

# Experimental Aspects of Neutron Diffraction

William Ratcliff

NCNR





MAY 15, 1939

PHYSICAL REVIEW

VOLUME 55

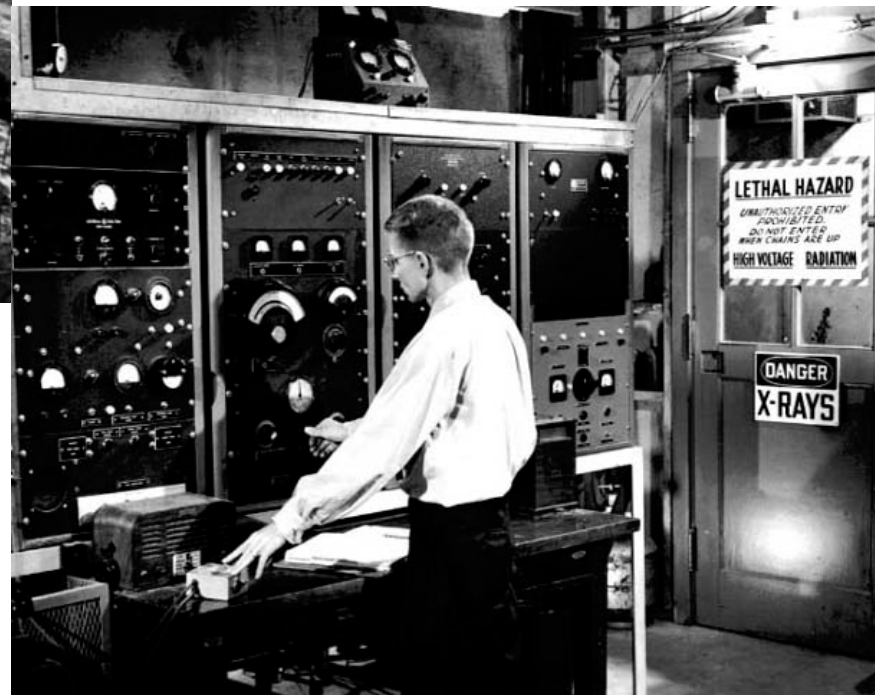
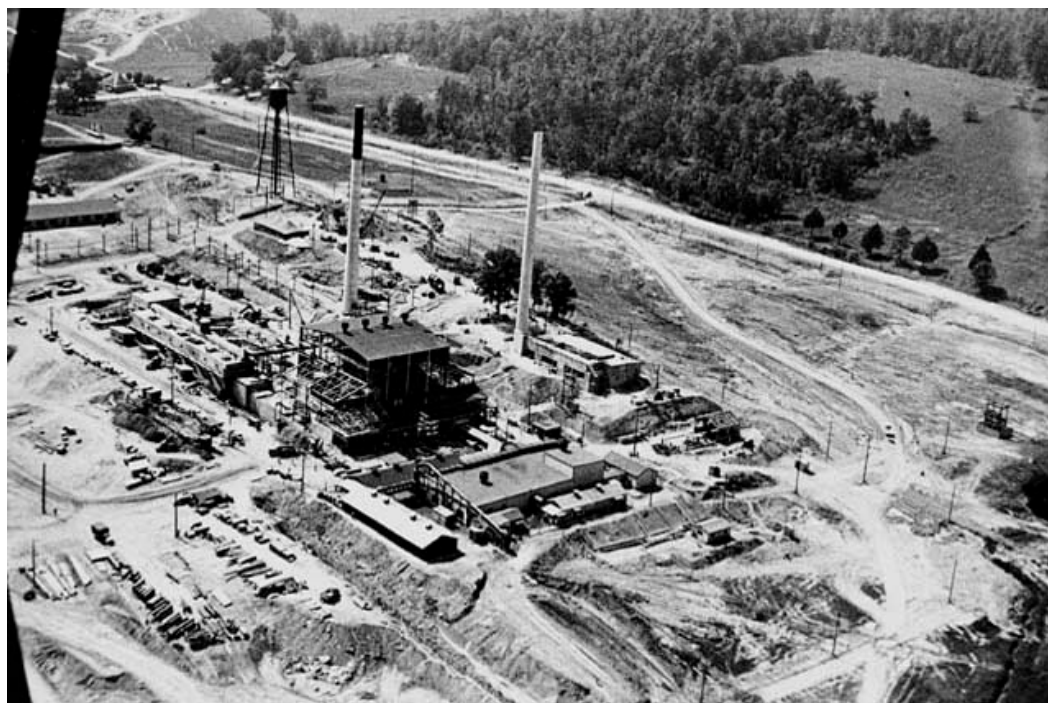
## On the Magnetic Scattering of Neutrons

O. HALPERN AND M. H. JOHNSON

*New York University, University Heights, New York, New York*

(Received December 3, 1938)

# ORNL Graphite Reactor 1943-1963

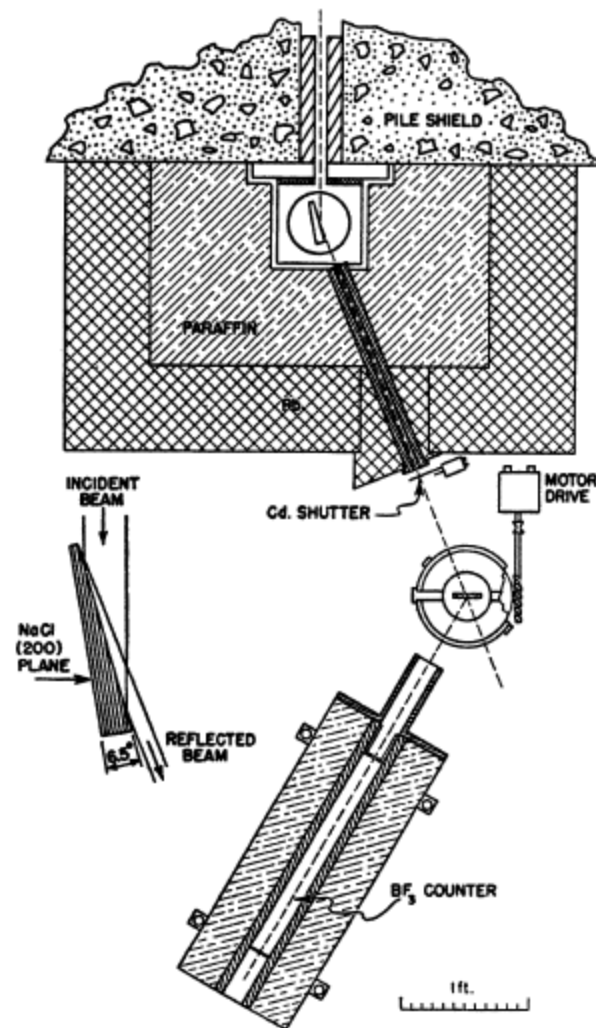
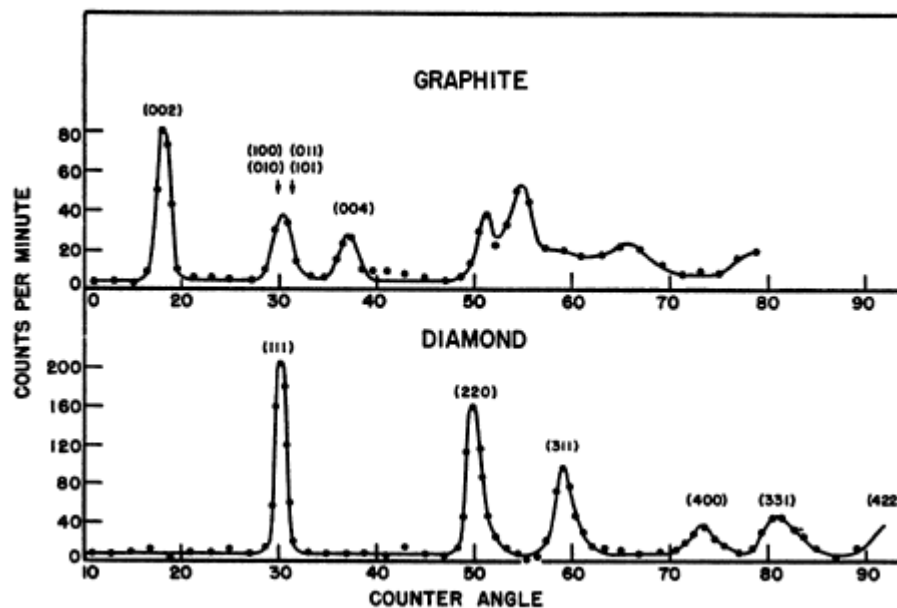
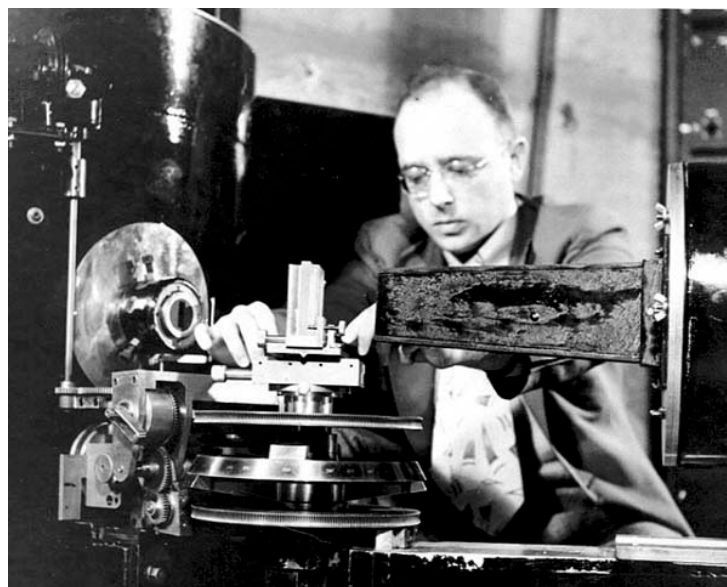


# The Diffraction of Neutrons by Crystalline Powders

E. O. WOLLAN AND C. G. SHULL

*Oak Ridge National Laboratory, Oak Ridge, Tennessee*

(Received January 5, 1948)





# The Nobel Prize in Physics 1994



Clifford G. Shull, MIT, Cambridge, Massachusetts, USA, receives one half of the 1994 Nobel Prize in Physics for development of the neutron diffraction technique.



**S** Shull made use of **elastic scattering** i.e. of neutrons which change direction without losing energy when they collide with atoms.

Because of the wave nature of neutrons, a diffraction pattern can be recorded which indicates where in the sample the atoms are situated. Even the placing of light elements such as hydrogen in metallic hydrides, or hydrogen, carbon and oxygen in organic substances can be determined.

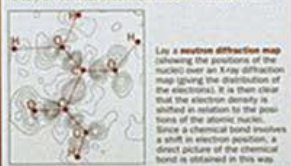
The pattern also shows how atomic dipoles are oriented in magnetic materials, since neutrons are affected by magnetic forces. Shull also made use of this phenomenon in his neutron diffraction technique.



An early (1950s) neutron diffractometer with flexible wavelength control here used by E.G. Wilson and C.G. Shull (standing) at Oak Ridge National Laboratory.

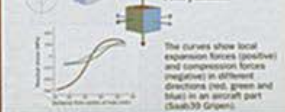
## Neutrons see more than X-rays

X-rays are scattered by electrons, neutrons by atomic nuclei. With X-rays it is easiest to see atoms that have many electrons. Hydrogen, for example, which has only one electron, is not so easy to see. With neutrons, all kinds of atoms are visible.



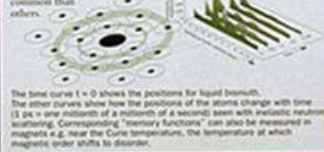
## Neutrons reveal inner stresses

A hole has been punched in an important metal aircraft part. Does the part match up? Neutron diffraction can show how much the distance between the atoms has changed and hence the internal forces remaining around the hole after it has been punched.



## Neutrons show what atoms remember

of their earlier positions when they move randomly in relation to each other in liquids and melts. Even here there is in fact some local order. The atoms cannot move infinitely close to each other. Some distances are more common than others.



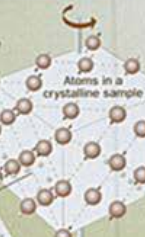
Neutrons behave as particles and as waves

# Neutrons reveal structure and dynamics

Neutrons bounce against atomic nuclei. They also react to the magnetism of the atoms.

Neutrons show where atoms are

When the neutrons collide with atoms in the sample material, they change direction (are scattered) - **elastic scattering**.



Crystal that sorts and forwards neutrons of a certain wavelength (energy) - **monochromatized neutrons**

Research reactor



Neutrons show what atoms do

3-axis spectrometer with rotatable crystals and rotatable sample



When the neutrons penetrate the sample they start or cancel oscillations in the atoms. If the neutrons create phonons or magnons they themselves lose the energy these absorb - **inelastic scattering**

Changes in the energy of the neutrons are first analysed in an analyser crystal...



...and the neutrons then counted in a detector.

**B** Brockhouse made use of **inelastic scattering** i.e. of neutrons, which change both direction and energy when they collide with atoms. They then start or cancel atomic oscillations in crystals and record movements in liquids and melts. Neutrons can also interact with spin waves in magnets. With his 3-axis spectrometer Brockhouse measured energies of phonons (atomic vibrations) and magnons (magnetic waves). He also studied how atomic structures in liquids change with time.



Bertram N. Brockhouse, McMaster University, Hamilton, Ontario, Canada, receives one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.

## How it started

Brockhouse and Shull made their pioneering contributions at the first nuclear reactors in the USA and Canada back in the 1940s and 1950s. It was then that the resources of the reactors became available for peacetime research.

## ... how it continues

Thousands of researchers are now working at the many neutron research centers throughout the world. New and very advanced neutron scattering installations have been built and more are planned in Europe, the USA and Asia. At these super-installations the researchers are studying the structure of new ceramic superconductors, molecular movements on surfaces of interest for catalytic exhaust cleaning, virus structures and the connection between the structure and the elastic properties of polymers.



KUNGL. VETENSKAPSAKADEMIEN  
THE ROYAL SWEDISH ACADEMY OF SCIENCES

© Information Department, Box 50005, S-104 05 Stockholm, Sweden. Tel +46 8 673 95 00, fax +46 8 673 95 75. Editors: Bengt Sjöström, Margareta Wångberg, The Royal Swedish Academy of Sciences. Authors: Professor Erik B. Sjöström and Professor Carl Norberg, Department of Physics, Uppsala University, Uppsala, Sweden. The Nobel Committee for Physics, Laddar och illustrationer: April Lundin, Explorare AB. Printed by Trycknord, 1994.

## Further reading:

- D.J. Hughes *The Nuclear Reactor as a Research Instrument*, SCIENTIFIC AMERICAN, VOL. 190, AUGUST 1955, P. 23.
- H. Lengeler and J.L. Finney *The European Spallation Source*, EUROPHYSICS NEWS, VOL. 25, P. 35, 1994.
- Information about the Nobel Prize in Physics 1994 (see also), THE ROYAL SWEDISH ACADEMY OF SCIENCES.

1932, Néel predicts Antiferromagnetic order

### Detection of Antiferromagnetism by Neutron Diffraction\*

C. G. SHULL

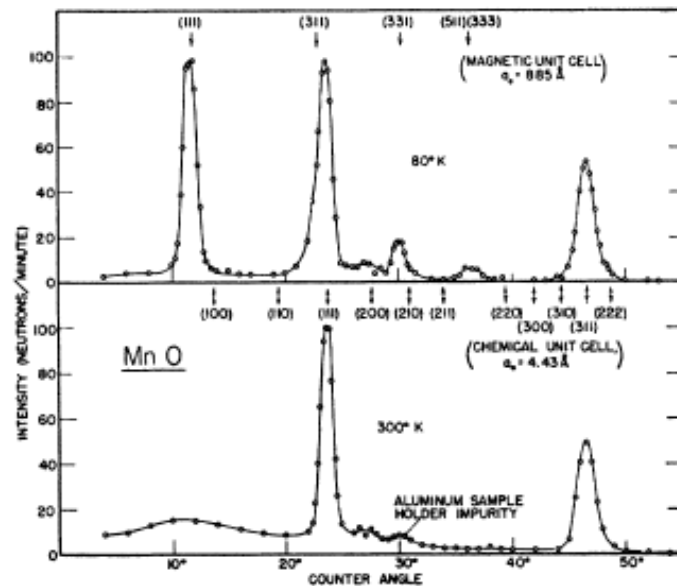
*Oak Ridge National Laboratory, Oak Ridge, Tennessee*

AND

J. SAMUEL SMART

*Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland*

August 29, 1949

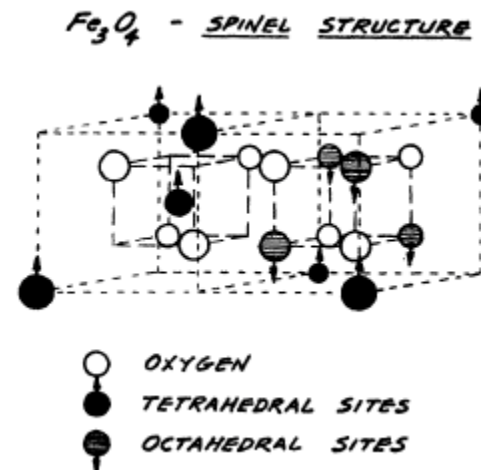


### Magnetic Structure of Magnetite and Its Use in Studying the Neutron Magnetic Interaction

C. G. SHULL, E. O. WOLLAN, AND W. A. STRAUSSER

*Oak Ridge National Laboratory, Oak Ridge, Tennessee*

December 8, 1950

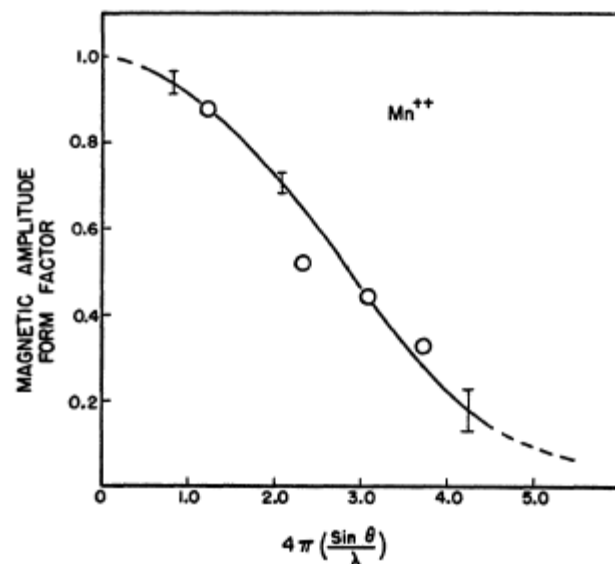




# Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. SHULL, W. A. STRAUSSER, AND E. O. WOLLAN  
Oak Ridge National Laboratory, Oak Ridge, Tennessee

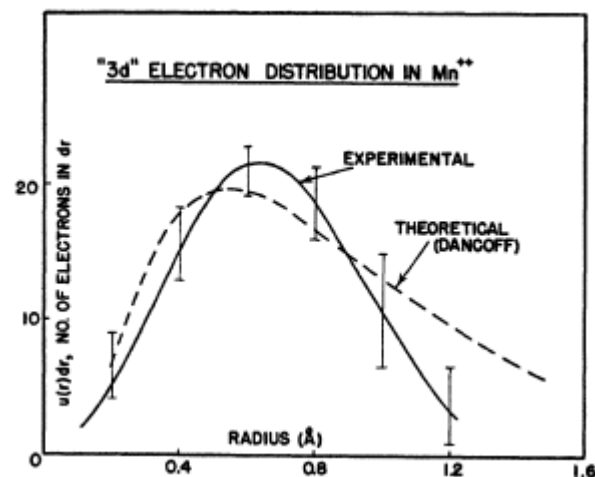
(Received March 2, 1951)



$$d\sigma_m = \frac{2}{3} S(S+1) (e^2 \gamma / mc^2) f^2 d\Omega,$$



$$u(r) = (2r/\pi) \int_0^\infty k f(k) \sin kr dk$$



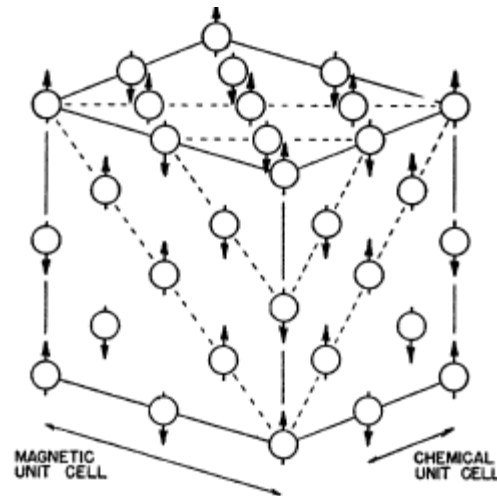
(a) The magnetic moments are aligned along arbitrary  $[100]$  directions, in other words, along the cube axes, as illustrated in Fig. 5. For this case it can be shown that  $q^2$  (average) =  $\frac{2}{3}$  for each of the four observed magnetic reflections in MnO.

(b) The magnetic moments are aligned perpendicular to the ferromagnetic  $(111)$  sheets. For this case,  $q^2$  vanishes for the  $(111)$  reflection and becomes  $32/33$  for the  $(311)$  and  $32/57$  for the  $(331)$  reflections.

(c) The magnetic moments are aligned arbitrarily in the ferromagnetic  $(111)$  sheets. Here  $q^2$  should be 1 for the  $(111)$  reflection and various odd values for the other reflections, depending upon the assignment of moment orientation within the sheet.

TABLE II. Comparison between observed MnO antiferromagnetic intensities and those calculated for various models of magnetic orientation with respect to crystallographic axes.

	Calculated for various oriented models			Observed (neutrons/min)
	(a)	(b)	(c)	
(111)	1038	0	1560	1072
(311)	460	675	...	308
(331)	129	109	...	132
(511) (333)}	54	24	...	70



# Neutron Scattering and Polarization by Ferromagnetic Materials

C. G. SHULL, E. O. WOLLAN, AND W. C. KOEHLER  
Oak Ridge National Laboratory, Oak Ridge, Tennessee

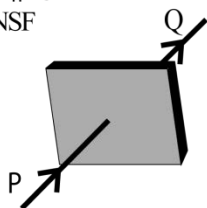
(Received August 20, 1951)

$$F^2 = C^2 + 2CD\mathbf{q} \cdot \boldsymbol{\lambda} + D^2q^2$$

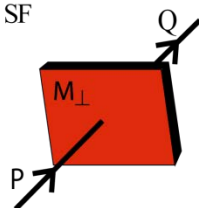
$$\mathbf{q} = \mathbf{e}(\mathbf{e} \cdot \boldsymbol{\kappa}) - \boldsymbol{\kappa} \quad \text{and} \quad q^2 = 1 - (\mathbf{e} \cdot \boldsymbol{\kappa})^2$$

$$D = (e^2/mc^2)\gamma Sf = 0.539 \times 10^{-12} Sf \text{ cm}$$

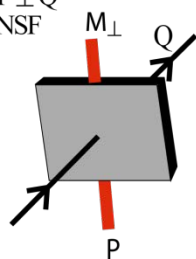
(a)  $P \parallel Q$   
NSF



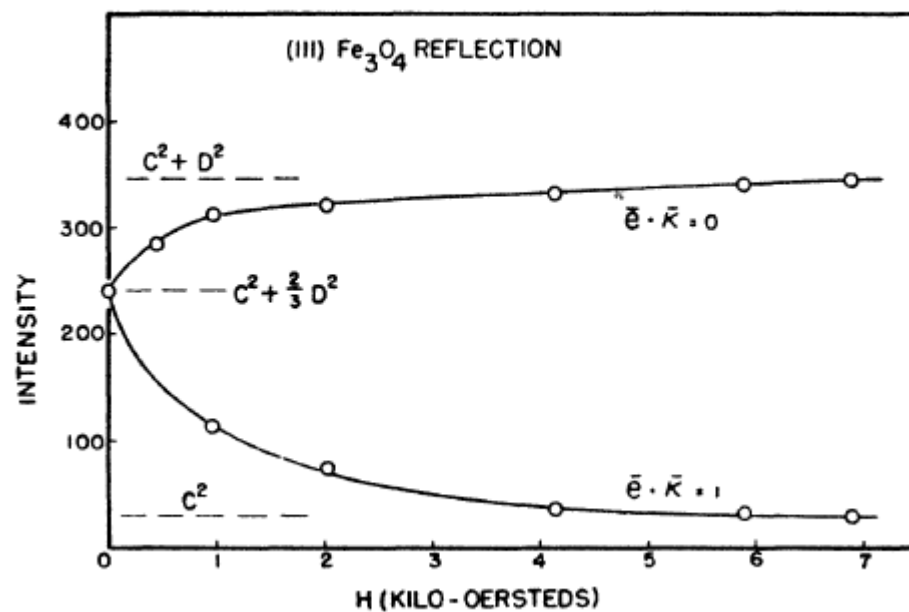
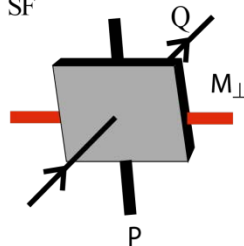
(b)  $P \parallel Q$   
SF



(c)  $P \perp Q$   
NSF



(d)  $P \perp Q$   
SF



# Neutron Diffraction Study of the Magnetic Properties of the Series of Perovskite-Type Compounds $[(1-x)\text{La}, x\text{Ca}]\text{MnO}_3^\dagger$

E. O. WOLLAN AND W. C. KOEHLER

Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received May 9, 1955)

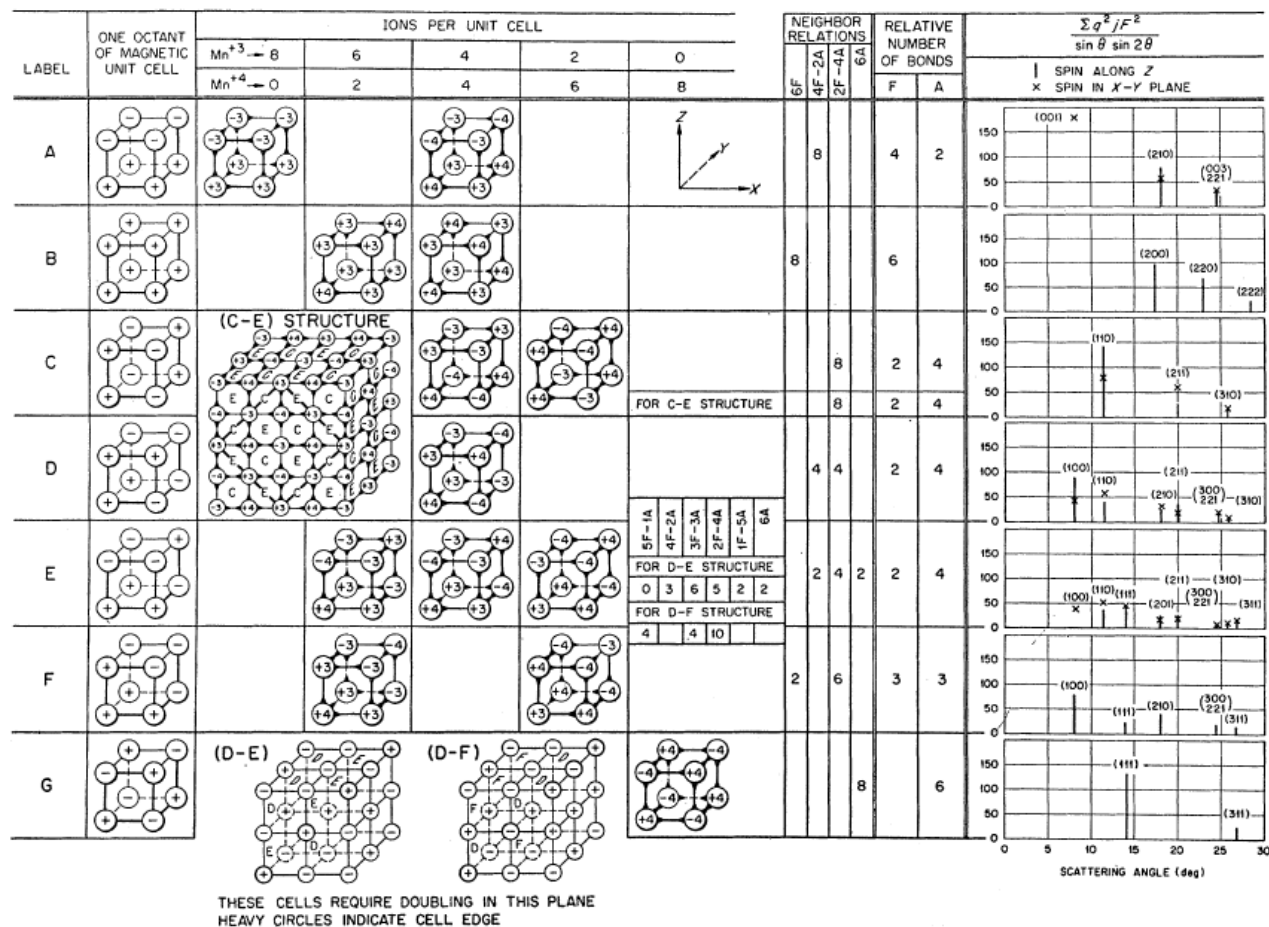


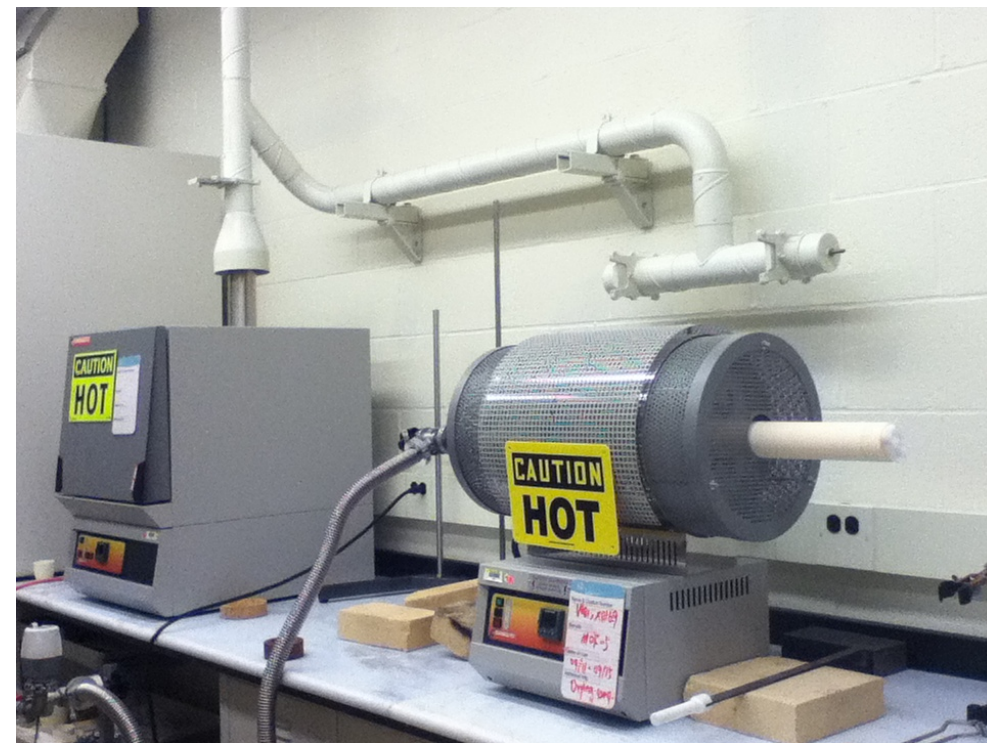
FIG. 18. Scheme of magnetic structures and related information. A, B, C, G, and (C-E) definitely observed and some evidence for D and F. Ion ordering schemes represent arrangements consistent with certain coupling criteria. Arrowheads are a schematic representation of Goodenough's semicovalent exchange coupling.



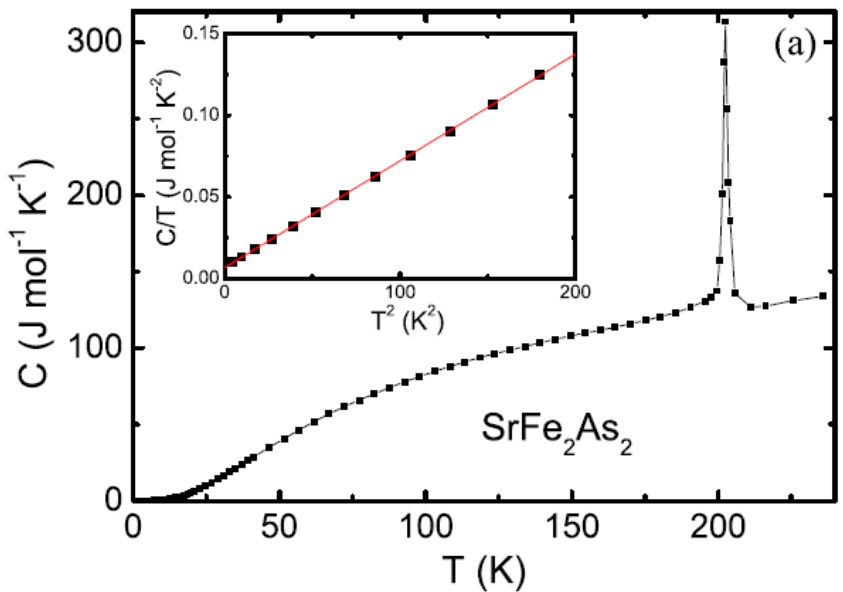
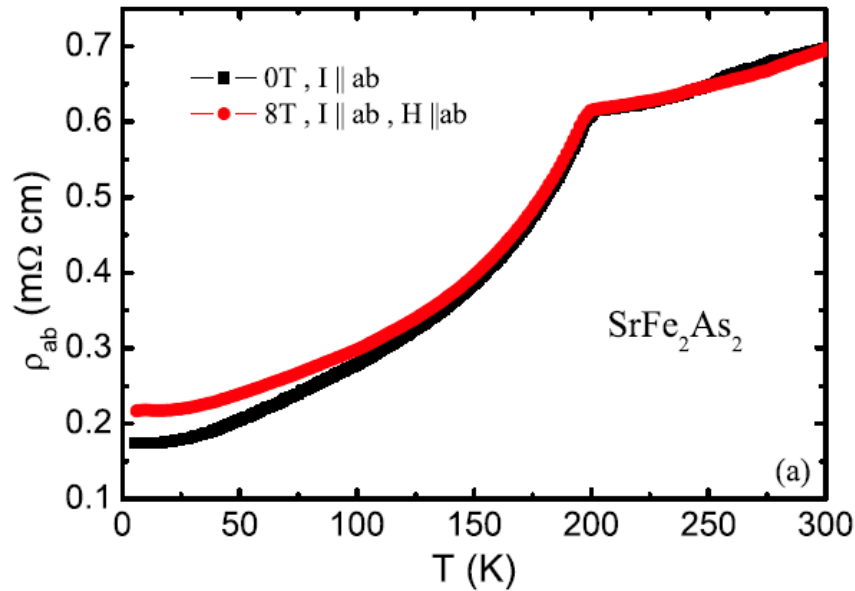
# Intermission



# How it starts?



# Bulk Data Comes In

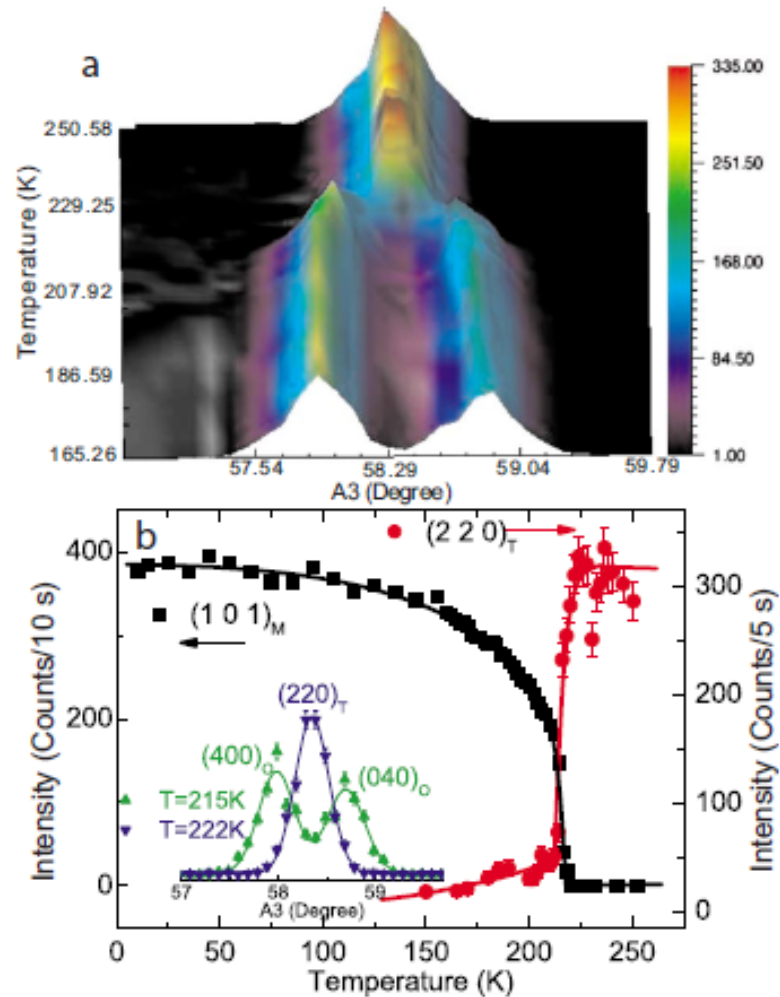


Physical Review B **78**, 22514 (2008)





# Neutrons to the Rescue

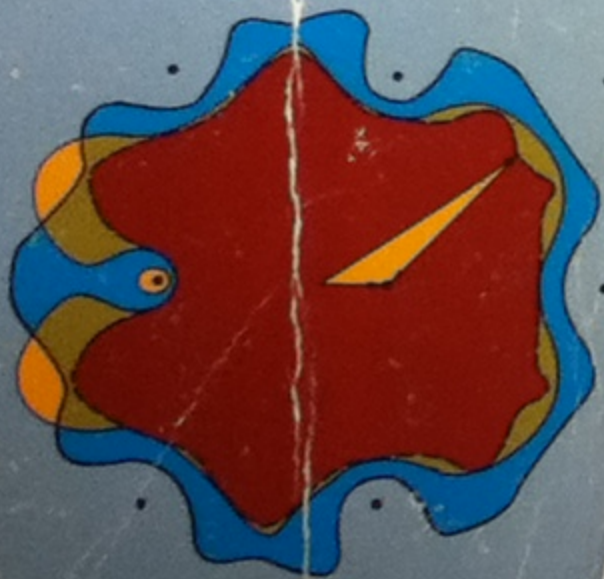


Physical Review B **78**, 140504 (2008)



how**stuff**works  
It's good to know

INTRODUCTION TO  
THE THEORY OF  
THERMAL  
NEUTRON  
SCATTERING



G.L. Squires

Harald Ibach Hans Lüth

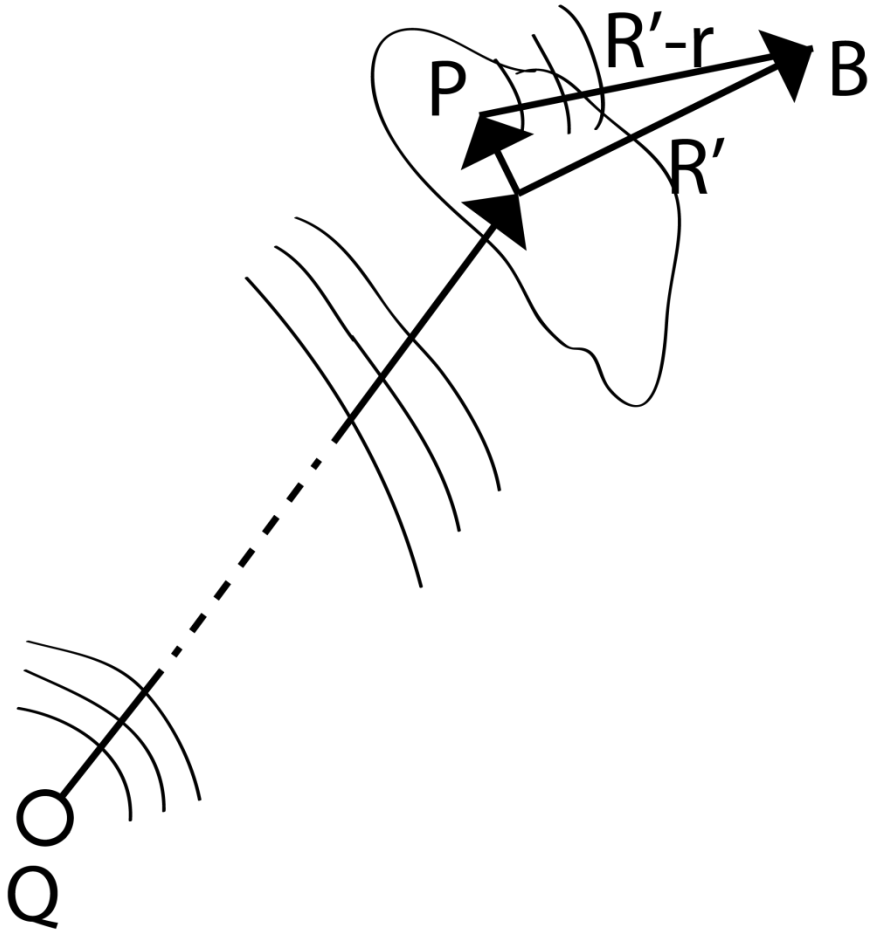
# Solid-State Physics

An Introduction to Principles of Materials Science

Second Edition



Springer



$$A_P = A_0 e^{i\vec{k}_0 \cdot (\vec{R} + \vec{r}) - i\omega_0 t}$$

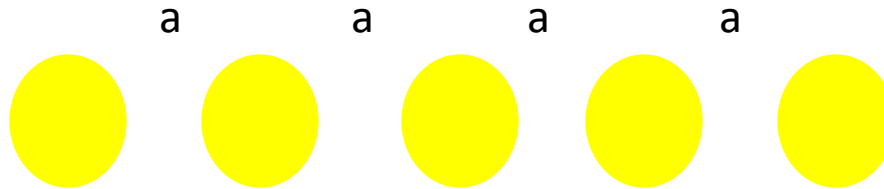
$$A_B = A_P(r, t) \rho(r) \frac{e^{i\vec{k} \cdot (\vec{R}' - \vec{r})}}{|\vec{R}' - \vec{r}|}$$

$$A_B = A_P(R' \gg r, t) \rho(r) \frac{e^{i\vec{k} \cdot (\vec{R}' - \vec{r})}}{|\vec{R}'|}$$

$$I(K) \propto |A_B|^2 \propto \left| \int \rho(r) e^{i\vec{K} \cdot \vec{r}} dr \right|^2$$



# Reciprocal Space



$$\rho(x) = \rho(x + na)$$

$$\rho(x) = \sum_n \rho_n e^{i(n2\pi/a)x}$$

$$\rho(\vec{r}) = \sum_n \rho_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}$$

$$\vec{G} \cdot \vec{r} = 2\pi m \quad g1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

# Here there be dragons...

THE LENOX GLOBE



$$I(K) \propto |A_B|^2 \propto \left| \int \rho(r) e^{i\vec{K} \cdot \vec{r}} d\vec{r} \right|^2$$

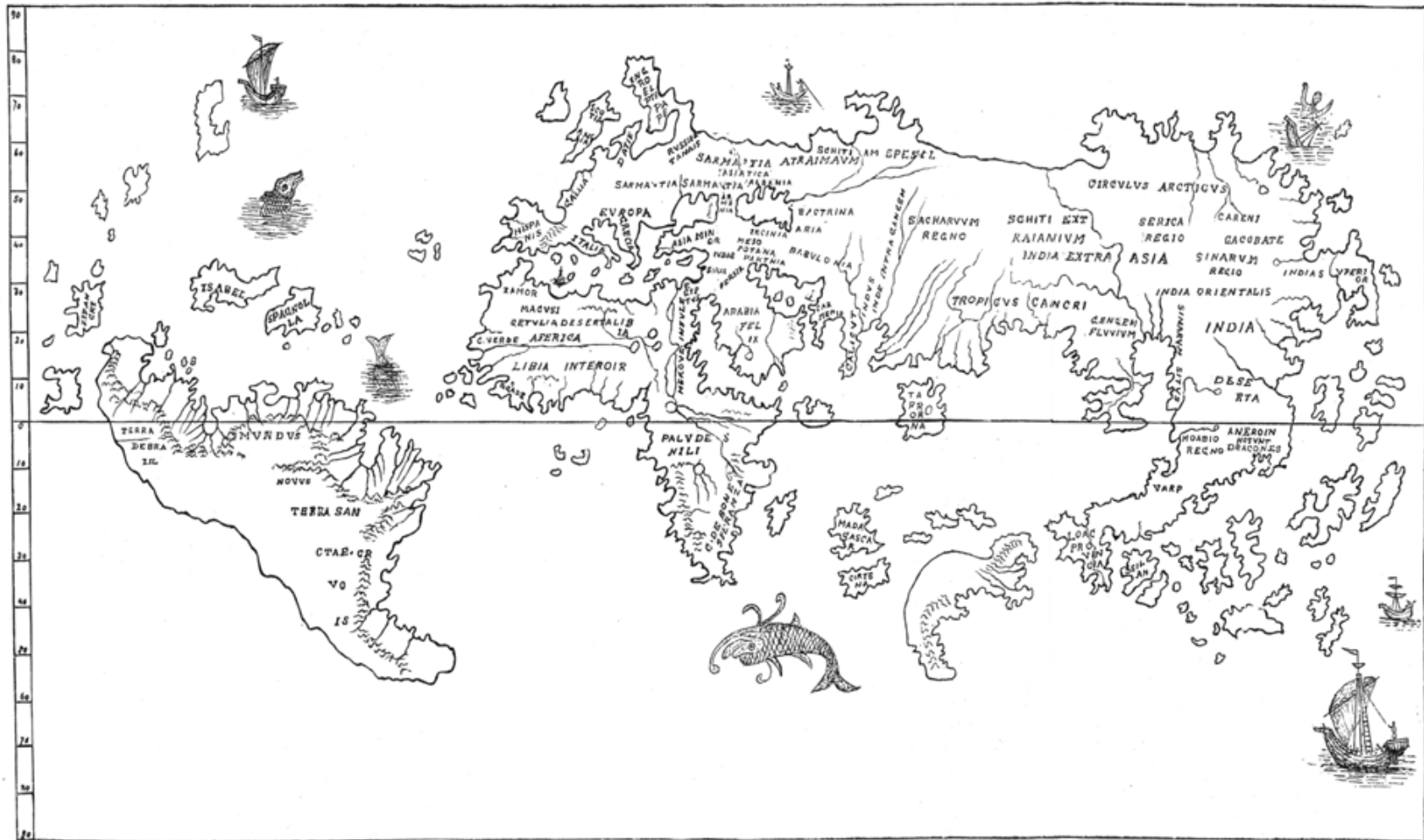


$$I(K) \propto \left| \sum_{\vec{G}} \rho_{\vec{G}}(r) \int e^{i(\vec{G}-\vec{K}) \cdot \vec{r}} d\vec{r} \right|^2$$

$$\int e^{i(\vec{G}-\vec{K}) \cdot \vec{r}} d\vec{r} = \begin{cases} V & \text{for } \vec{G} = \vec{K} \\ \sim 0 & \text{otherwise} \end{cases} \quad \text{Laue Condition}$$

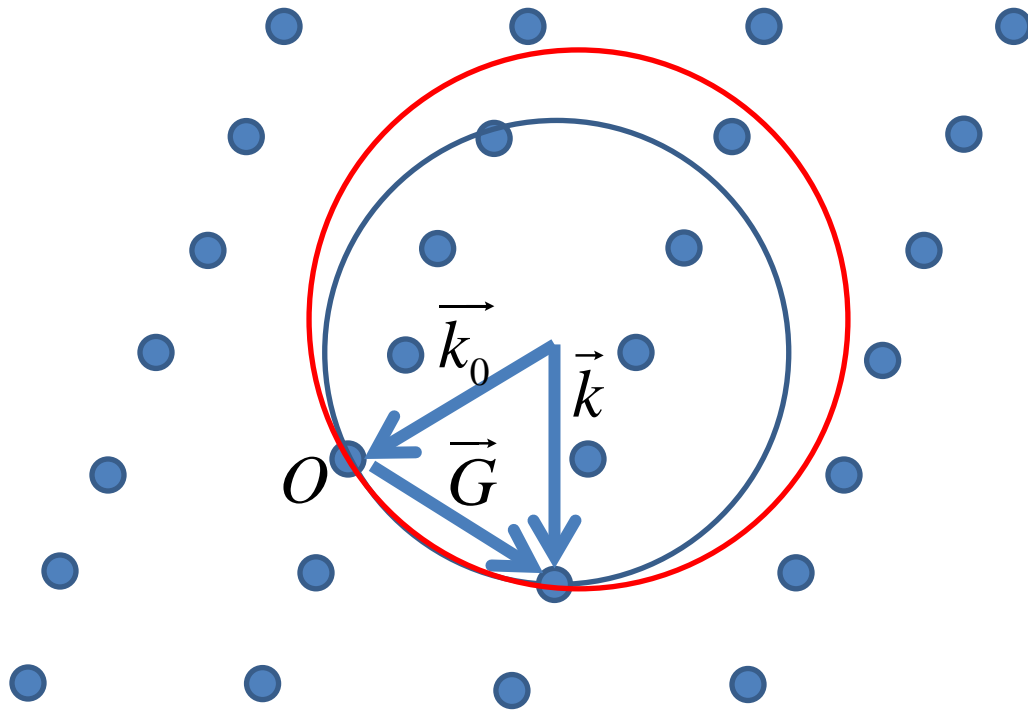
# Here there be dragons...

THE LENOX GLOBE



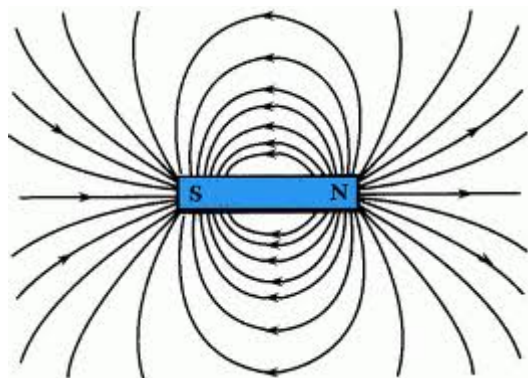


# Ewald Sphere



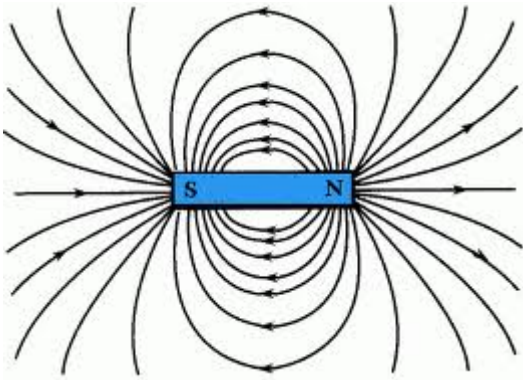
# So...

- See scattering where reciprocal lattice point lies on Ewald Sphere
- But, whither magnetism???

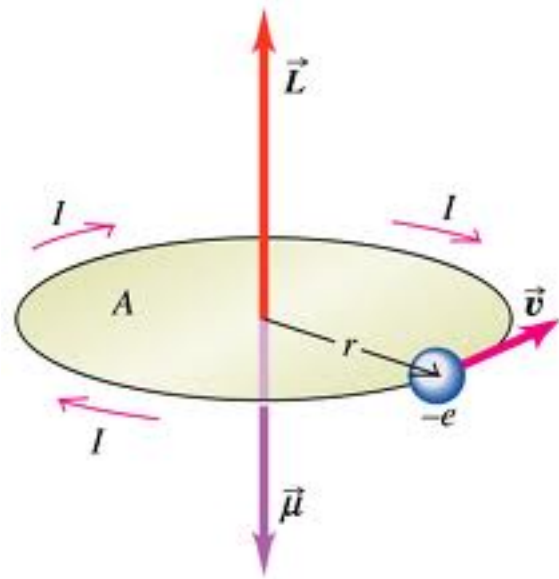


$$\boldsymbol{\mu}_N = -\gamma \mu_N \boldsymbol{\sigma} \quad \mu_N = \frac{e\hbar}{2m_p}$$

$$\boldsymbol{\mu}_e = -2\mu_B \mathbf{s} \quad \mu_B = \frac{e\hbar}{2m_e}$$



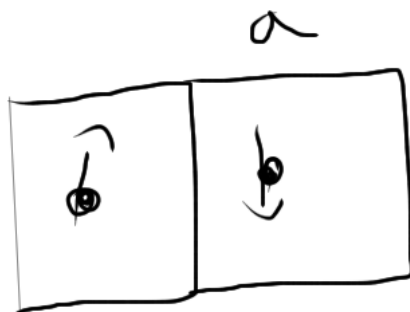
$$\mathbf{B}_s = \vec{\nabla} \times \vec{A} \quad \mathbf{A} = \frac{\mu_0}{4\pi} \frac{\vec{\mu}_e x \hat{R}}{R^2}$$



$$\mathbf{B}_L = \frac{\mu_0}{4\pi} I \frac{d\mathbf{l} x \hat{R}}{R^2}$$

$$q\mathbf{v} = I d\mathbf{l} = -\frac{e}{m_e} \mathbf{p} = -\frac{2\mu_B}{\hbar} \mathbf{p}$$

$$V = -\mu_N \bullet (B_L + B_S)$$



$$\vec{K} = \left( \frac{1}{2} \ 0 \ 0 \right)$$



$$\vec{K} = \left( 0 \ \frac{1}{2} \ 0 \right)$$

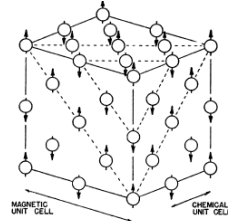
After a lot of math and Quantum Mechanics...

$$\frac{d\sigma}{d\Omega} = (\gamma r_0)^2 N \frac{(2\pi)^3}{v_0} \sum_{\tau_m} |F_m(\tau_m)|^2 \delta(\kappa - \tau_m)$$

$$F_m(\tau_m) = \frac{1}{2} \sum_d F_d(\tau_m) s_{\perp,d} e^{i\boldsymbol{\tau}_m \bullet \mathbf{d}}$$



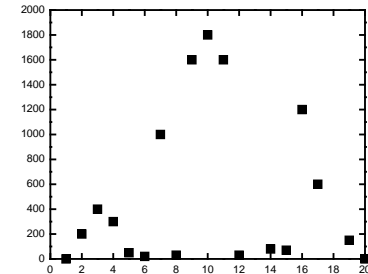
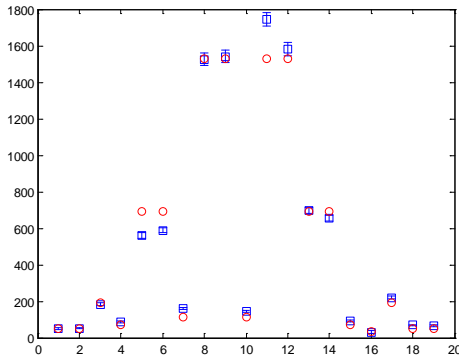
# Guess and Check (Refinement)



Update model

Predict Intensities from model

Compare predicted intensities to data



Choices

# Goodness of Fit

$$\chi^2 = \sum_1^n w_i (y_i - y_{ci}(\alpha))^2 \qquad w_i = \frac{1}{\sigma_i^2}$$

or

$$R_{wp} = 100 \left( \frac{\sum_1^n w_i (y_i - y_{ci}(\alpha))^2}{\sum_1^n w_i (y_i)^2} \right)^{\frac{1}{2}}$$

# Optimization Approaches

Simulated Annealing

Marquardt-Levenberg

Genetic Algorithm

# How I proceed

- Think about the problem
- Powder diffraction
- Think some more
- Try Representational Analysis
- Single crystal diffraction
- Think a lot!!!
- Polarized diffraction
- Spherical polarimetry
- Think some more...

# YMn<sub>2</sub>O<sub>5</sub>

PRL 96, 097601 (2006)

PHYSICAL REVIEW LETTERS

week ending  
10 MARCH 2006

## Ferroelectricity Induced by Acentric Spin-Density Waves in YMn<sub>2</sub>O<sub>5</sub>

L. C. Chapon,<sup>1</sup> P. G. Radaelli,<sup>1,2</sup> G. R. Blake,<sup>1,3</sup> S. Park,<sup>4</sup> and S.-W. Cheong<sup>4</sup>

Powder

Journal of the Physical Society of Japan  
Vol. 76, No. 7, July, 2007, 074706  
©2007 The Physical Society of Japan

## Spiral Spin Structure in the Commensurate Magnetic Phase of Multiferroic RMn<sub>2</sub>O<sub>5</sub>

Hiroyuki KIMURA\*, Satoru KOBAYASHI<sup>1</sup>, Yoshikazu FUKUDA, Toshihiro OSAWA,  
Youichi KAMADA, Yukio NODA, Isao KAGOMIYA<sup>2</sup>, and Kay KOHN<sup>3</sup>

xtal

PHYSICAL REVIEW B 78, 245115 (2008)

## Spiral spin structures and origin of the magnetoelectric coupling in YMn<sub>2</sub>O<sub>5</sub>

J.-H. Kim,<sup>1</sup> S.-H. Lee,<sup>1,\*</sup> S. I. Park,<sup>2</sup> M. Kenzelmann,<sup>3</sup> A. B. Harris,<sup>4</sup> J. Schefer,<sup>3</sup> J.-H. Chung,<sup>5</sup> C. F. Majkrzak,<sup>6</sup>  
M. Takeda,<sup>7</sup> S. Wakimoto,<sup>7</sup> S. Y. Park,<sup>8</sup> S.-W. Cheong,<sup>8</sup> M. Matsuda,<sup>7</sup> H. Kimura,<sup>9</sup> Y. Noda,<sup>9</sup> and K. Kakurai<sup>7</sup>

Xtal+spherical polarimetry

PHYSICAL REVIEW B 79, 020404(R) (2009)

## Incommensurate magnetic structure of YMn<sub>2</sub>O<sub>5</sub>: A stringent test of the multiferroic mechanism

P. G. Radaelli,<sup>1,2</sup> C. Vecchini,<sup>1,3</sup> L. C. Chapon,<sup>1</sup> P. J. Brown,<sup>4</sup> S. Park,<sup>5</sup> and S.-W. Cheong<sup>5</sup>

Xtal+more representation analysis



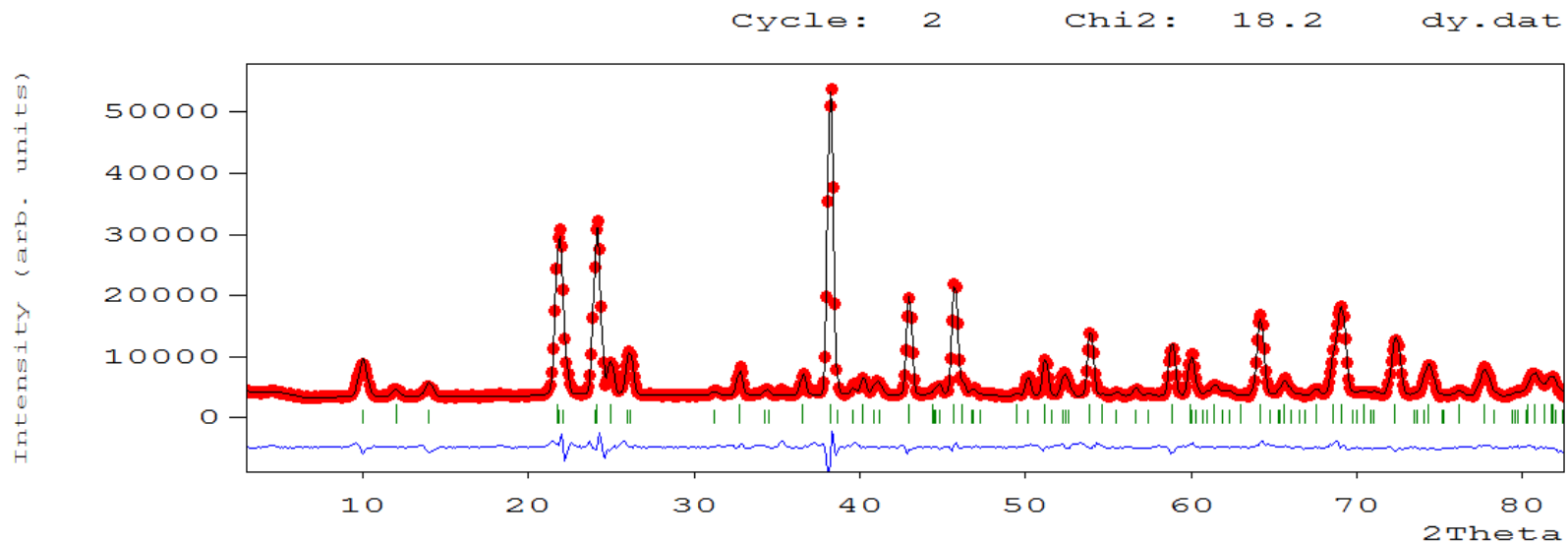
# Powder Diffraction

## Advantages

- You get the big picture
- Can get the propagation vector
- Avoids the muss and fuss of extinction
- It's often Good Enough™

## Disadvantages

- Can be hard to truly index  $k$ — is it  $[3\ 4\ 0]$  or  $[0\ 0\ 5]$ ?
- You average over all symmetry equivalent  $k$  at any particular Bragg angle
- You lose information in the powder averaging
- No domain info
- No multi- $k$  info
- Can be very hard to determine phase



- Determine the propagation vector
- Use symmetry analysis to constrain the possible magnetic structures
- Refine the moment directions and magnitudes

# Single Crystal Diffraction

## Advantages

- Can fully determine  $\mathbf{k}$
- Can investigate domain populations
- Can apply probes (magnetic field, E-field, pressure, etc.) along a particular direction to see effect on magnetic ordering

## Disadvantages

- Extinction
- Absorption depends on shape
- Reciprocal space is large...
- Crystal growth is hard...

# Where Do I Go?



# <http://www.neutron.anl.gov/facilities.html>

## Neutron Scattering Facilities

### Asia and Australia

**Bragg Institute**, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia  
**High-flux Advanced Neutron Application Reactor (HANARO)**, Korea  
**Japan Atomic Energy Research Institute (JAERI)**, Tokai, Japan  
**Japan Proton Accelerator Research Complex (J-PARC)**, Tokai, Japan  
**Kyoto University Research Reactor Institute (KURRI)**, Kyoto, Japan  
**Reactor Triga Puspatti (RTP)**, Malaysian Nuclear Agency, Malaysia

### Europe

**Budapest Neutron Centre**, AEKI, Budapest, Hungary  
**Berlin Neutron Scattering Center**, Helmholtz-Zentrum Berlin, Germany  
**Delft Neutron & Positron Research**, Delft University of Technology, Netherlands  
**Frank Laboratory of Neutron Physics**, Joint Institute of Nuclear Research, Dubna, Russia  
**FRJ-2 Reactor**, Forschungszentrum Jülich, Germany  
**FRM-II Research Reactor**, Garching, Germany  
**GEMS Research Reactor**, Geesthacht, Germany  
**Institut Laue Langevin**, Grenoble, France  
**ISIS Pulsed Neutron and Muon Facility**, Rutherford-Appleton Laboratory, Oxfordshire, UK  
**JEEP-II Reactor**, IFE, Kjeller, Norway  
**Laboratoire Léon Brillouin**, Saclay, France  
**Ljubljana TRIGA MARK II Research Reactor**, J. Stefan Institute, Slovenia  
**Nuclear Physics Institute (ASCR)**, Řež nr Prague, Czech Republic  
**St. Petersburg Nuclear Physics Institute**, Gatchina, Russia  
**Swiss Spallation Neutron Source (SINQ)**, Villigen Switzerland

### North and South America

**Centro Atomico Bariloche**, Rio Negro, Argentina  
**Canadian Neutron Beam Centre**, Chalk River, Ontario, Canada  
**High Flux Isotope Reactor (HFIR)**, Oak Ridge National Laboratory, Tennessee, USA  
**Los Alamos Neutron Science Center (LANSCE)**, New Mexico, USA  
**Low Energy Neutron Source (LENS)**, Indiana University Cyclotron Facility, USA  
**McMaster Nuclear Reactor**, Hamilton, Ontario, Canada  
**MIT Nuclear Reactor Laboratory**, Massachusetts, USA  
**NIST Center for Neutron Research**, Gaithersburg, Maryland, USA  
**Peruvian Institute of Nuclear Energy (IPEN)**, Lima, Peru  
**Spallation Neutron Source**, Oak Ridge National Laboratory, Tennessee, USA  
**University of Missouri Research Reactor**, Columbia, Missouri, USA

### Planned Facilities

**Austron Spallation Neutron Source**, Vienna, Austria  
**China Advanced Research Reactor (CARR)**, Beijing, China  
**China Spallation Neutron Source (CSNS)**, Dongwan, Guangdong, China  
**European Spallation Source (ESS)**, Lund, Sweden

### Closed Facilities

**Intense Pulsed Neutron Source (IPNS)**, Argonne National Laboratory, Illinois, USA  
**KENS Neutron Scattering Facility**, KEK, Tsukuba, Japan  
**Risø National Laboratory**, Denmark  
**Studsvik Neutron Research Laboratory (NFL)**, Studsvik, Sweden  
**University of Illinois Triga Reactor**, Urbana-Champaign, Illinois, USA

# North America



# Powder Diffractometers (Reactor)

	BT1	HB2A	C2
2 $\theta$	0-167	2-155	0-120
detectors	32	44 He3	800-wire BF3 PSD
Detector spacing	5 degrees	2.7 degrees	0.1 degrees
flux	10 <sup>6</sup> (n/cm <sup>2</sup> /s)	5x10 <sup>6</sup> (n/cm <sup>2</sup> /s)	7x10 <sup>7</sup> (n/cm <sup>2</sup> /s)
Sample Environment	.05-2000K 7 T magnet Pressure	0.3-1800K 7T magnet	1.5K-800K 7.5 T Vertical, 2.7 T Horizontal
Monochromators	Cu, Ge	Ge	Cu, Ge, Be, Al, PG, Si, Heussler

LUJAN: HIPD, HIPPO

# Powder Diffractometers (Spallation)

- POWGEN (SNS)
- $Q=0.5-20 \text{ \AA}^{-1}$
- Detector  $25 < 2\theta < 150$
  
- NOMAD (SNS)
- $Q=0.5-50 \text{ \AA}^{-1}$
- Detector  $3 < 2\theta < 175$

# Single Xtal Diffractometers

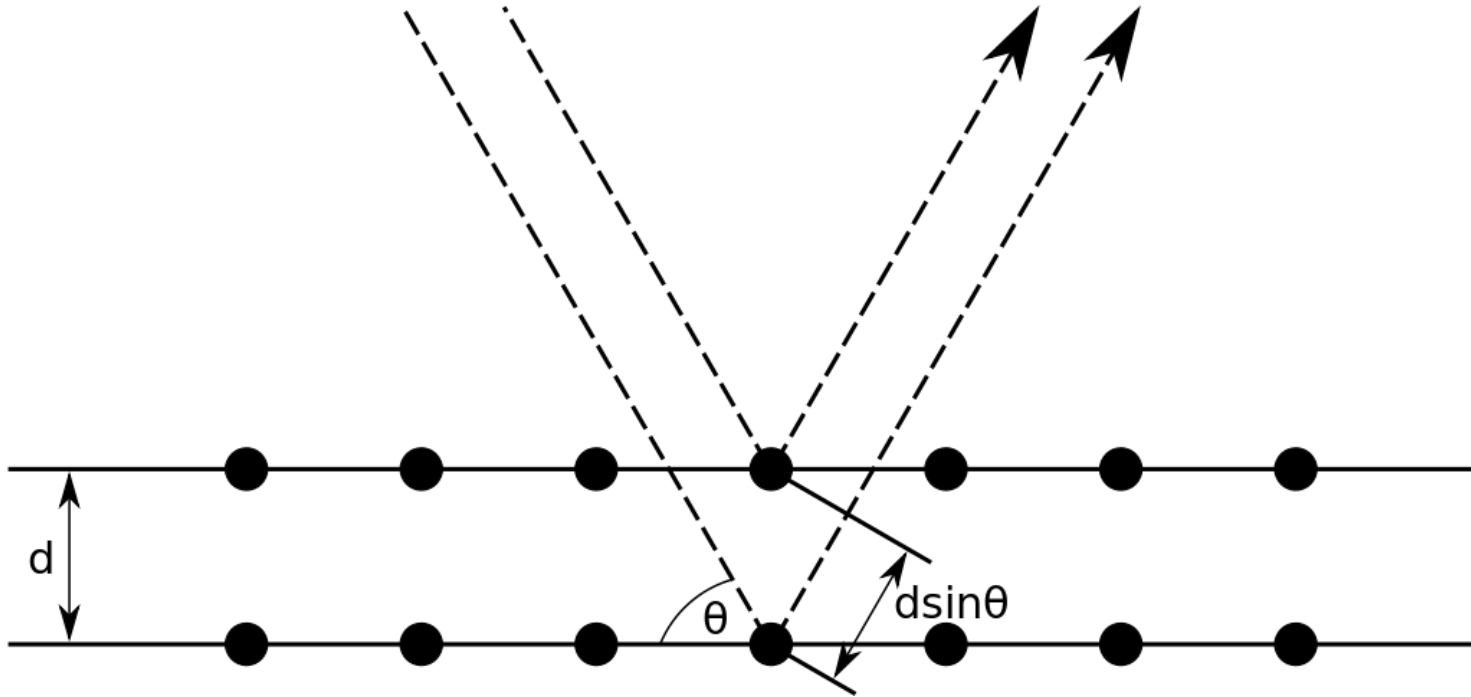
- HFIR—HB3A
- SNS – TOPAZ (operational next year?)
- LUJAN – SCD (No longer in user program)
- Chalk River—E3, N5
- NIST -- Hopeful...

# Triple Axis Spectrometers

- NIST—BT4, BT7, SPINS
- HFIR – HB1A, HB1, HB3, C4
- Chalk River – C5, N5

Questions?

# Bragg's Law



$$\vec{G} = \vec{K}$$

$$|\vec{G}| = |\vec{K}|$$

$$\frac{2\pi}{d h k l} =$$