Applications of Powder Diffraction Methods

Jim Rhyne
Lujan Neutron Scattering Center, LANL
Los Alamos, NM 87545

- Scattering sources, instruments, line shapes, resolution
- Rietveld Structure Refinement Analysis
- Magnetic Structures and Diffraction
- Example Refinement $Ho_6Fe_{23}D_x$

What do we need to do neutron scattering?

- **Neutron Source – produces neutrons**
- **Diffractometer or Spectrometer**
  - Allows neutrons to interact with sample
  - Sorts out discrete wavelengths by monochromator (reactor) or by time of flight (pulse source)
  - Detectors pick up neutrons scattered from sample
- **Analysis methods to determine material properties**
- **Brain power to interpret results**

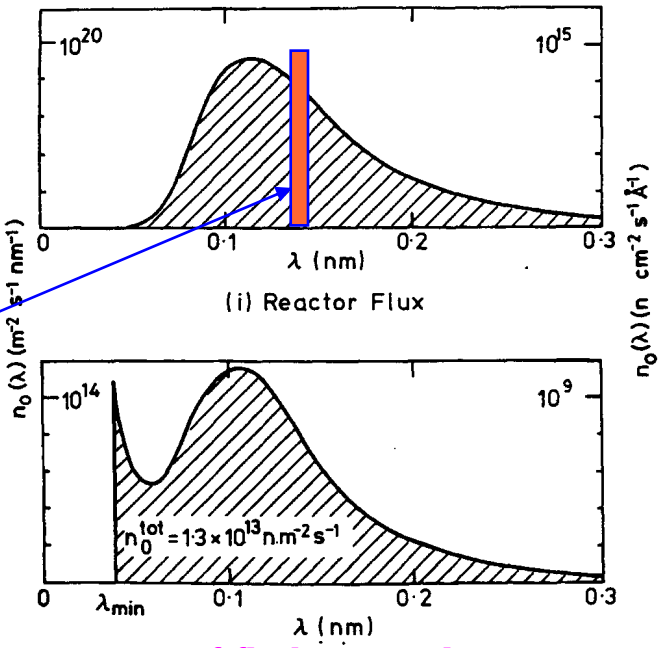
Powder Diffraction Experimental View

- Two types of diffactometers
  - Fixed Wavelength Diffraction (x rays, neutrons at a Reactor [HFIR, NCNR])
  - Variable wavelength (white beam neutrons) [beam may be pulsed (LANSCE [20 Hz], ISIS [50 Hz], SNS [60 Hz]) or continuous (PNS, Geneva)]
- Objective (determine "d" or "2θ")

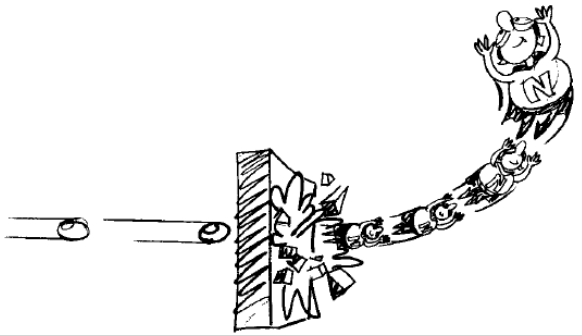
  Bragg Law $\lambda = 2d \sin\theta$
  - $d = \lambda/(2 \sin \theta)$
    - » pulse neutron source - vary λ, keep θ fixed
    - » x-ray or reactor neutron source -- vary θ, keep λ fixed

Neutron sources – steady state (Reactors) and pulsed (Spallation)

- Reactor
  - Fission of U^{235} produces neutrons
  - Fission spectrum moderated (slowed down) by either D_2O or H_20 (less good moderator) and neutrons are extracted through beam tubes for spectrometers – fixed wavelength used
- Spallation source
  - High E protons (e.g., 800 MeV) impinge on target (W, Hg or U)
  - Nucleus of target is raised to excited state and subsequent decay produces neutrons (+ γs, neucleons and neutrinos) – 15 – 25 neutrons produced per proton with average E = 55 MeV
  - Neutrons moderated by liquid H, H_20 or methane
  - Spallation sources generally operate in pulse mode – 20 Hz at LANSCE, 60 Hz at new SNS



Time of flight is used to sort out wavelengths

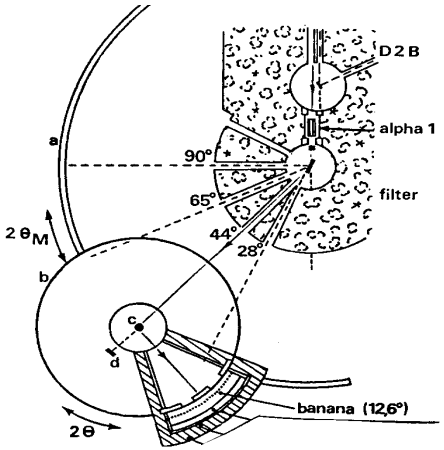


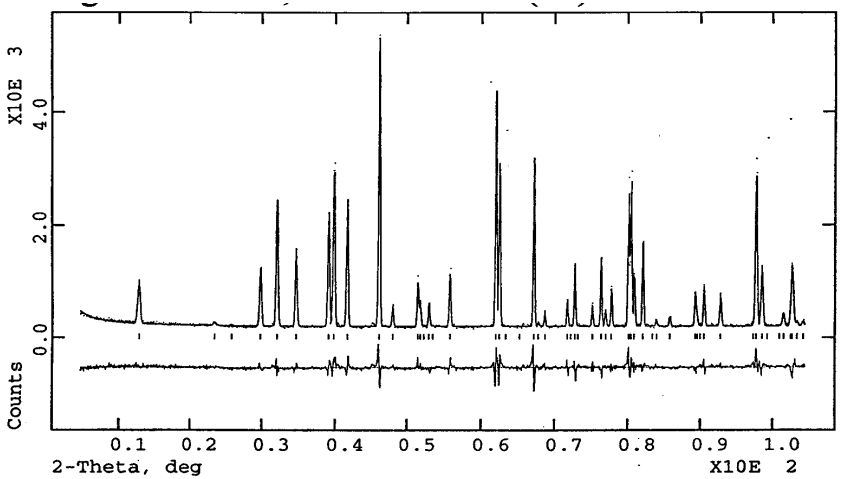
COMPARISON OF POWDER DIFFRACTION INSTRUMENTS

**** Bragg Scattering: $\lambda = 2d \sin\theta$ [we need "d"] ****

Reactor Source -- Monochromator selects near mono-energetic neutrons, detector moves (2θ) to collect discrete diffraction data

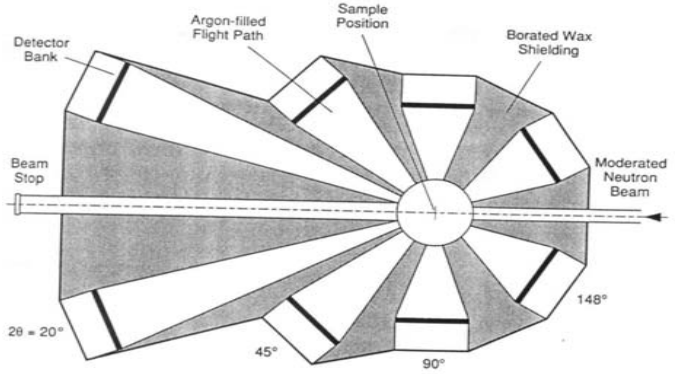
•*(λ fixed, vary θ)*



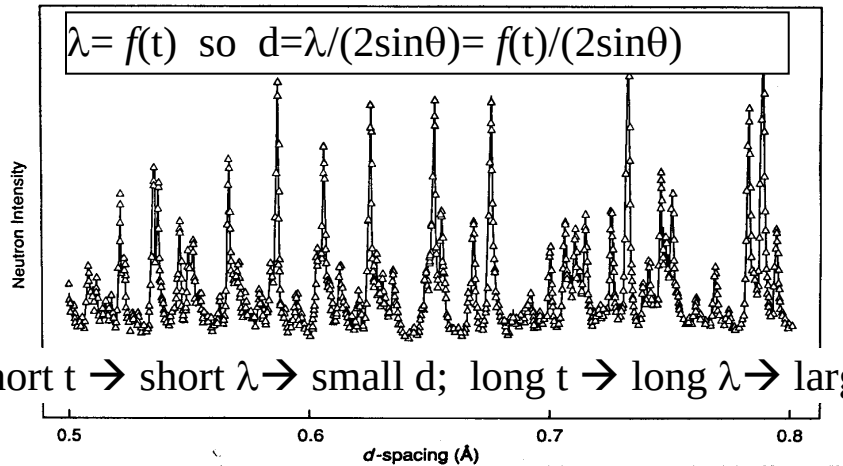


•*Pulse Source* -- White beam of moderated neutrons used, neutron time-of-flight selects wavelength, detectors grouped in banks, no moving parts

(θ fixed, vary λ)



$\lambda = f(t)$ so $d = \lambda/(2\sin\theta) = f(t)/(2\sin\theta)$

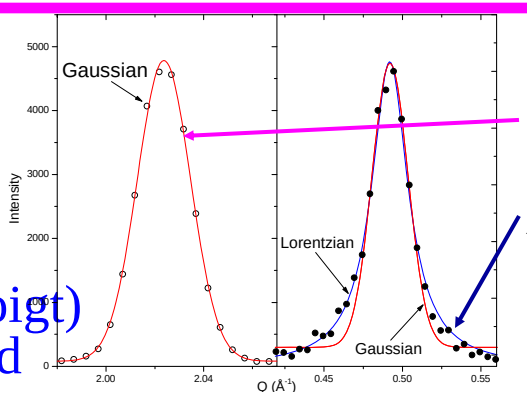


short t → short λ → small d; long t → long λ → large d

Using Powder Diffraction

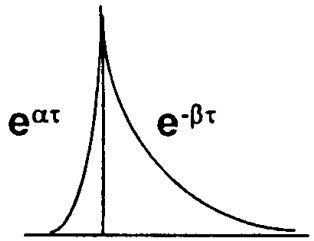
Input Information -- Structure Determination

- Know instrument-dependent scattering line-shape
  - Gaussian for λ fixed
  - Sample distortions (pseudo Voigt) linear comb. of Lorentzian and Gaussian
  - Convolution of rising and falling exponentials with Gaussian for TOF
- Dependence of resolution on "d" [or Q] varies widely with instrument design
  - For pulse sources Δd/d near constant
  - For reactor – resolution has minimum



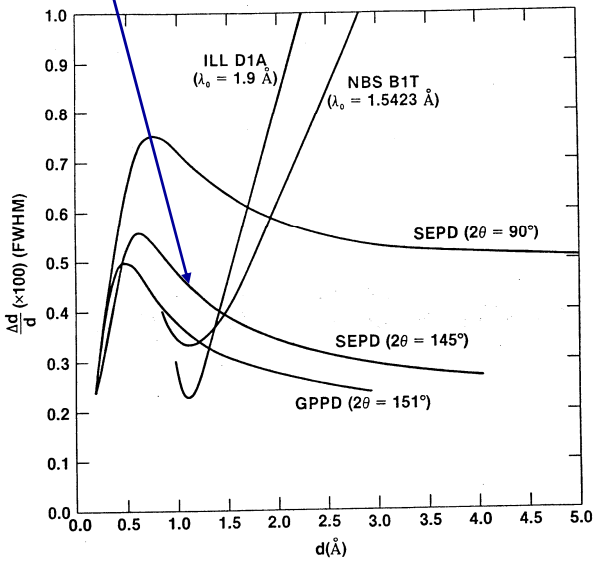
$$R(Q) = \sqrt{\frac{4\ln 2}{\pi\Gamma^2}}\; e^{-\left(\frac{4\ln 2(Q-Q_o)^2}{\Gamma^2}\right)}$$

$$R(Q) = \frac{2}{\pi\Gamma'}\,\frac{1}{1+\left(\frac{2(Q-Q_o)}{\Gamma'}\right)^2}$$



$$R(T) = N\left[e^{u}erfc(y) + e^{v}erfc(z)\right]$$

(VonDreele, Jorgensen & Windsor)



Rietveld Profile Refinement

Least Squares Fitting Procedure for Powder Data

- Input Data
  - Powder scattering pattern data
  - Trial structure space group and approximate lattice parameters and atomic positions [coordinates of atoms in cell - may be variables x,y,z]
  - Line shape function and Q-dependence of resolution

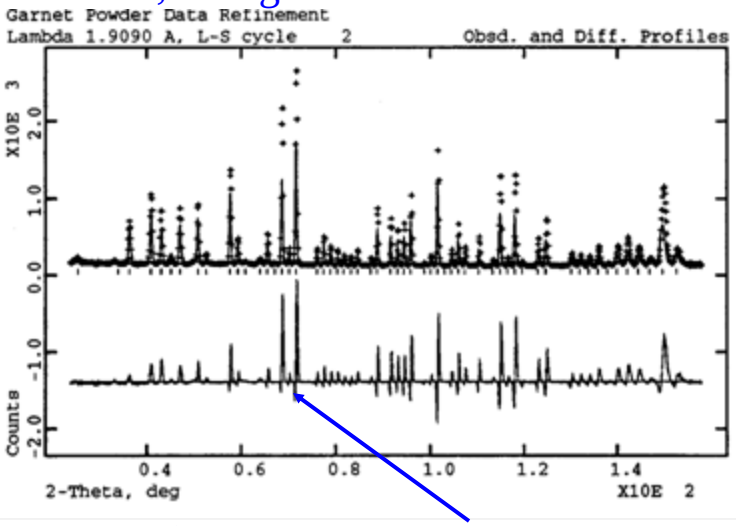
e.g., Caglioti, Paoletti & Rice

$$\Gamma^2 = U\tan^2\theta + V\tan\theta + W$$

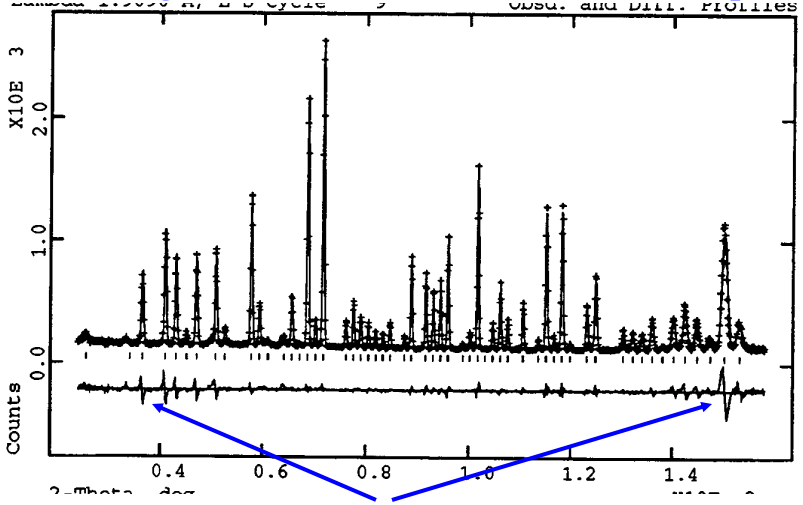
- Output Results
  - Lattice Parameters
  - Refined atomic positions and occupancies
  - Thermal parameters (Debye Waller) for each atom site
  - Line shape parameters (may reflect sample strains, etc.)
  - Background parameters
  - R factors of fit (and other measures of fit precision)
  - Preferential orientation, absorption, etc.
- More than one phase can be separately refined

Progress of a Refinement

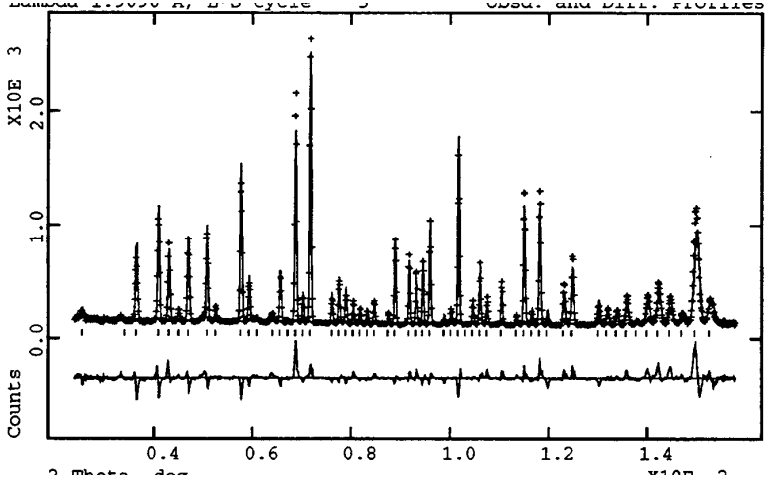
First Cut -- Input data and basic info and refine scale factor, background.



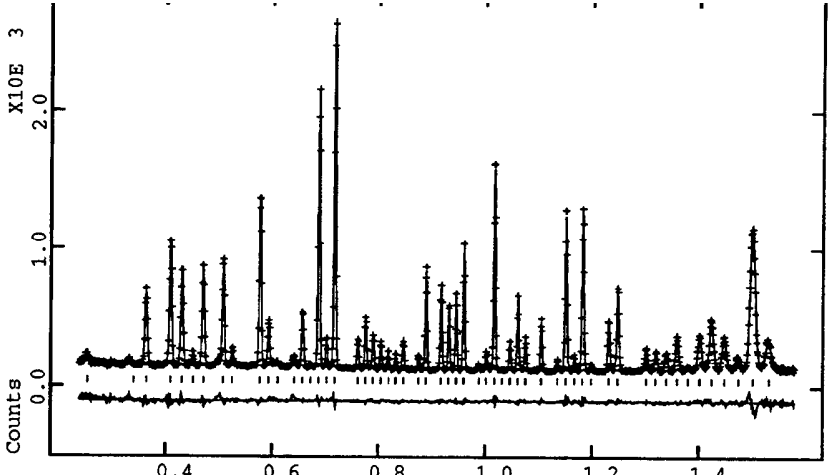
Refining Atom Pos., Therm.Factrs, Occup.



Next Refine Lattice Parameters and Zero Point



Refine Resolution Parameters, Peak Asymmetry, More background coefficients



Cautions with Rietveld (i.e. don't blindly believe the results)

- Hazards
  - Incorrect space group -- may only slightly degrade R factors, symptoms -- unrealistically large thermal factors, misfit on some peaks not others
  - Parameter correlation and compensation -- e.g., absorption and thermal parameters may correlate -- look at variance-covariance matrix (if available from program)
  - Refining multiple phases may be unrealistic -- get a better sample!
  - Over parameterization -- Simultaneous refining of too many parameters may lead to lack of uniqueness

Profile Fitting Programs

- Original Description of Method -- H.M. Rietveld, J. Appl. Cryst. **2**, 65 (1969)
- *FULLPROF* [good for magnetic structures] -- Juan Rodriguez-Carvajal, ILL
- Defacto World Standard -- *Generalized Structure Analysis System [GSAS]* -- A.C. Larson & R.B. Von Dreele, LANL and ANL

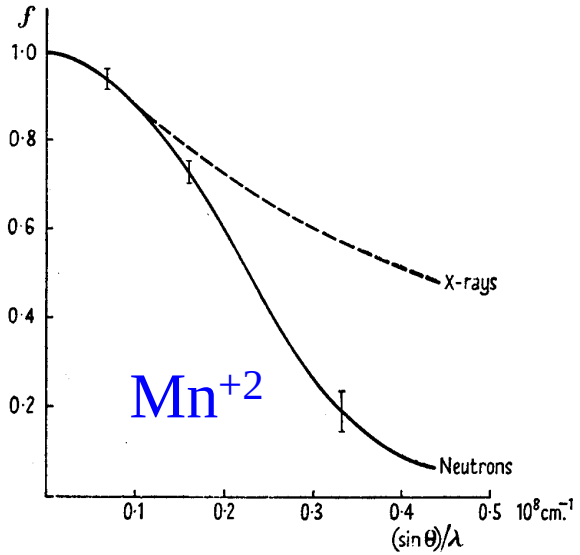
Magnetic Powder Diffraction

- Neutron has a magnetic moment -- will interact with any magnetic fields within a solid, e.g., exchange field
- Equivalent (to b) magnetic scattering amplitude for an atom

$$p = \left(\frac{e^2 \gamma}{2mc^2} \right) fgJ = 0.269 x 10^{-12}\ fgJ\,(cm)$$

where g = Lande "g" factor, J = total spin angular momentum, f = magnetic electrons form factor

- Magnetic scattering comes from polarized spins (e.g., 3d [Fe] or 4f [RE]) not from nucleus -- Therefore scattering amplitude is Q-dependent (like for x-rays) via f
- at Q = 0 for Fe μ = gJ = 2.2 Bohr magneto p = 0.6 (comparable to nuclear b = 0.954) all in units of 10^{-12}cm

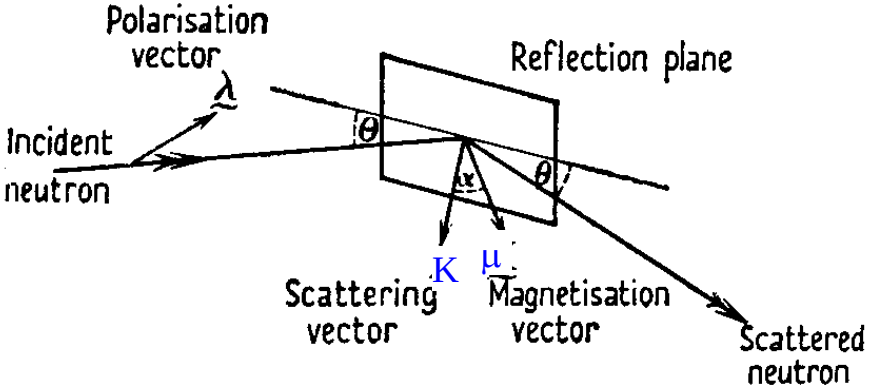


Magnetic Powder Diffraction II

- In diffraction with unpolarized neutrons (polarized scattering is a separate topic) the nuclear and magnetic cross sections are independent and additive:

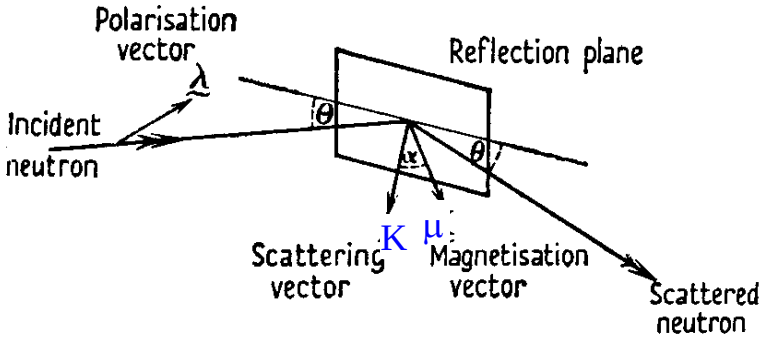
$$\frac{d\sigma}{d\Omega} \propto S(Q) = S_{nucl} + q^2 S_{magn} = S_{nucl} + \left(1 - \cos^2\alpha\right) S_{magn}$$

- q^2 is a "switch" reflecting fact that only the component of the magnetic moment $\mu \perp$ scattering vector **K** (or **Q**) contributes to the scattering



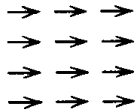
q^2 "switch" affects intensity on Bragg peaks in a polycrystal (powder)

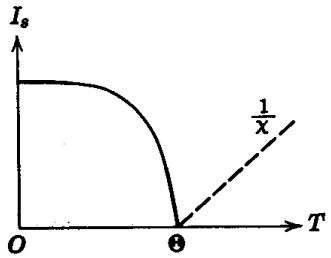
- **Polycrystalline averaging** over $q^2 = (1 - \cos^2\alpha)$ for various symmetries
  - Cubic: $q^2 = 2/3$ [no moment direction information]
  - Tetragonal: $q^2 = 1 - d^2[1/2(h^2+k^2)a^{*2}\sin^2\varphi + l^2c^{*2}\cos^2\varphi]$
    φ = angle between μ and c axis
  - Hexagonal: $q^2 = 1 - d^2[1/2(h^2+k^2+hk)a^{*2}\sin^2\varphi + l^2c^{*2}\cos^2\varphi]$
  - ...

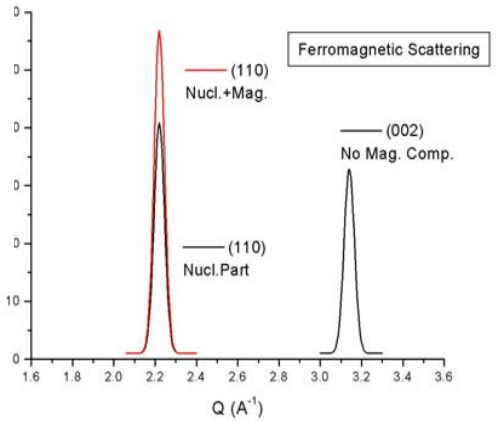


How is magnetism reflected in a scattering pattern?

- **Long-range ordered**
  - Ferromagnet (Fe, Ni, Gd)
  - Spins parallel on lattice







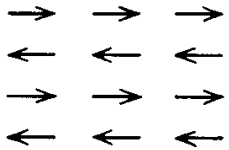
Scattering only at Bragg peak positions (adds to nuclear), but not necessarily all (q^2 switch)

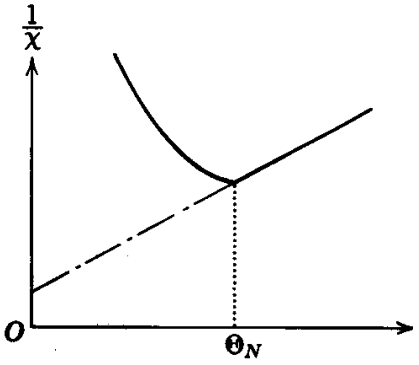
  - Ferrimagnet ($TbFe_2$, Fe_3O_4)

- Spins parallel on each site
- Sites can reverse spin direction
- $\Sigma\mu \neq 0$ on each site, but overall $\Sigma\mu$ could = 0

  - Antiferromagnet (MnO, MnF_2)

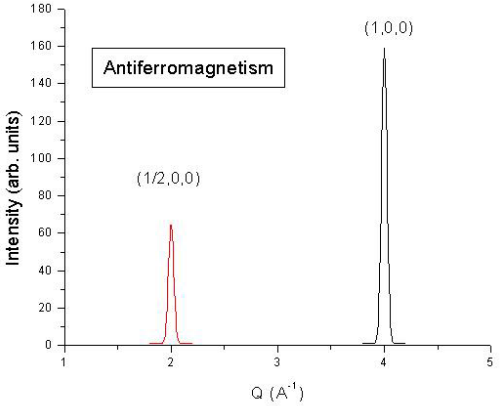
(parallel spins with alternate sites reversed in direction)





Net moment = 0

Job security for neutron scatterers

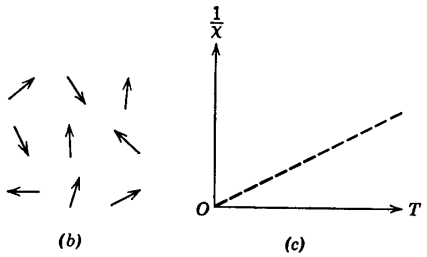


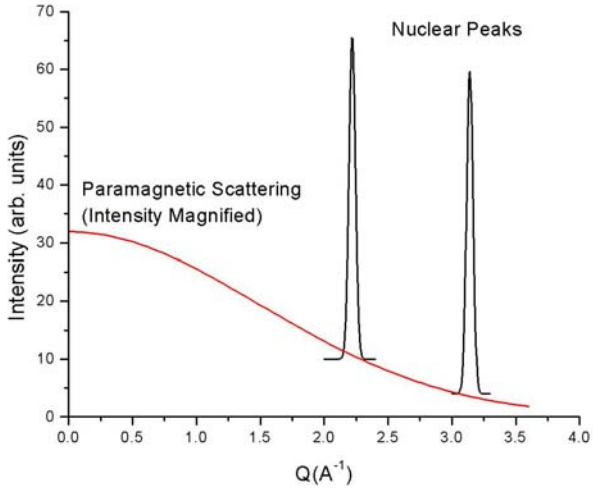
–Magnetic unit cell doubled wrt crystal cell

–Purely magnetic scattering peaks at half Miller index positions

How is magnetism reflected in a powder pattern?

- **Paramagnetism (T > TC)**
  - spins thermally disordered





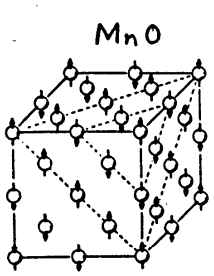
– no coherent magnetic scattering

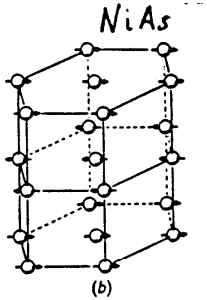
– Incoherent neutron scattering (weak) has form factor dependence

We can make life more complicated with magnetic structures

- Complex antiferromagnetic cells (multi-site, but on each site $\Sigma\mu = 0$)

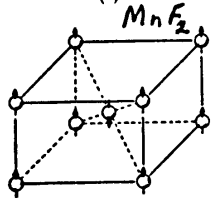
(111) FM Sheets

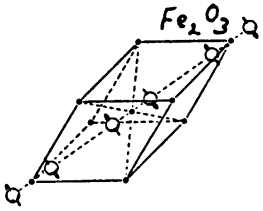




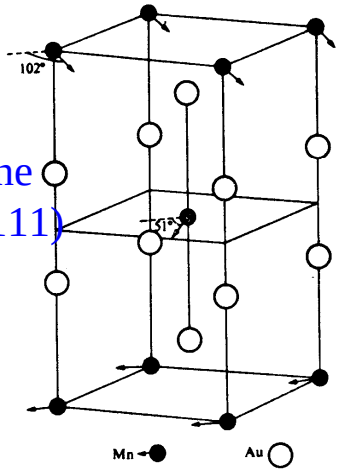
FM layers along (0001)

bcc site antiparallel to corners

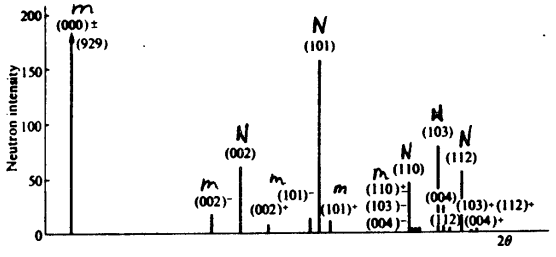




AFM line along (111)



- Periodic Moment Structures (e.g., Er, Au_2Mn)
  - $\Sigma\mu = 0$, but periodic spin arrangement gives rise to magnetic scattering satellites (+, -) of nuclear Bragg peaks



Magnetic structure refinement

- Nuclear and magnetic intensity are additive

$$\frac{d\sigma}{d\Omega} \propto S(Q) = S_{nucl} + q^2 S_{magn} = S_{nucl} + \left(1 - \cos^2 \alpha\right) S_{magn}$$

- Magnetic structure can be refined using GSAS as a separate "phase" alongside the atomic structure
- General magnetic structure factor depends on Shubnikov-Dehaas groups

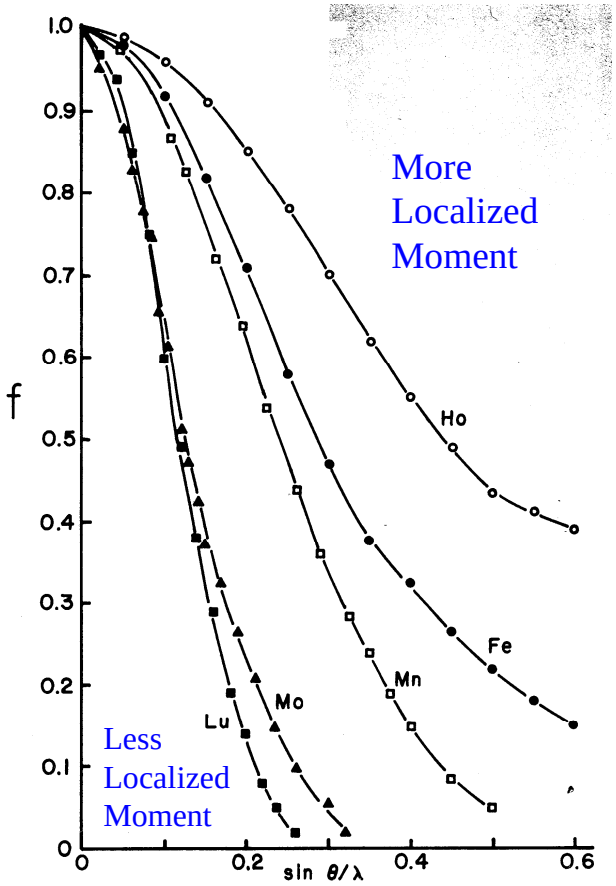
- Magnetic scattering amplitude depends on moment and form factor

$$p = \left(\frac{e^2 \gamma}{2mc^2}\right) fgJ = 0.269 x 10^{-12}\ fgJ\,(cm)$$

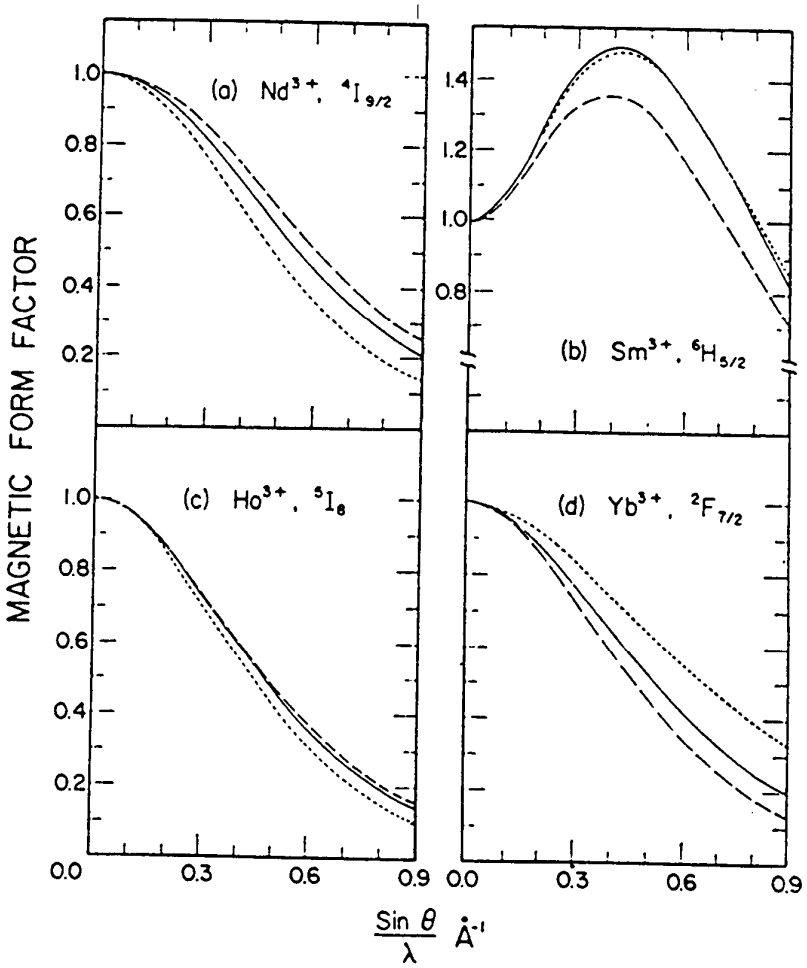
- Form factors, f, are detemined experimentally for most magnets (e.g., RE's) -- can be calculated from electronic band structure and other techniques
- Refinement gives moment magnitudes on each site and x,y,z components (if symmetry permits)

Form Factors

- Experimental



- Calculated



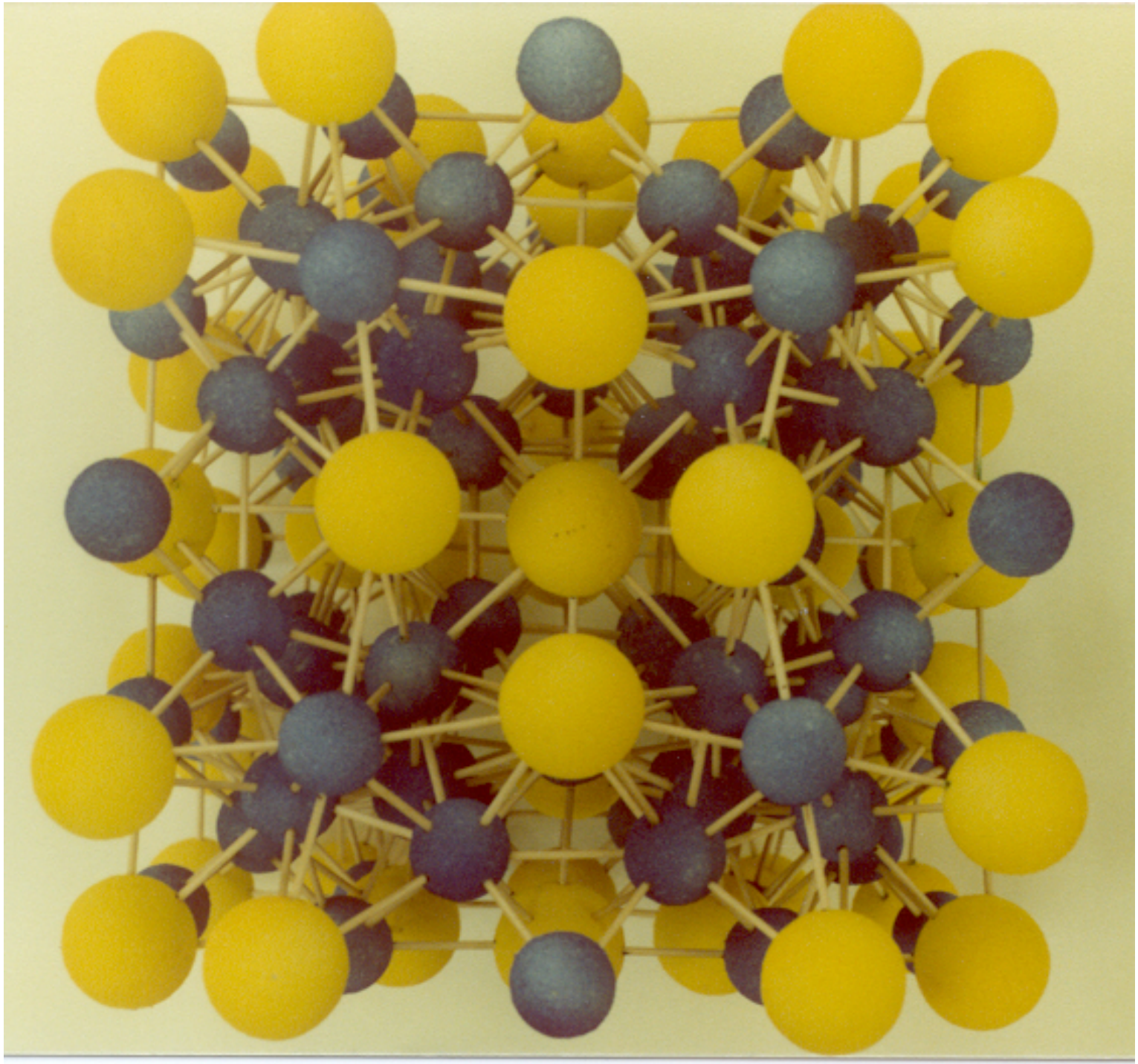
Structure determination case study

Rare earth intermetallic compounds

Ho_6Fe_{23} and $Ho_6Fe_{23}D_x$

Structure Refinement Example Ho_6Fe_{23} and $Ho_6Fe_{23}D_x$

- Rare Earth Intermetallic Compound
- fcc cell - Fm3m structure (space group)
- 4 Formula Units per Unit Cell
- Large Unit Cell -- a = 12 Å
- Absorbs H (or D) from 1 up to 16 atoms/FU -- forms stable hydride compounds
- Also magnetic (both Ho and Fe)



Ho_6Fe_{23} and $Ho_6Fe_{23}D_x$ (Fm3m) Unit Cell

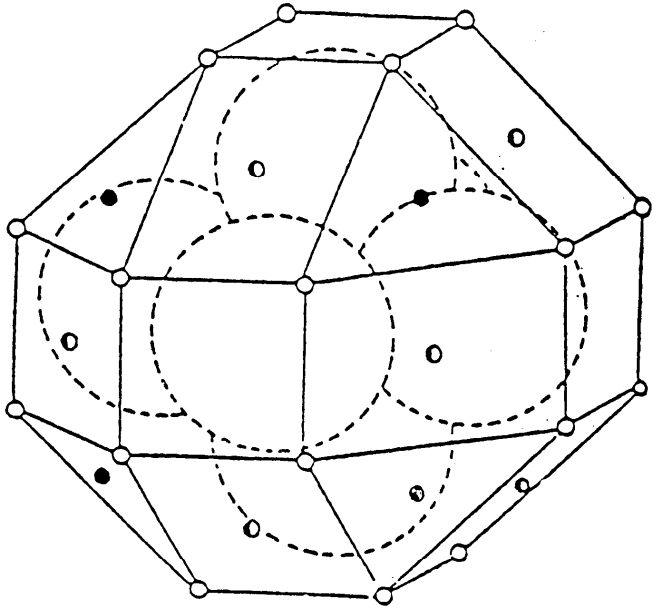
4 F.U./cell

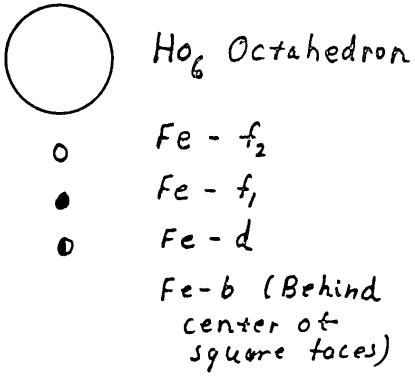
16 metal atoms (4 sites - all full)

324 possible D atoms (5 sites) – only 64 D atoms in fact

-- some sites are empty or

-- some sites are partially occupied





ATOM	FCC (FM3M) WYCOFF NOTATION	PARAMETERS
HO	(24E)	(x,0,0)
FE	(4B)	(.5,.5,.5)
FE	(24D)	(0,.25,.25)
FE	($32F_{1,2}$)	(x,x,x)

$Ho_6Fe_{23}D_x$

Occupied Crystallographic Sites (13 allowed)

F.c.c. (Fm3m)		
Atom	***Wyckoff notation***	***Parameters***
Ho	24e	$(x, 0, 0)$
Fe	4b	$(0.5, 0.5, 0.5)$
Fe	24d	$(0, 0.25, 0.25)$
Fe	$32f_{1,2}$	(x, x, x)
D	4a	$(0, 0, 0)$
D	$32f_3$	(x, x, x)
D	$96j_{1,2}$	$(0, y, z)_{1,2}$
D	96k	(x, x, z)

- Reitveld least squares refinement procedure determines
  - Lattice parameters
  - Atomic position coordinates
  - Site occupation numbers vs. maximum
  - Thermal (Debye-Waller) factors for each atom
  - Instrumental parameters (background, peak shape parameters

- Note: Ho, Fe sites all full 4x(6+23) – 116
- D sites not full – 324 allowed > max 4x16 = 64

$Ho_6Fe_{23}D_{15.7}$ Refinement Parameters I

Lattice Parameters, Volume Expansion relative to Ho_6Fe_{23},

Ho_6Fe_{23}:

T(K)	a_0	$\Delta V/V_0$	R_e	R_{wp}	χ
295	12.029	0	6.1	11.5	1.9
4.2	12.000	0	8.9	18.0	2.0

$Ho_6Fe_{23}D_{15.7}$:

T(K)	a_0	$\Delta V/V_0$(%)	R_e	R_{wp}	χ
295	12.423	9.8	5.1	9.2	1.8
4.2	12.406	10.2	3.1	9.8	3.2

R_e = statistical variance for a perfect fit with taking into account the statistical precision of the data.

R_{wp} = weighted profile variance of the fit (big pks. vs little pks.)

χ = ratio of R_{wp}/R_e (values near 2 are generally indicative of a good profile fit to the model structure)

$Ho_6Fe_{23}D_{15.7}$ Refinement Parameters II

Refined atomic coordinates, thermal factors, and occupancy factors

(D) – Values are per formula unit – 4 formula units/unit cell

Atom	Wyckoff Site **Max. Occup.**	N	X(or Y)	Z	B
Ho	$24e_{(x,0,0)}$	6	0.205	(f)	--
Fe	$4b_{(0.5,.0.5,0.5)}$	1	(f)	(f)	--
Fe	$24d_{(0,0.25,0.25)}$	6	(f)	(f)	--
Fe	$32f_{1(x,x,x)}$	8	0.177	=x	--
Fe	$32f_{2(x,x,x)}$	8	0.372	=x	--
D	$4a_{(0,0,0)}$	0	(f)	(f)	n/a
D	$32f_{3(x,x,x)}$	7.2	0.096	=x	0.55
D	$96j_{1(0,y,z)}$	4.9	0.135	0.340	0.19
D	$96j_{2(0,y,z)}$	3.1	0.076	0.385	0.29
D	$96k_{(x,x,z)}$	1.4	0.159	0.047	0.94

All sites full

Sites part full

$Ho_6Fe_{23}D_{15.7}$ Magnetic Moments

- Refined magnetic structure confirms a colinear spin arrangement
- Ho moments (1 site – 24e) antiparallel to Fe moments (4 sites – 4b, 24d, $32f_1$, $32f_2$)
- Refinement produces site specific values of magnetic moment [Note: Total magnetic moment may have large errors due to compounding of errors from each site.]
- Moments at 4.2 K:

Atom	Wyckoff Site	N	Mom. (μ_B)
Ho	24e	6	-10.2
Fe	4b	1	2.2
Fe	24d	6	2.4
Fe	$32f_1$	8	2.0
Fe	$32f_2$	8	2.2