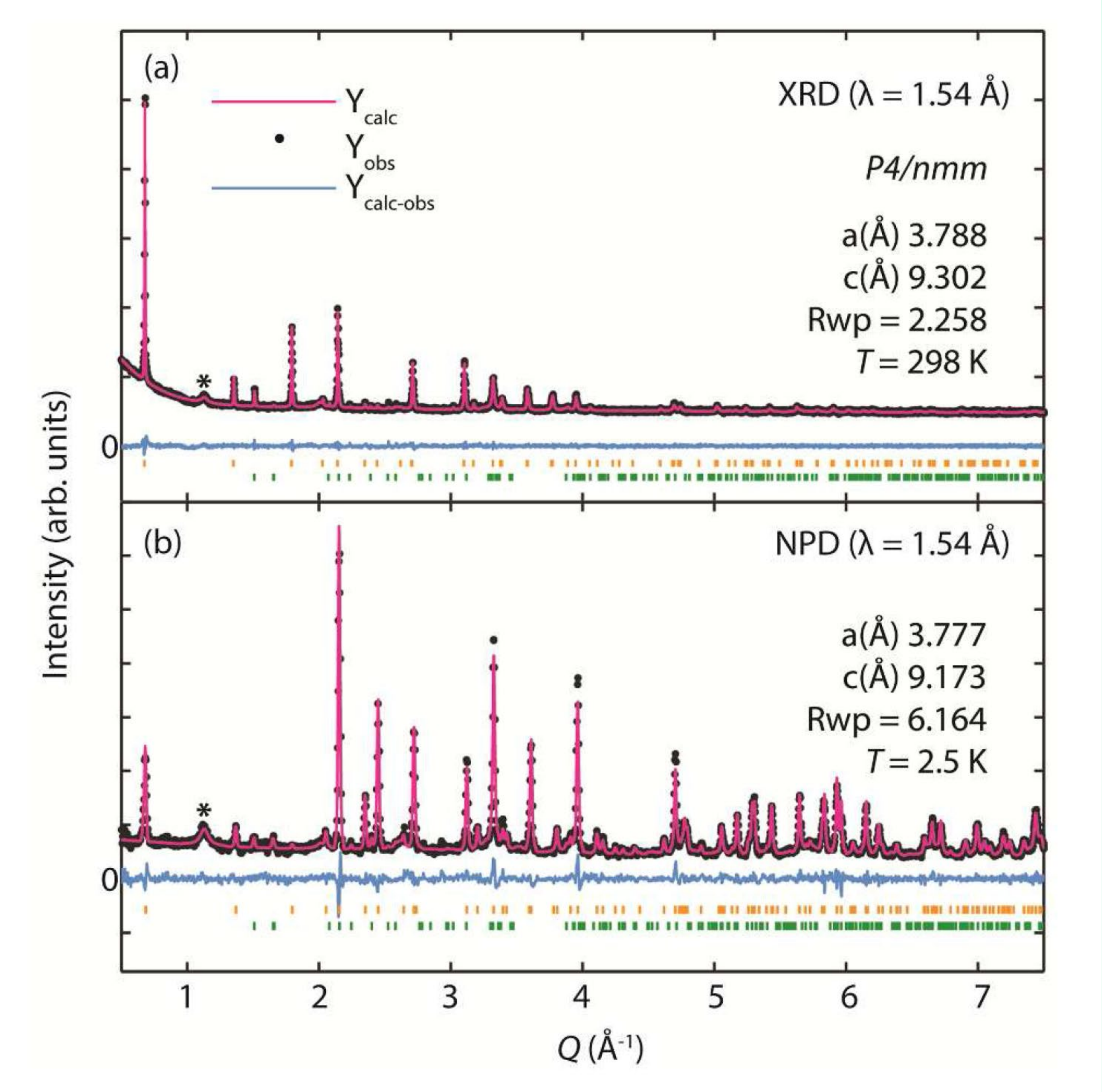
Synthesis and Structure



K + Fe + Mn + Se
self-flux method

Neutron and X-ray Diffraction



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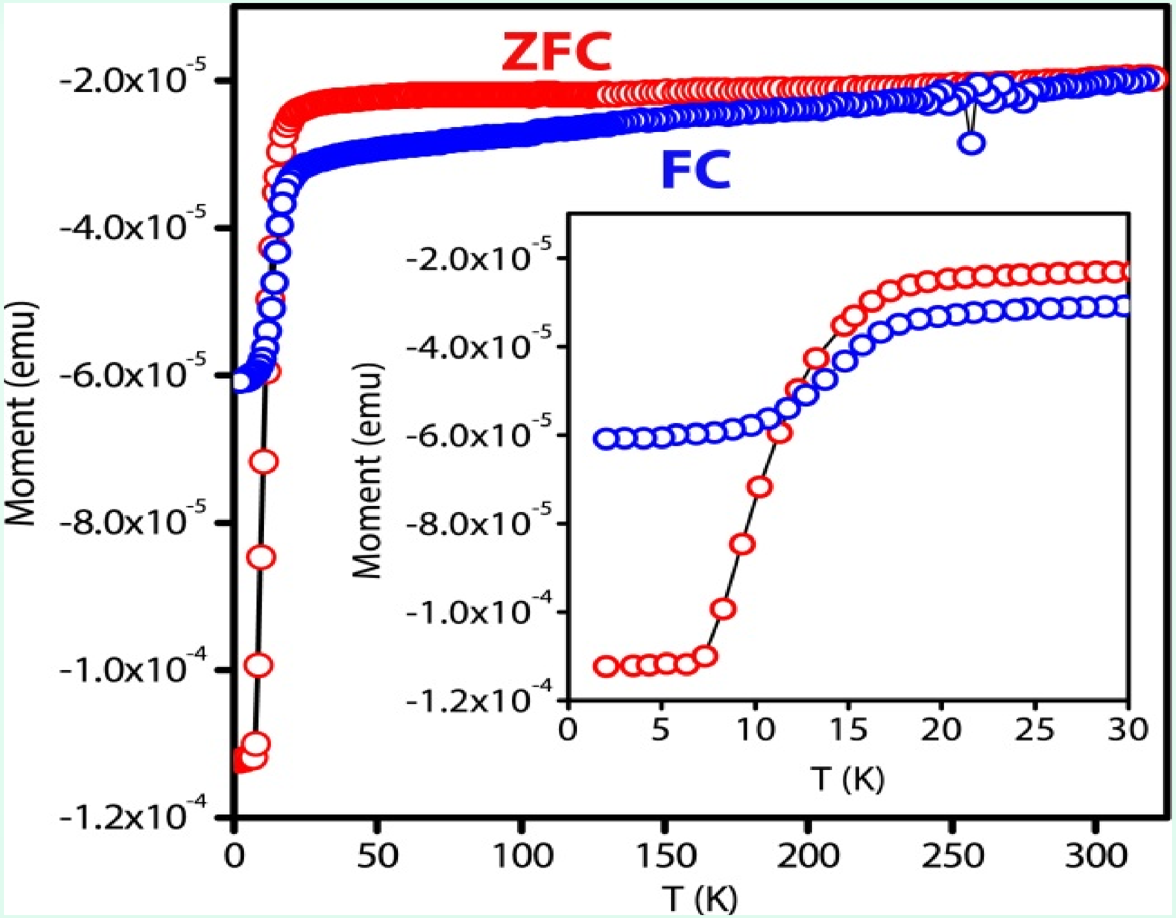
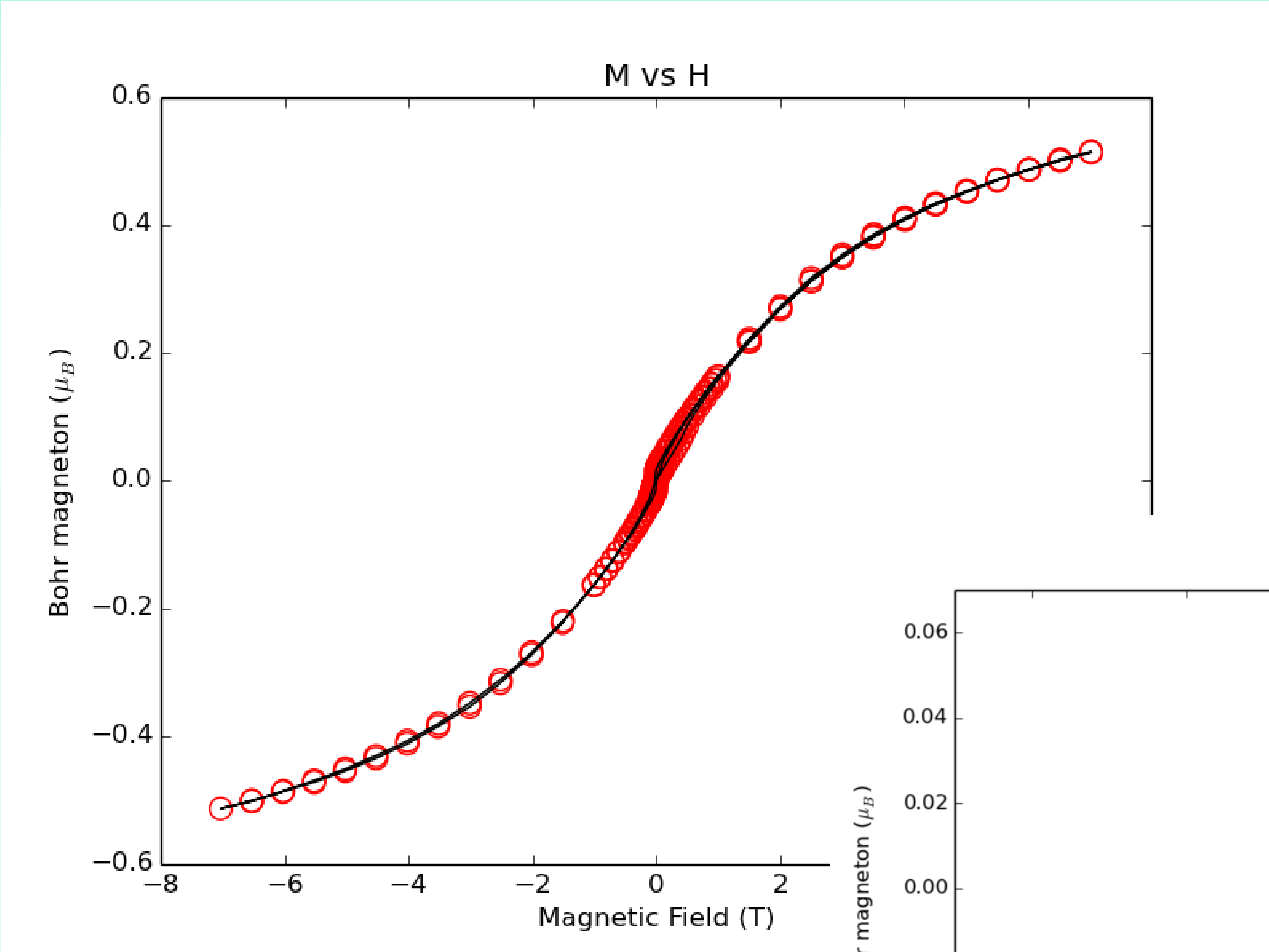
Magnetization for Tc = 18 K

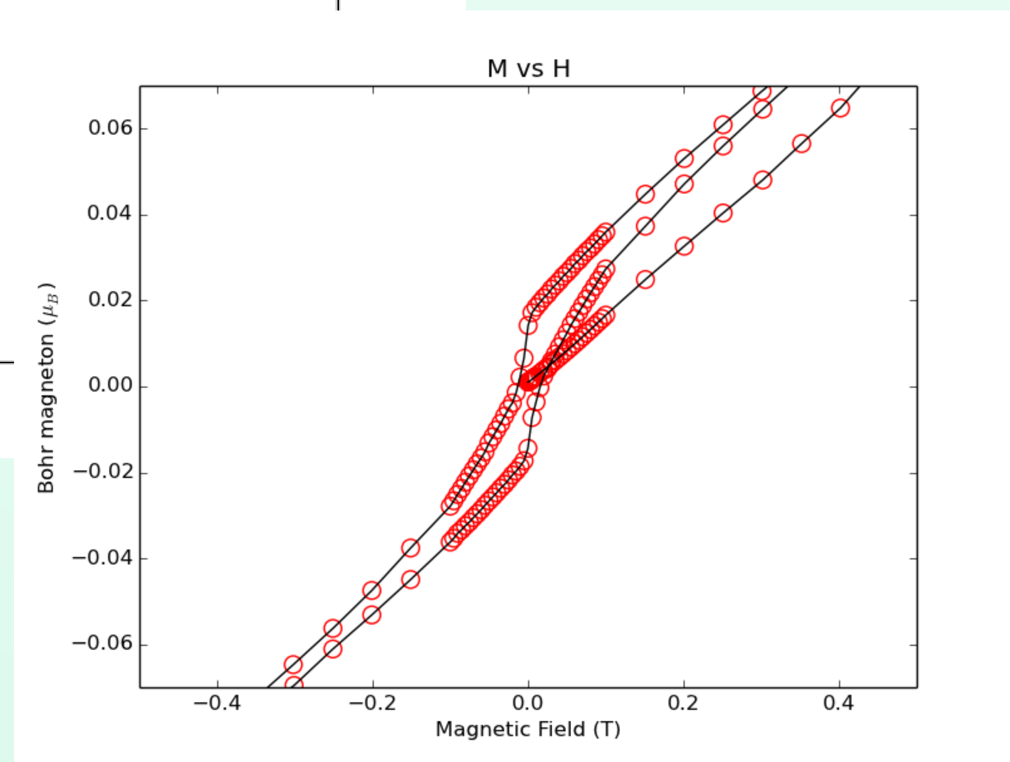
(polycrystalline sample)



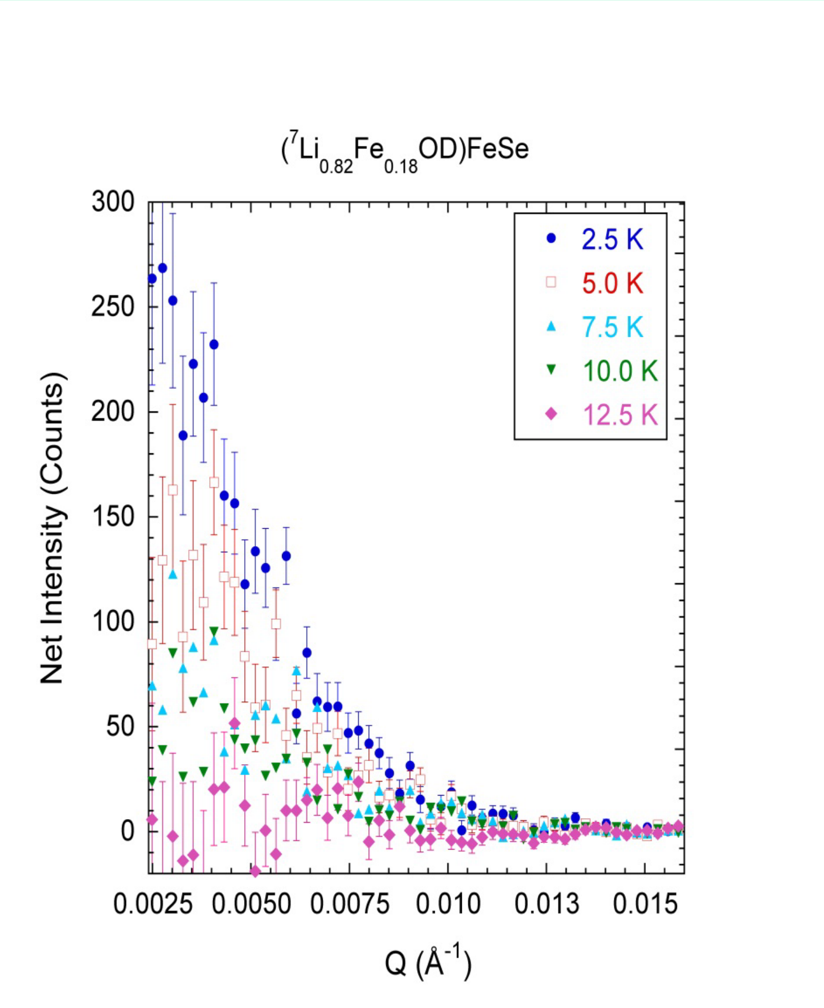
Ferromagnetic Magnetization

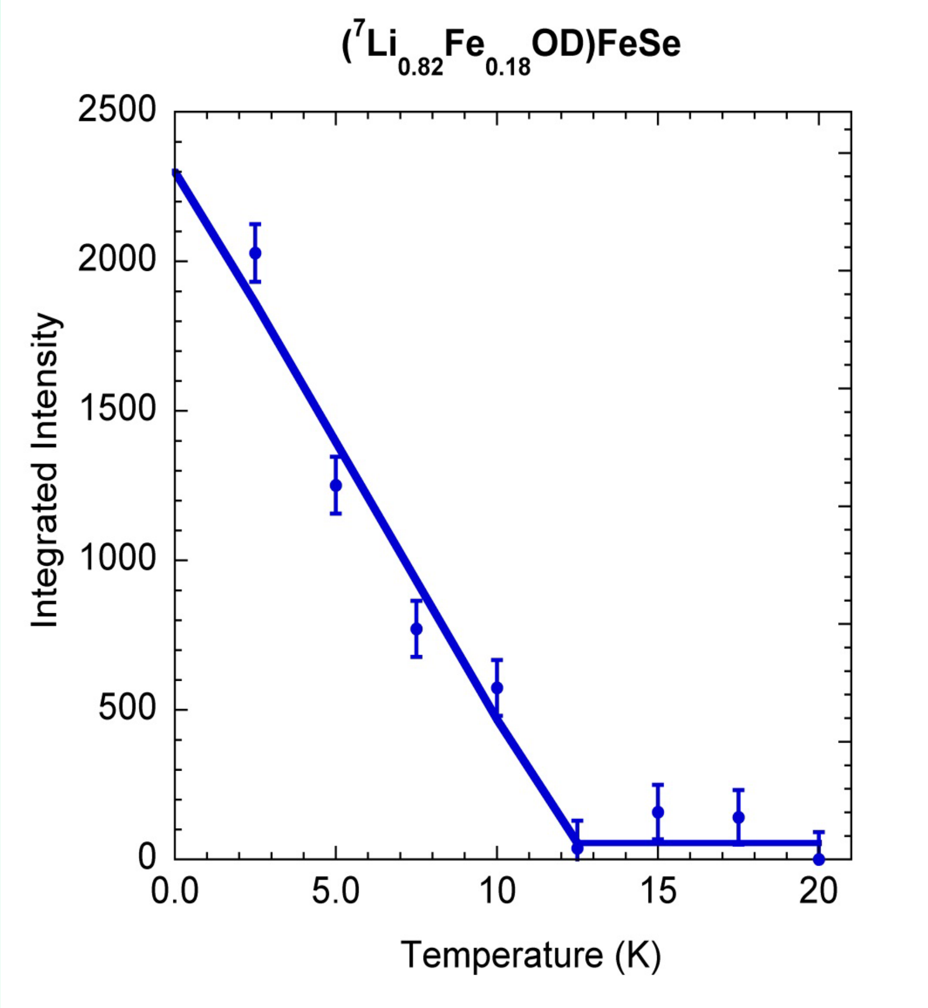


2 K

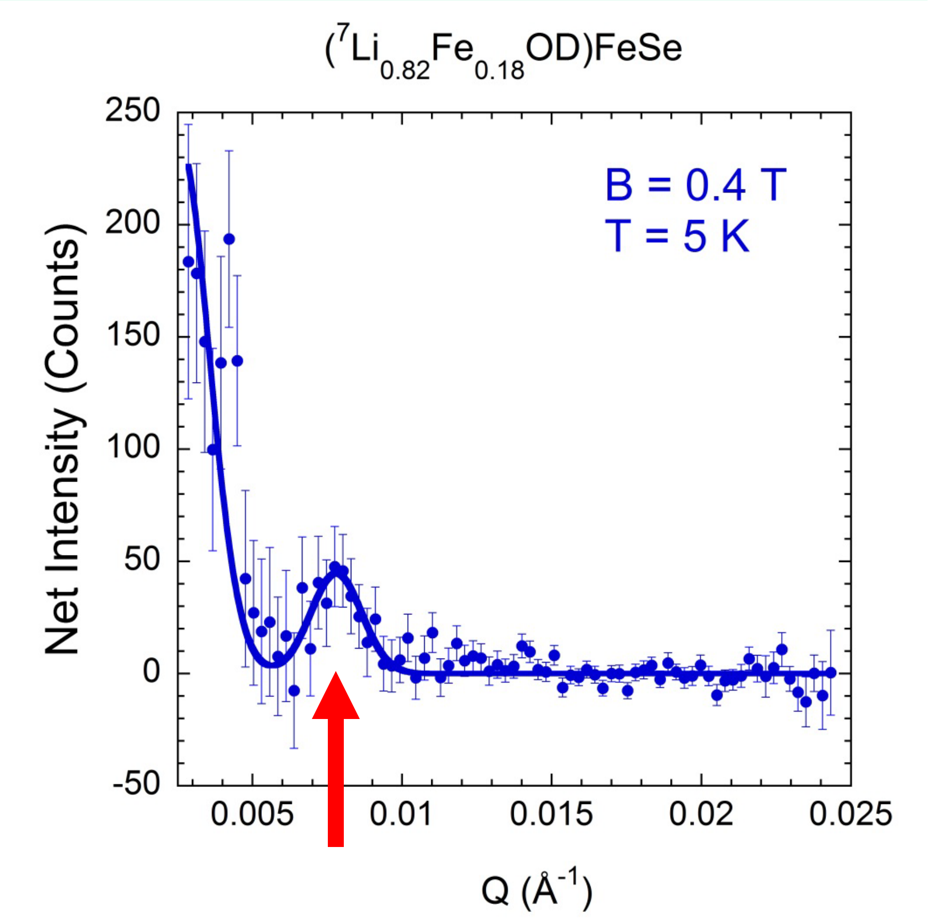


No Applied Magnetic Field

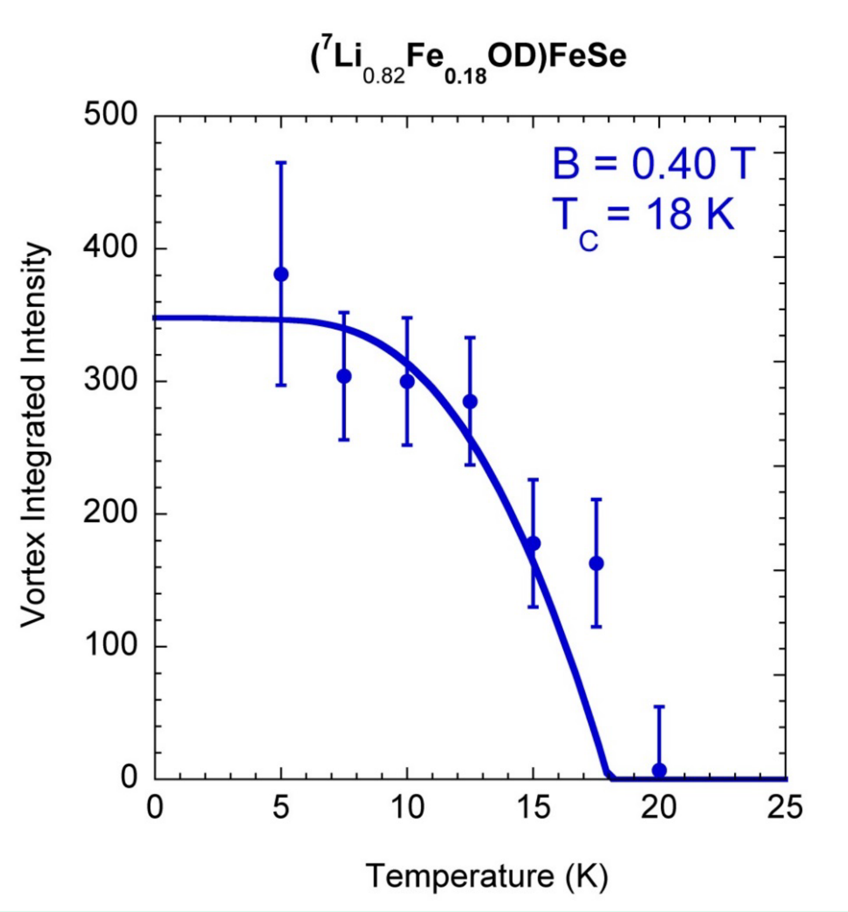




B = 0.4 T



($^7Li_{0.82}Fe_{0.18}OD$)FeSe
B = 0.4 T
T = 5 K
Net Intensity (Counts)
Q (Å^{-1})
250
200
150
100
50
0
-50
0.005
0.01
0.015
0.02
0.025



($^7Li_{0.82}Fe_{0.18}OD$)FeSe
B = 0.40 T
T_C = 18 K
Vortex Integrated Intensity
Temperature (K)
500
400
300
200
100
0
0
5
10
15
20
25

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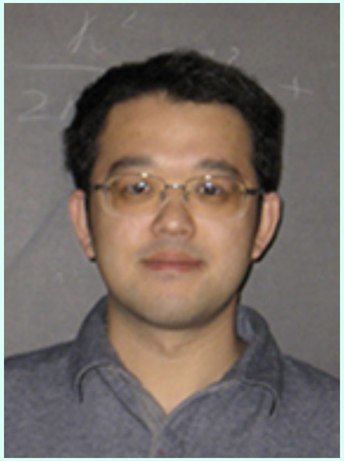
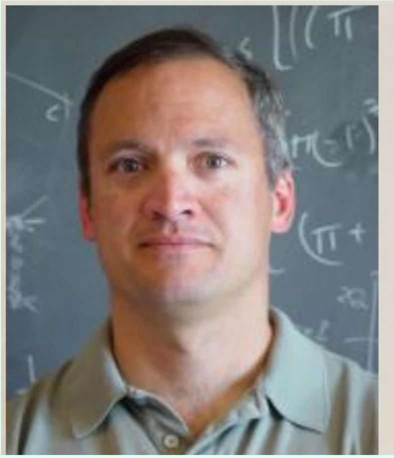
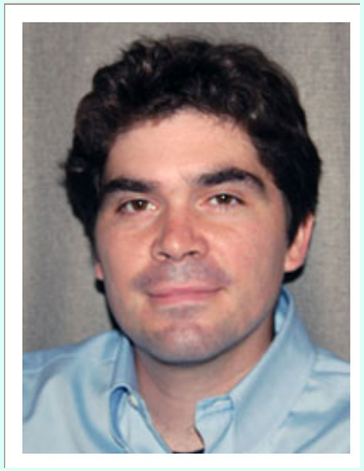
Singular angular magnetoresistance in a magnetic nodal semimetal

by T. Suzuki, L. Savary, J.-P. Liu, J. W. Lynn, L. Balents, and J. G. Checkelsky



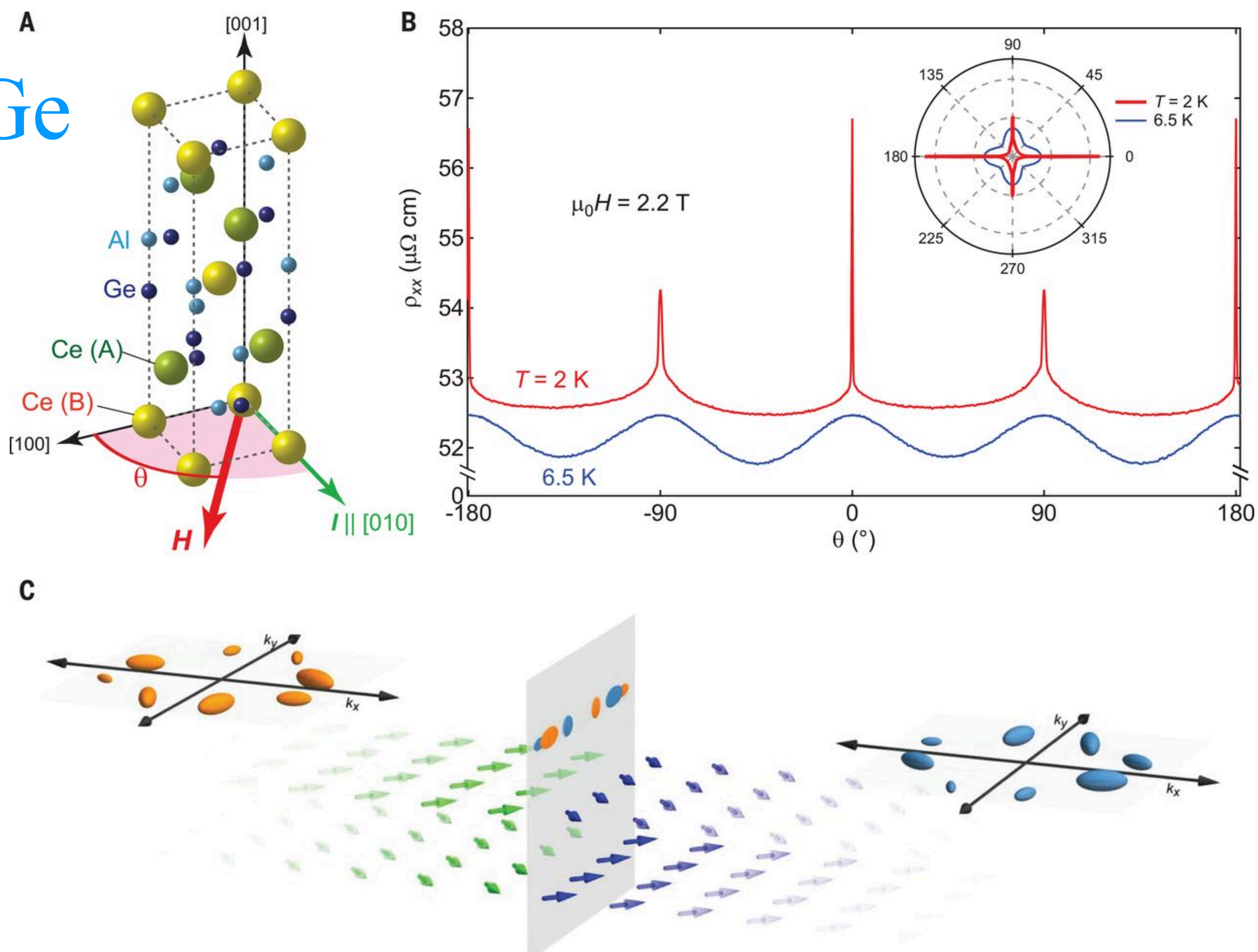




Science
Volume 365(6451):377-381
July 26, 2019

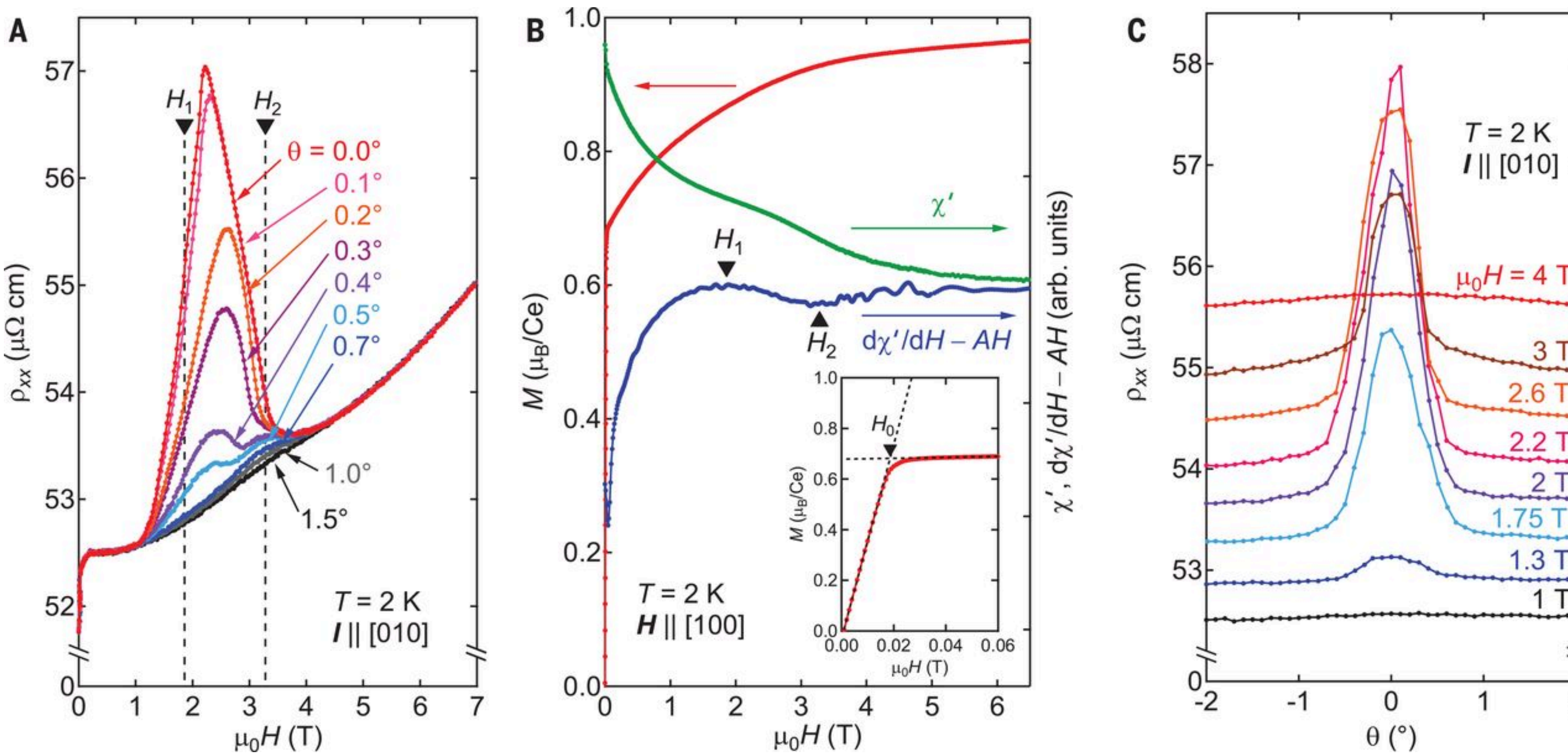
Fig. 1 Singular angular magnetoresistance (SAMR).

CeAlGe



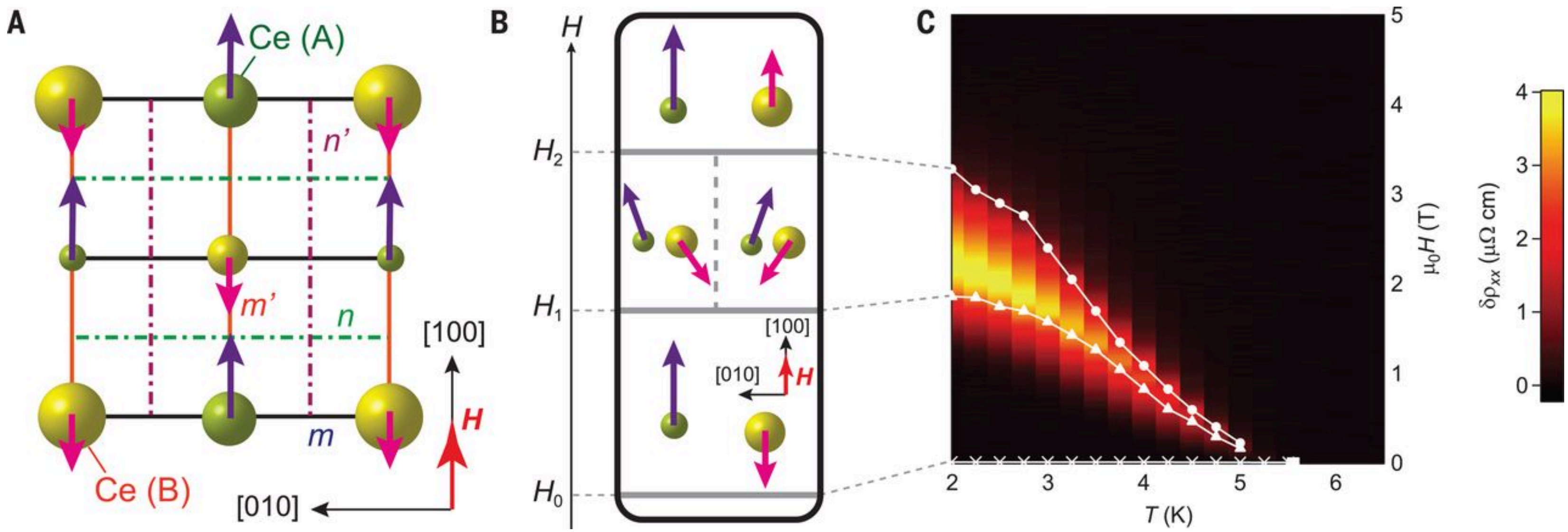
T. Suzuki et al. Science 2019;365:377-381

Fig. 2 Magnetic field dependence of SAMR.



T. Suzuki et al. Science 2019;365:377-381

Fig. 3 Phase diagram of SAMR.



T. Suzuki et al. Science 2019;365:377-381

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Magnetic Topological Properties in YMn_6Sn_6

- Competing magnetic states and fluctuation-driven scalar spin chirality in the kagome metal YMn_6Sn_6, **Nirmal J. Ghimire, Rebecca L. Dally**, L. Poudel, D. C. Jones, D. Michel, N. Thapa Magar, M. Bleuel, Michael A. McGuire, J. S. Jiang, John F. Mitchell, Jeffrey W. Lynn, and **I. I. Mazin**, Science Advances **6**, eabe2680 (2020).

- Chiral properties of the zero-field spiral state and field-induced magnetic phases of the itinerant kagome metal YMn_6Sn_6, **Rebecca L. Dally**, Jeffrey W. Lynn, Nirmal J. Ghimire, Dina Michel, Peter Siegfried, and Igor I. Mazin, Phys. Rev. B **103**, 094413 (2021).

Fig. 2 Magnetization and Hall effect of YMn6Sn6.

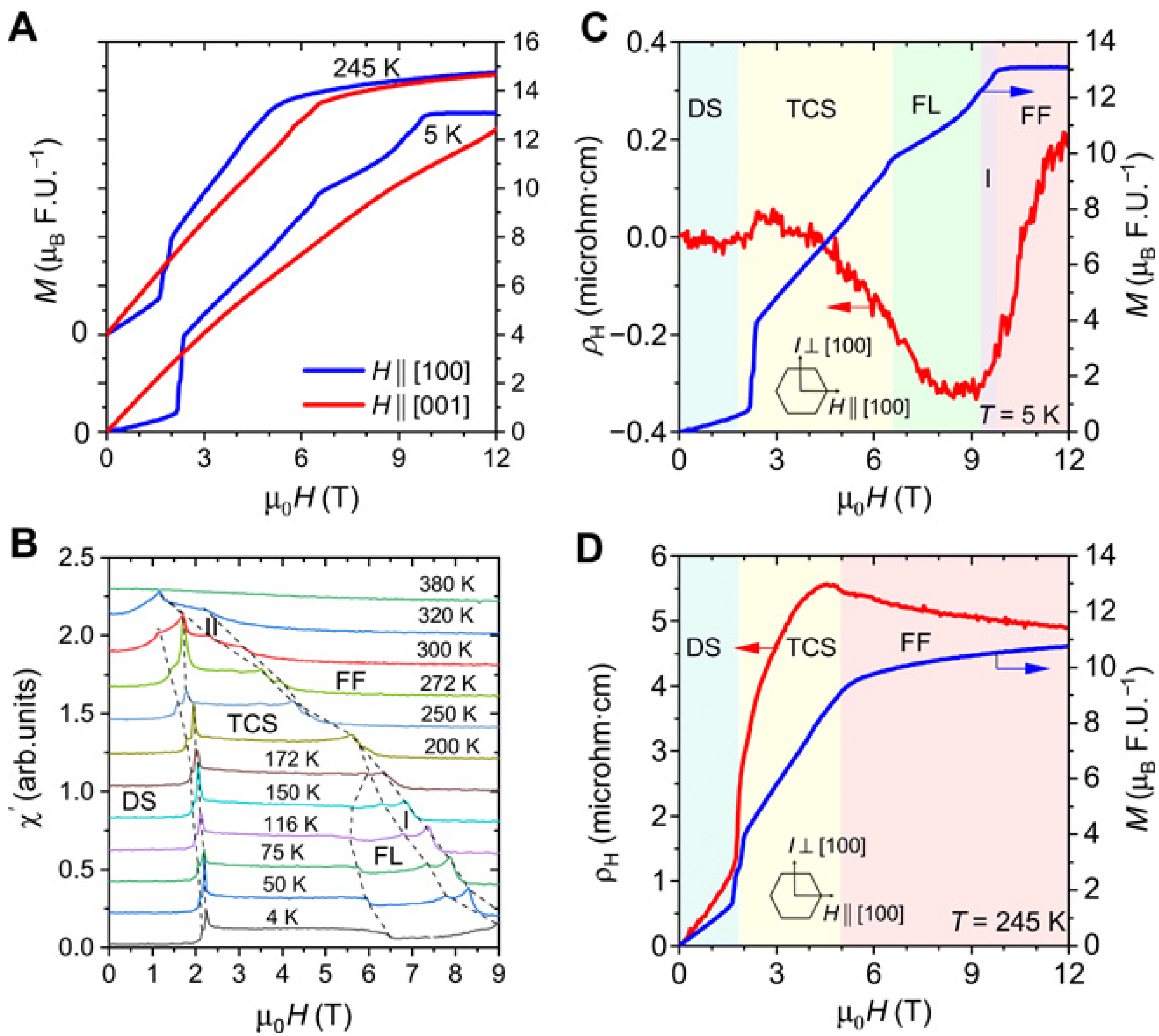

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Fig. 1 Crystal structure and electrical and magnetic properties of YMn6Sn6.

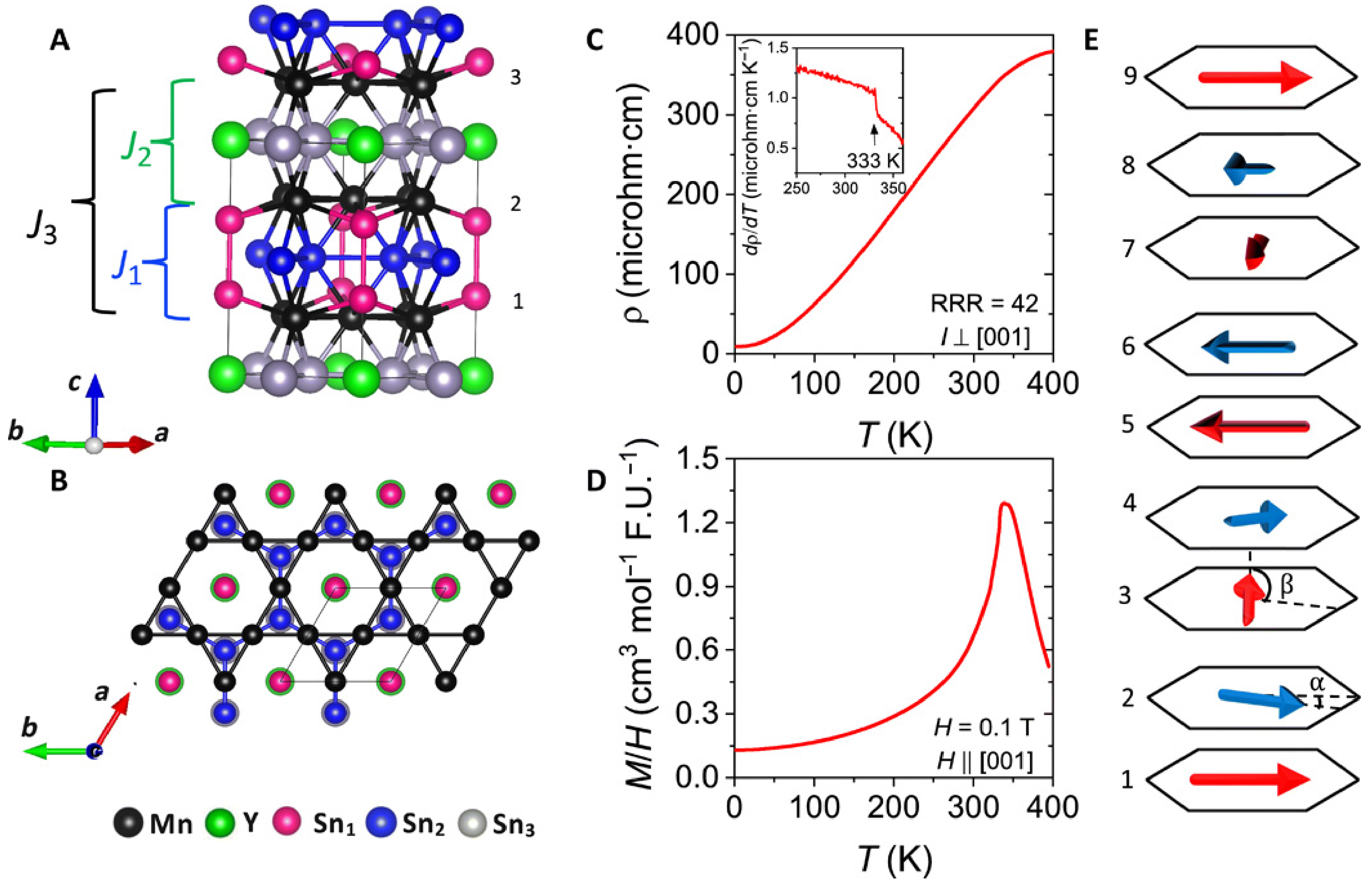

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Fig. 3 Single-crystal neutron diffraction of YMn6Sn6.

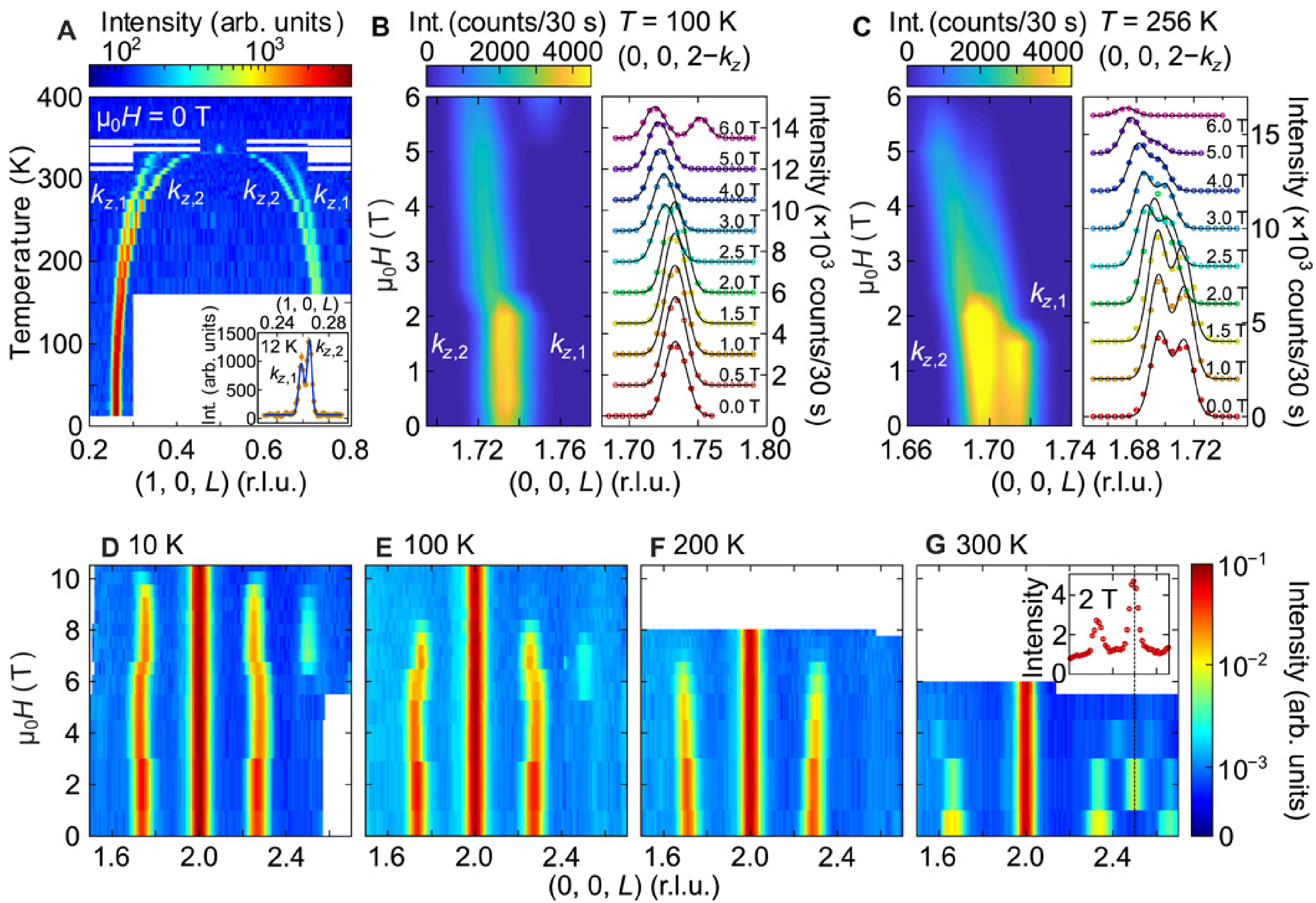

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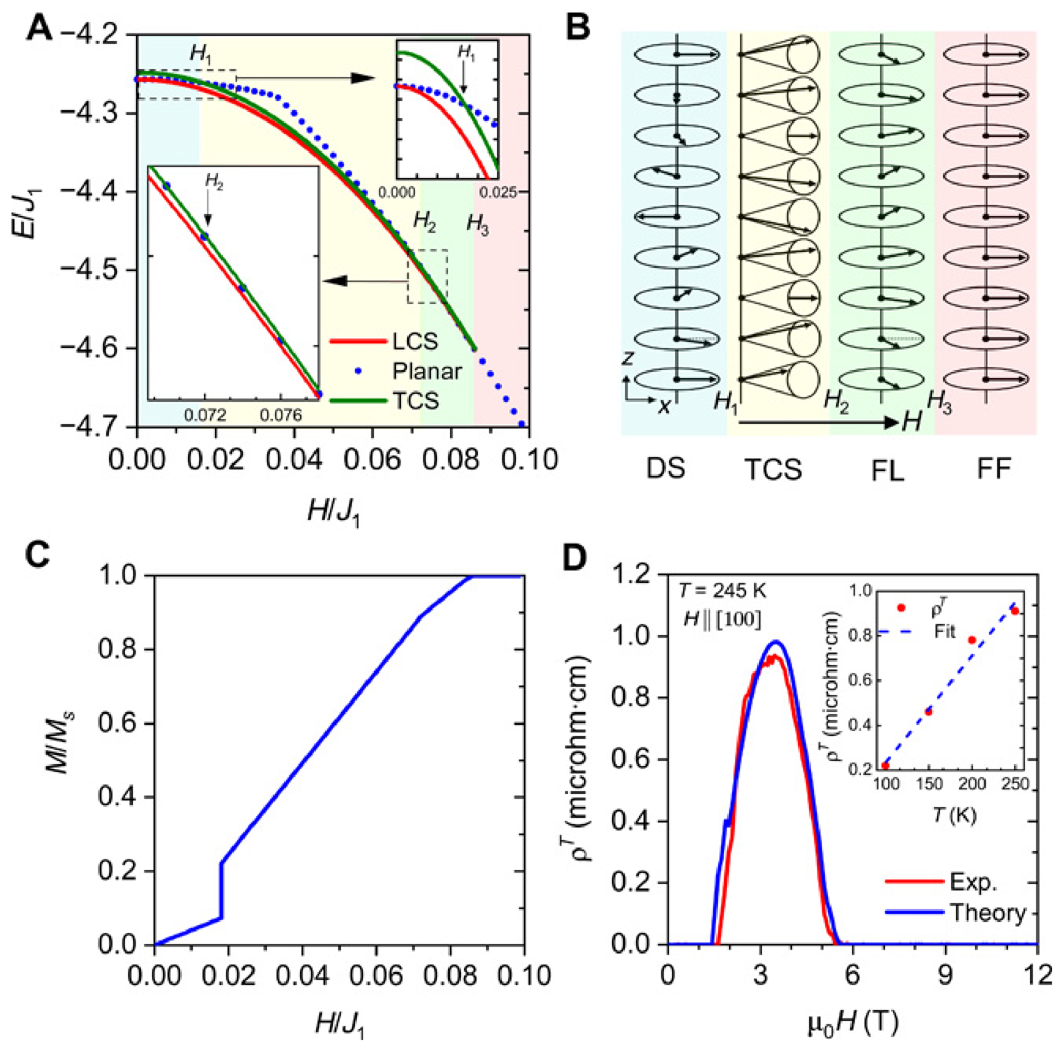
Fig. 4 First-principles calculation and phenomenological model of spin chirality for THE.



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Summary

- Neutron scattering is a powerful tool investigate crystal and magnetic structures, and lattice and magnetic excitations, over six orders of magnitude in length scale and energy scale.
- Neutron and X-ray scattering are complementary experimental tools.
- National user facilities are available on a proposal basis to everyone.

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Magnetic Form Factors

https://www.ill.eu/sites/ccsl/ffacts/ffachtml.html

JWL website: https://www.nist.gov/people/jeffrey-w-lynn