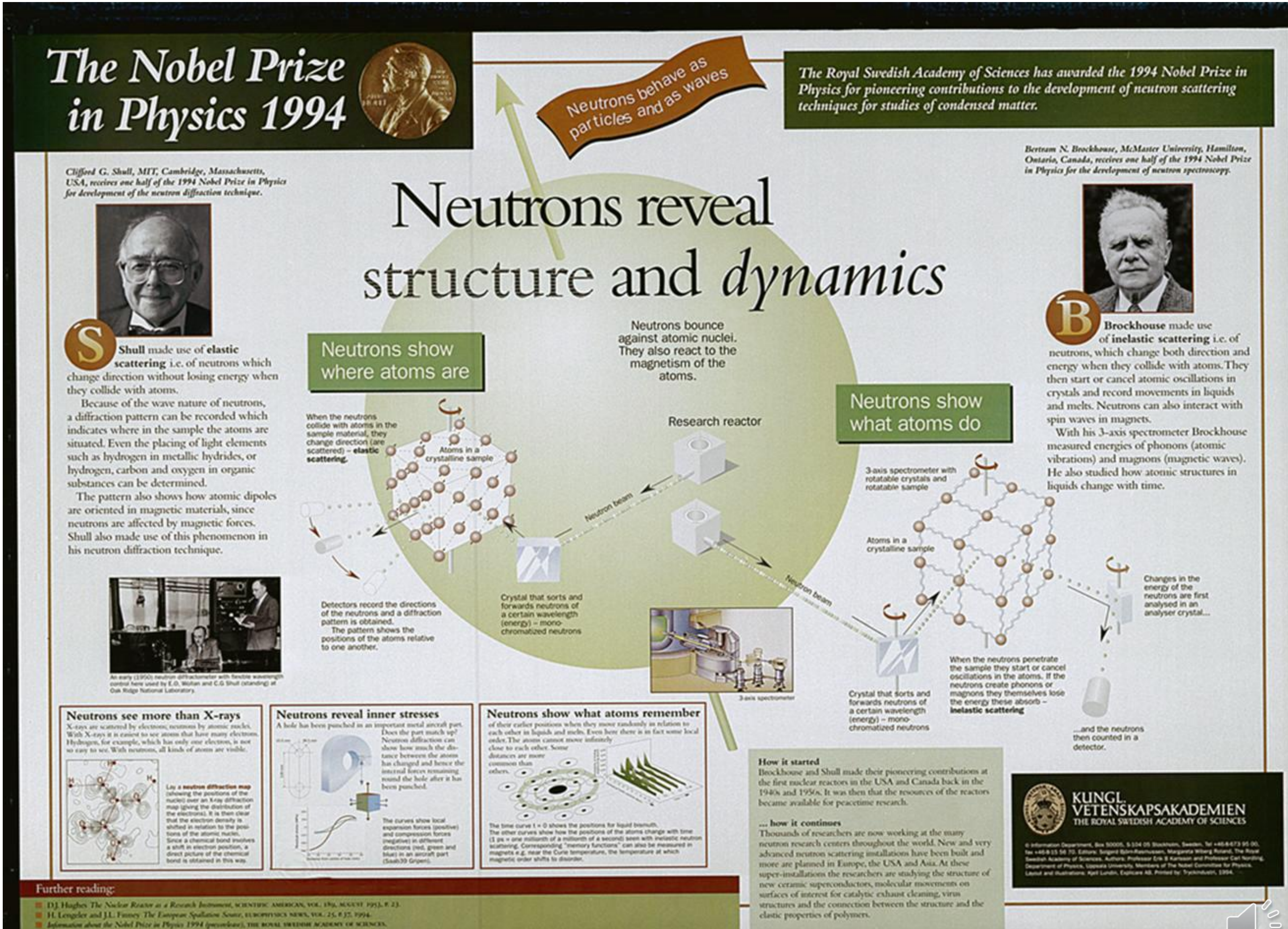
Experimental Aspects of Neutron Diffraction

William Ratcliff
NCNR



The Nobel Prize in Physics 1994
Neutrons behave as particles and as waves
The Royal Swedish Academy of Sciences has awarded the 1994 Nobel Prize in Physics for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter.
Clifford G. Shull, MIT, Cambridge, Massachusetts, USA, receives one half of the 1994 Nobel Prize in Physics for development of the neutron diffraction technique.
Bertram N. Brockhouse, McMaster University, Hamilton, Ontario, Canada, receives one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.
Neutrons reveal structure and dynamics
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.
Neutrons show where atoms are
Neutrons bounce against atomic nuclei. They also react to the magnetism of the atoms.
Research reactor
Neutrons show what atoms do
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.
When the neutrons collide with atoms in the sample material, they change direction (are scattered) – elastic scattering.
Atoms in a crystalline sample
Neutron beam
Detectors record the directions of the neutrons and a diffraction pattern is obtained. The pattern shows the positions of the atoms relative to one another.
Crystal that sorts and forwards neutrons of a certain wavelength (energy) – monochromatized neutrons
3-axis spectrometer with rotatable crystals and rotatable sample
Atoms in a crystalline sample
Changes in the energy of the neutrons are first analysed in an analyser crystal...
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
...and the neutrons then counted in a detector.
3-axis spectrometer
Neutrons see more than X-rays
Neutrons reveal inner stresses
Neutrons show what atoms remember
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
Further reading:


POLICE
PUBLIC
CALL
BOX

1932 Neutrons Discovered by Chadwick

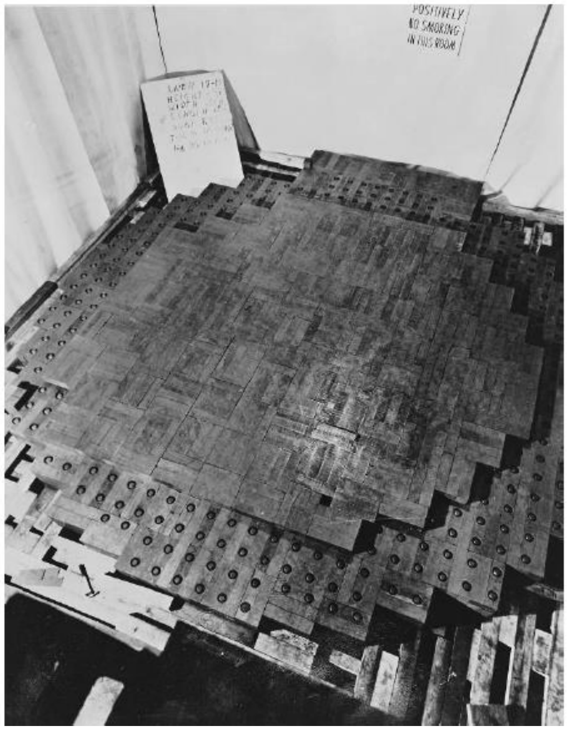
MAY 15, 1939 PHYSICAL REVIEW VOLUME 55

On the Magnetic Scattering of Neutrons

O. Halpern and M. H. Johnson
New York University, University Heights, New York, New York

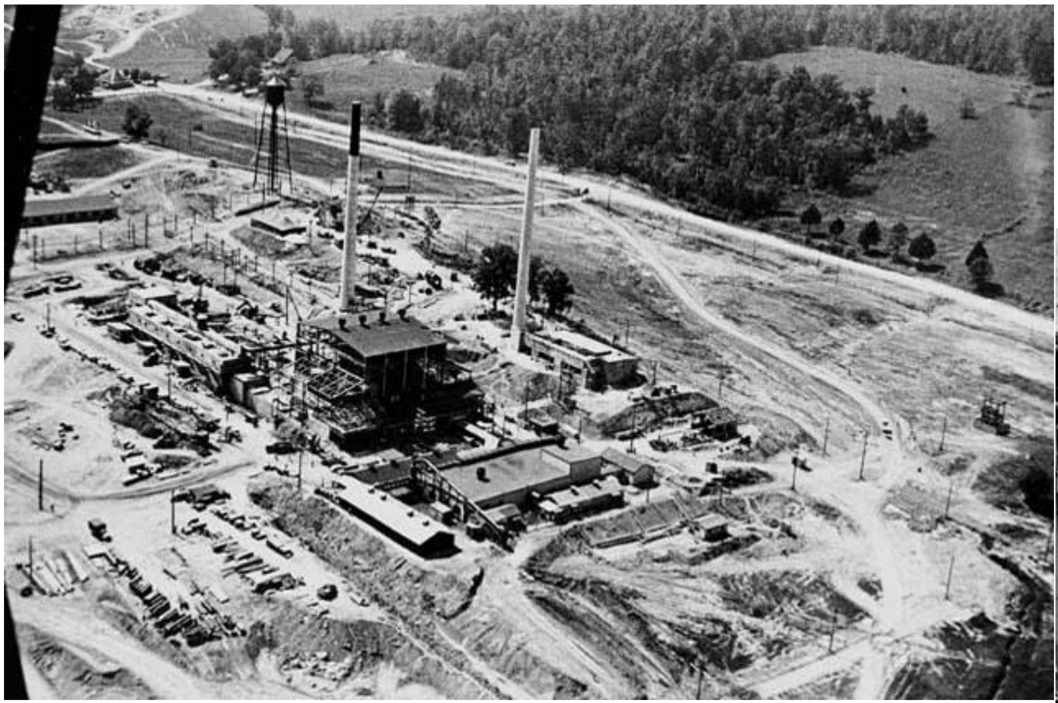
(Received December 3, 1938)

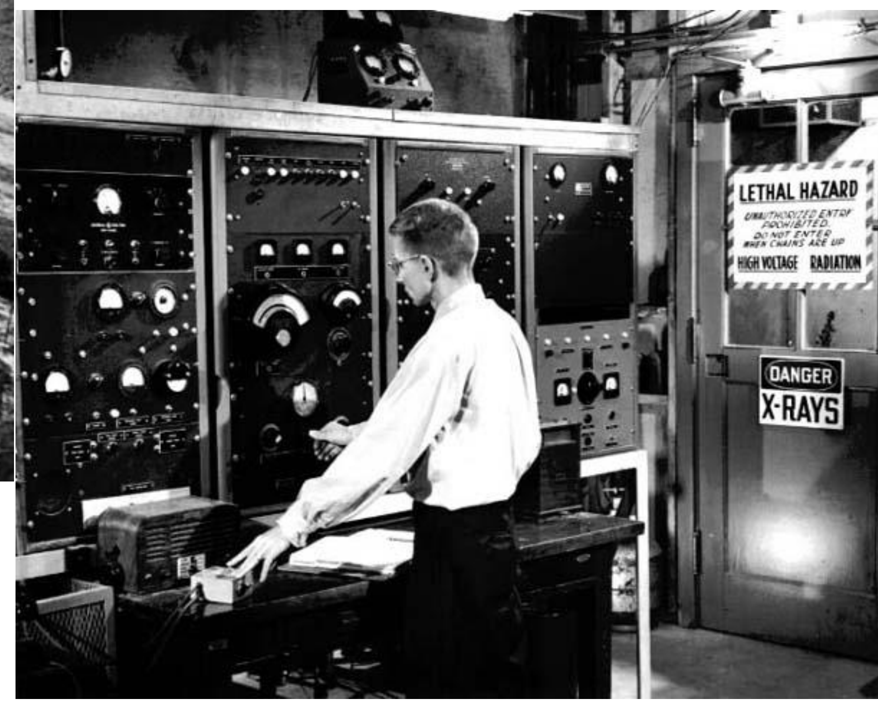
1942 Fermi's 30th pile goes critical



An Account of Oak Ridge National Laboratory's Thirteen Nuclear Reactors August 2009
https://info.ornl.gov/sites/publications/Files/Pub20808.pdf

ORNL Graphite Reactor
1943-1963





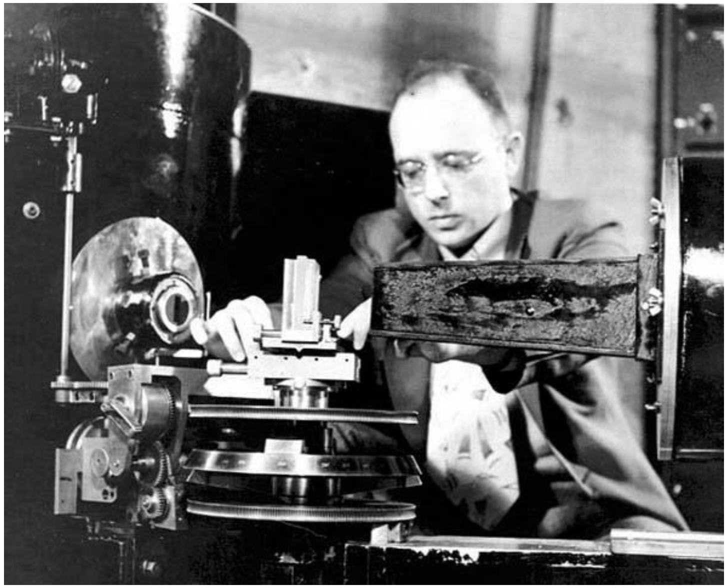
An Account of Oak Ridge National Laboratory’s Thirteen Nuclear Reactors August 2009
https://info.ornl.gov/sites/publications/Files/Pub20808.pdf

PHYSICAL REVIEW VOLUME 73, NUMBER 8 APRIL 15, 1948

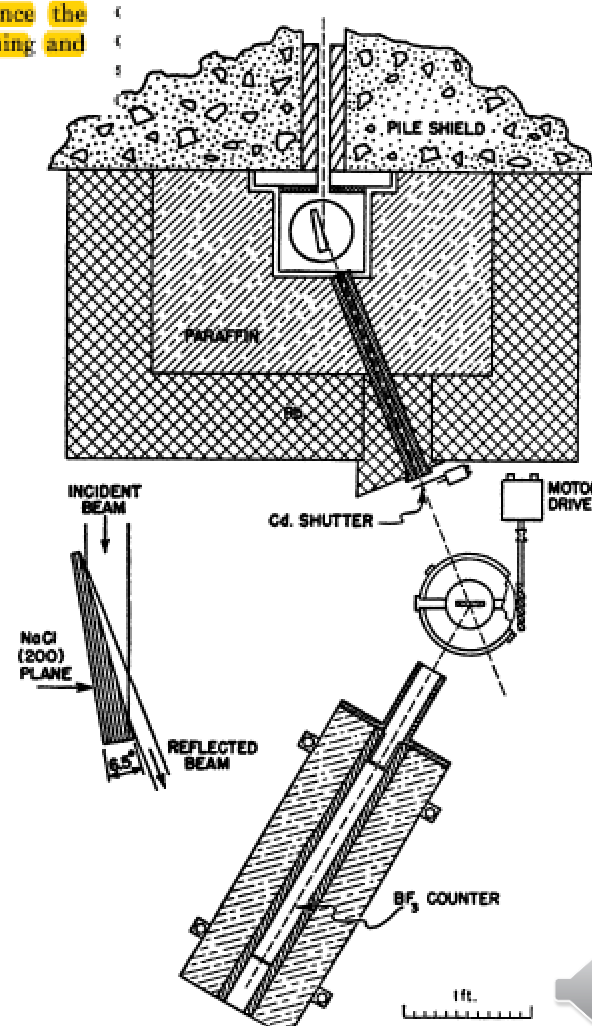
The Diffraction of Neutrons by Crystalline Powders

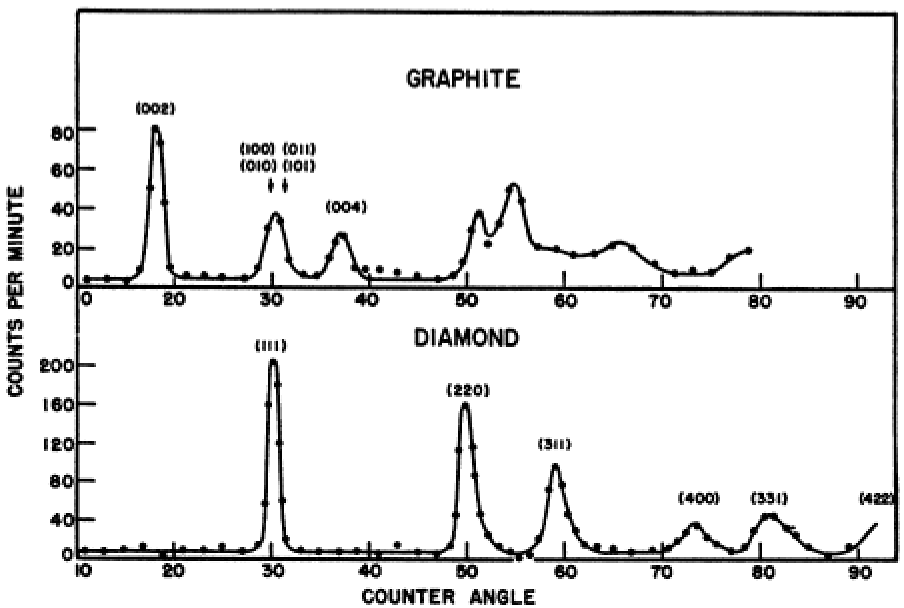
E. O. Wollan and C. G. Shull
Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received January 5, 1948)

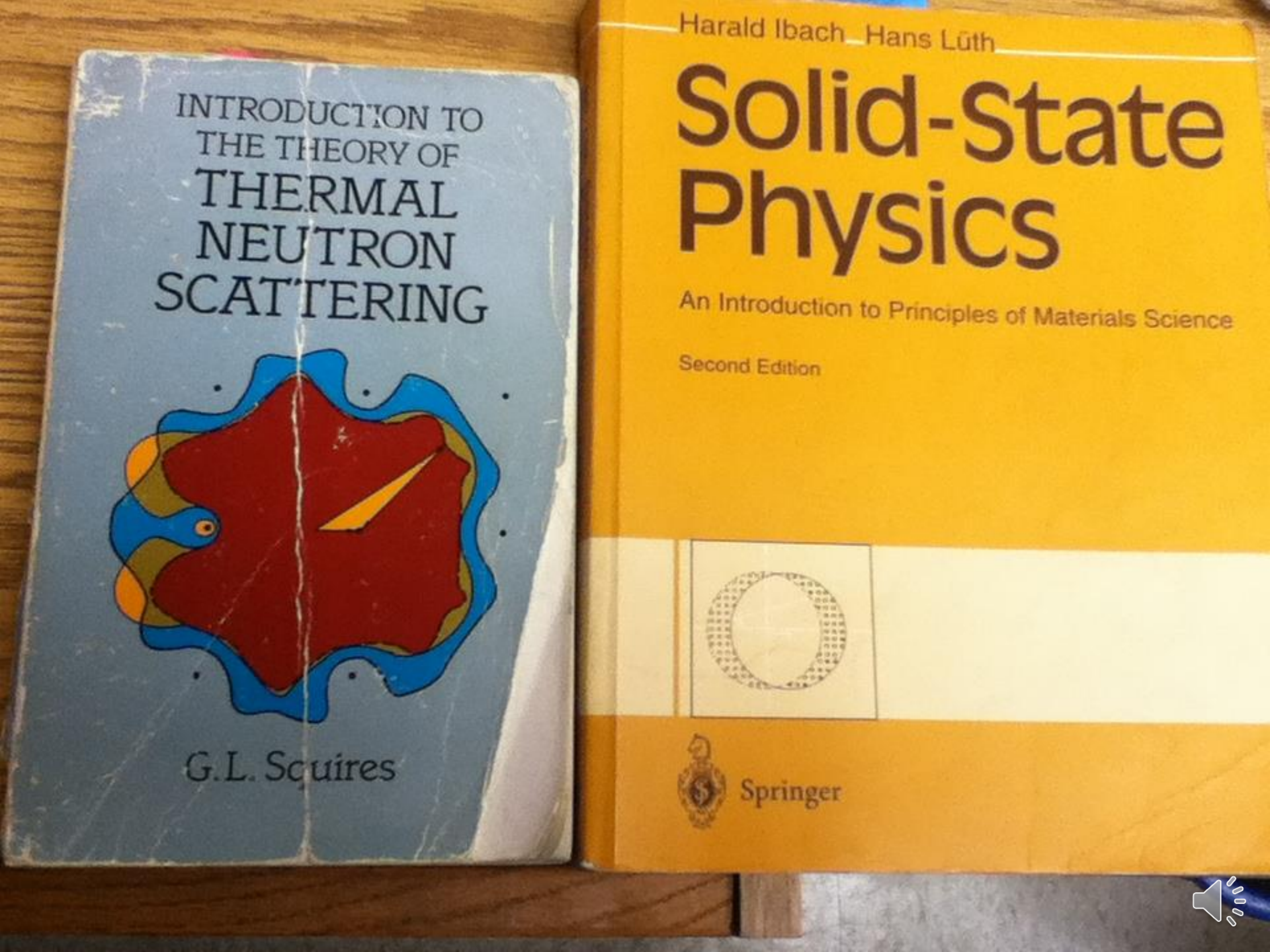


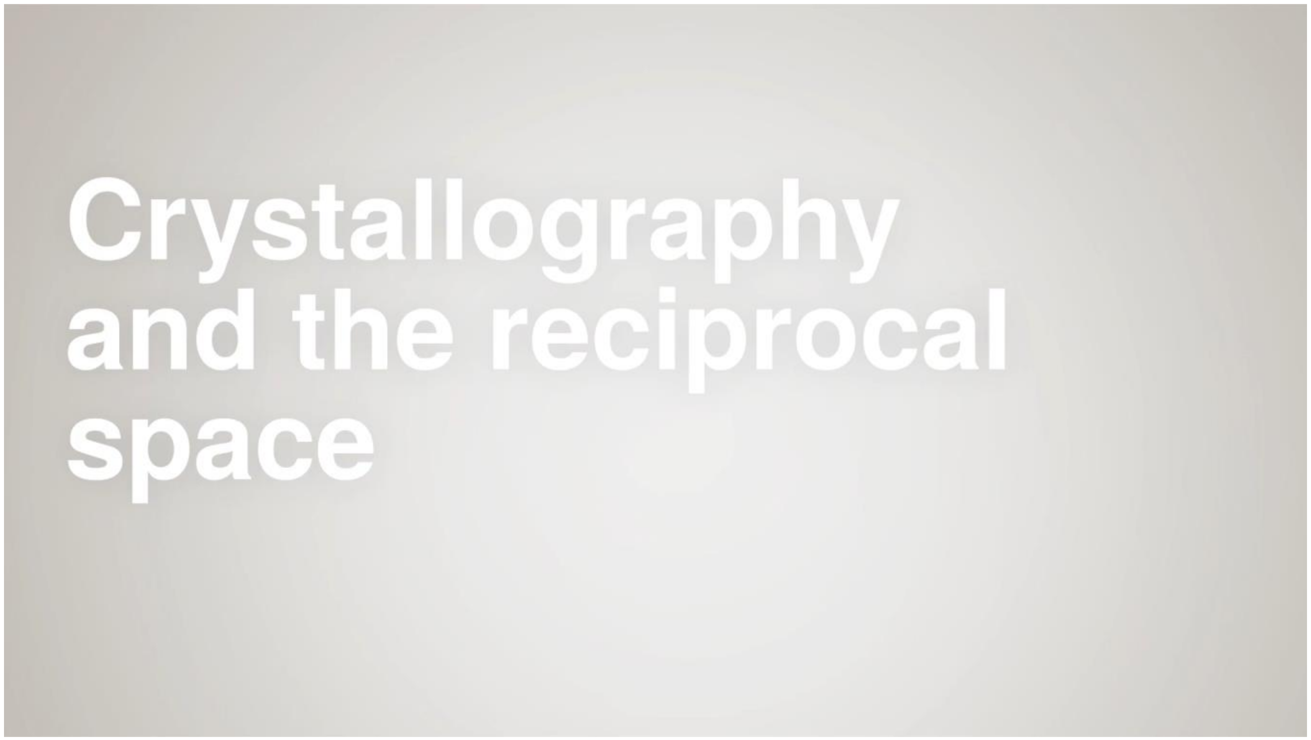
angular range. The advantage of automatic operation cannot be overestimated since the best data can be taken during the evening and night shifts.



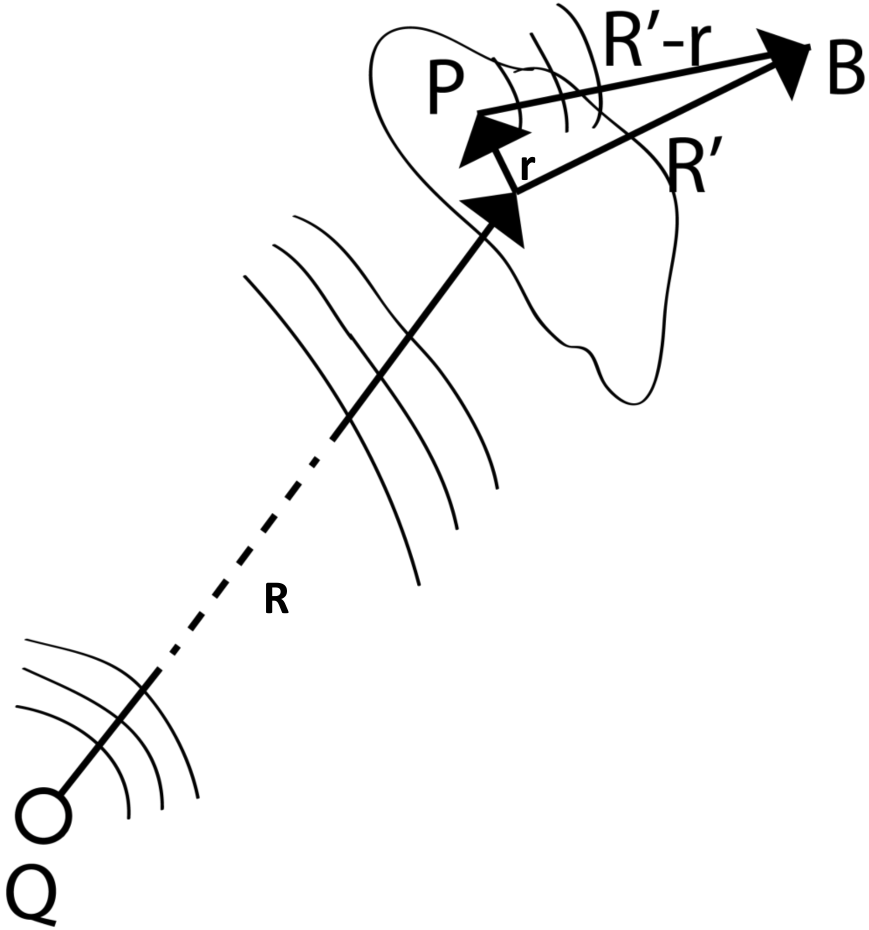


howstuffworks
It’s good to know


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



http://toutestquantique.fr/en/



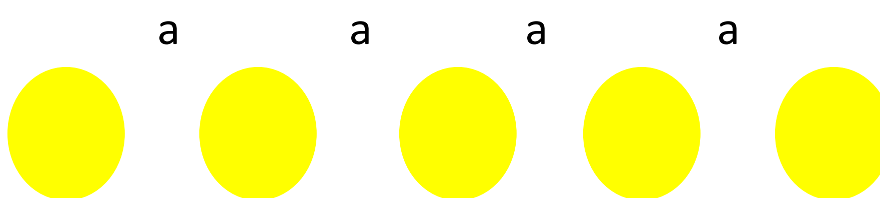
$$A_P = A_0 e^{i\overrightarrow{k_0}\bullet(\overrightarrow{R+r})-i\omega_0 t}$$

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

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

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

Reciprocal Space



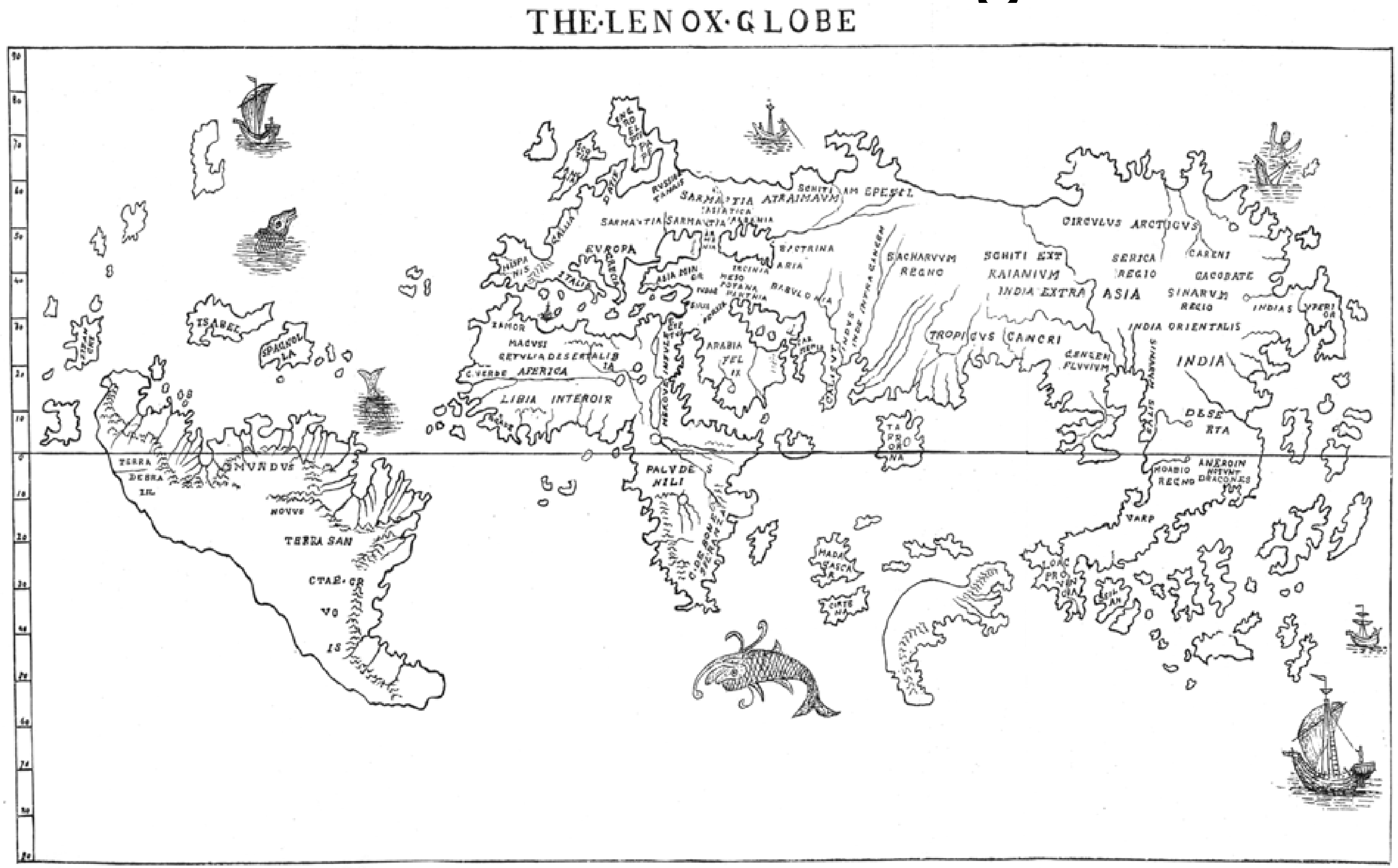
$$\rho(x) = \rho(x + na)$$

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

$$\rho(\vec{r}) = \sum_n \rho_{\vec{G}} e^{i\vec{G}\bullet\vec{r}} \qquad \vec{r_n} = n_1\vec{a_1} + n_2\vec{a_2} + n_3\vec{a_3}$$

$$\vec{G} \bullet \vec{r} = 2\pi m \qquad g_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \bullet (\vec{a}_2 \times \vec{a}_3)}$$

Here there be dragons…



The Hunt-Lenox Globe, as transcribed by B.F. da Costa

https://www.theatlantic.com/technology/archive/2013/12/no-old-maps-actually-say-here-be-dragons/282267/

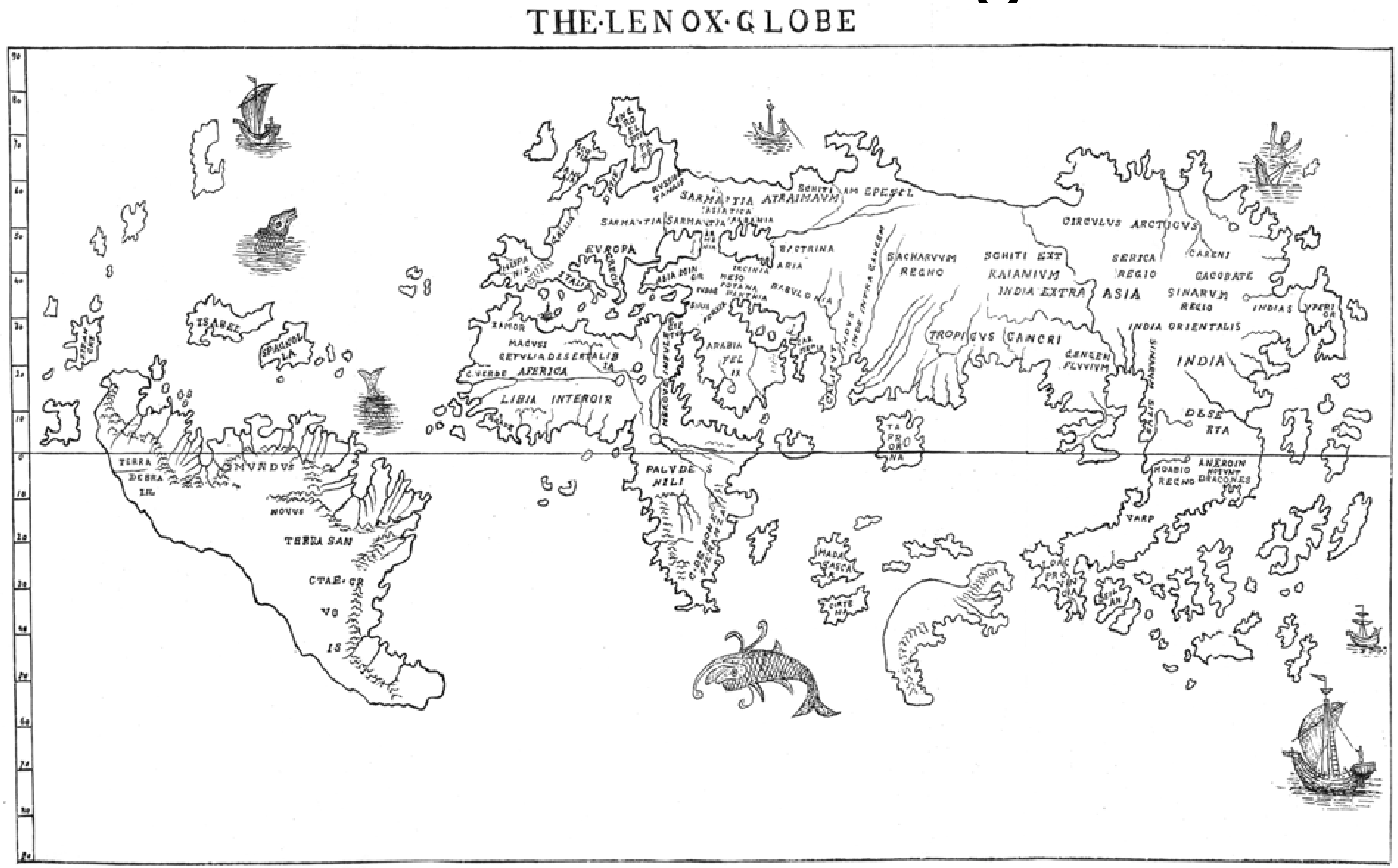
$$I(K) \propto \left|A_B\right|^2 \propto \left|\int \rho(r) e^{-i\vec{K}\bullet\vec{r}} dr\right|^2$$

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

$$\int e^{i\overrightarrow{(G-K)}\bullet\vec{r}} dr = \begin{cases} V \text{ for } \vec{G} = \vec{K} \\ \sim 0 \text{ otherwise} \end{cases}$$

Laue Condition

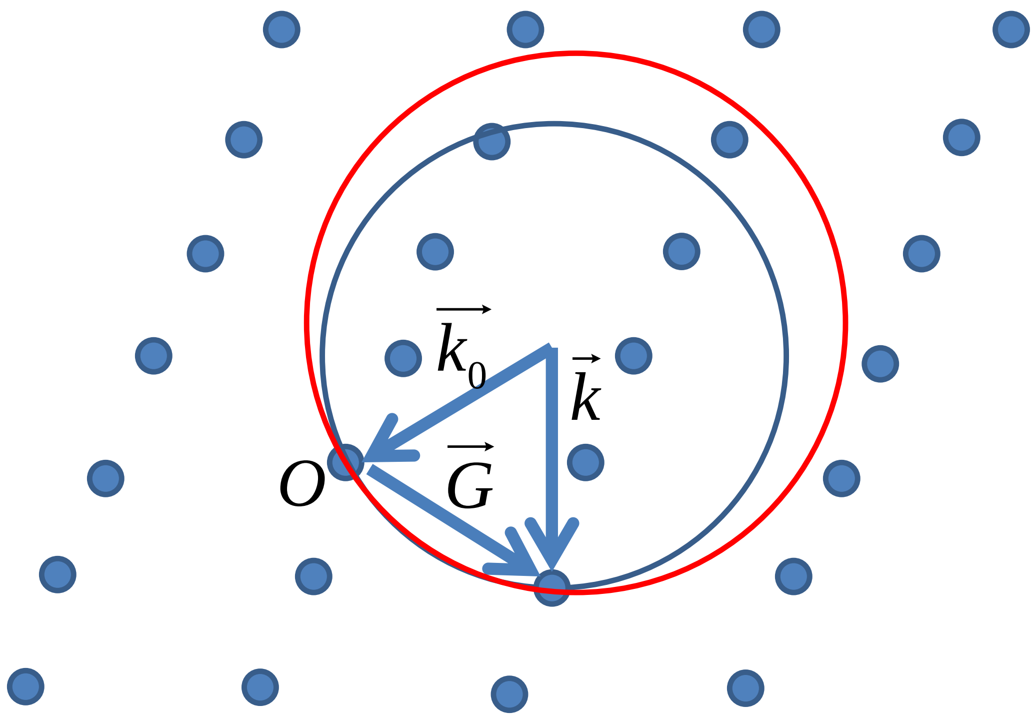
Here there be dragons…



The Hunt-Lenox Globe, as transcribed by B.F. da Costa

https://www.theatlantic.com/technology/archive/2013/12/no-old-maps-actually-say-here-be-dragons/282267/

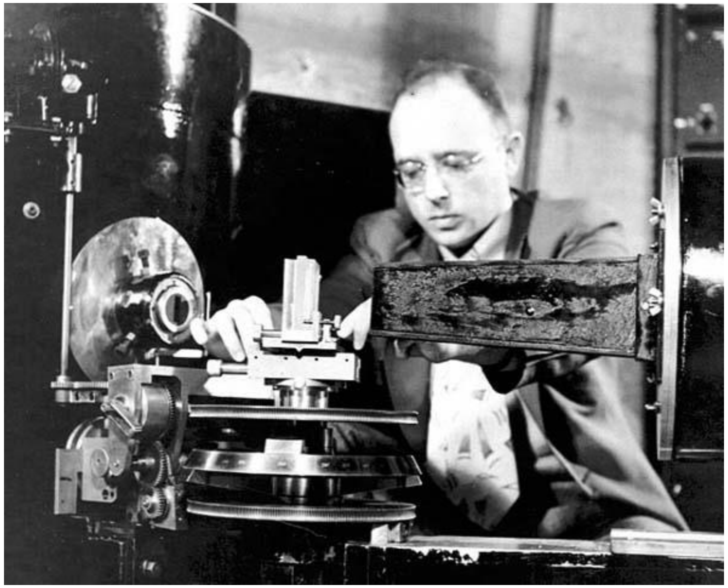
Ewald Sphere

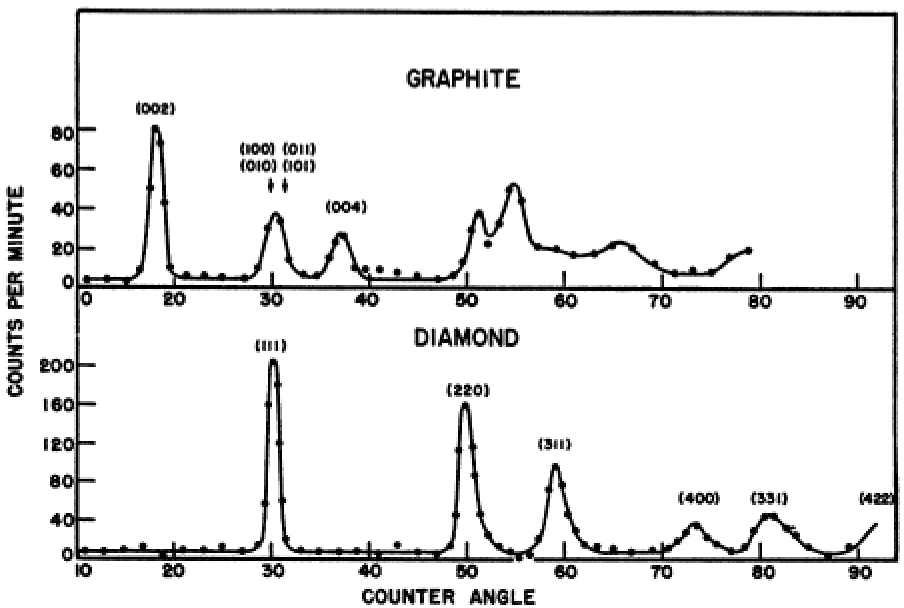


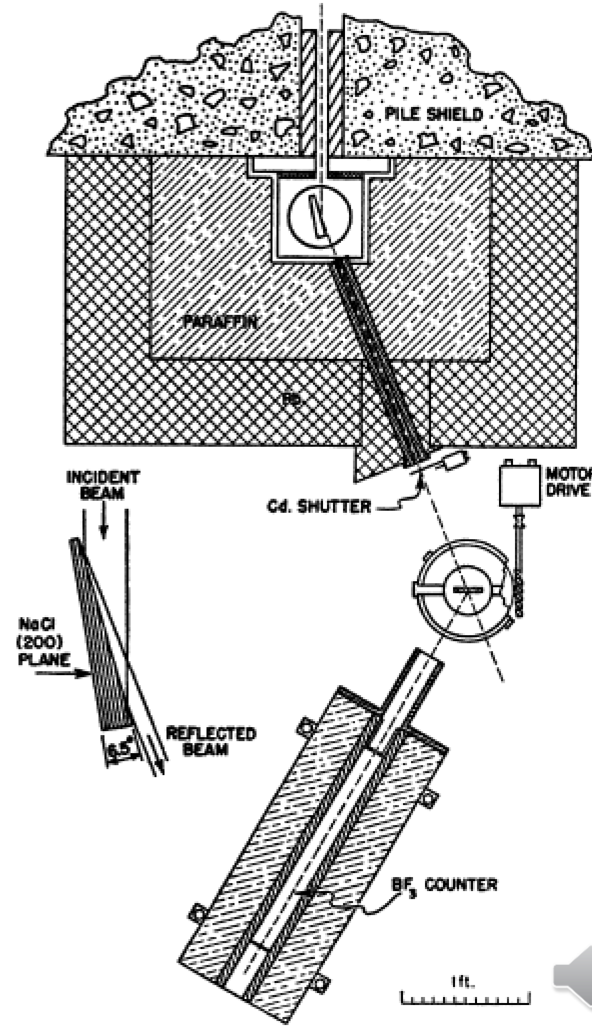
PHYSICAL REVIEW VOLUME 73, NUMBER 8 APRIL 15, 1948

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)







So…

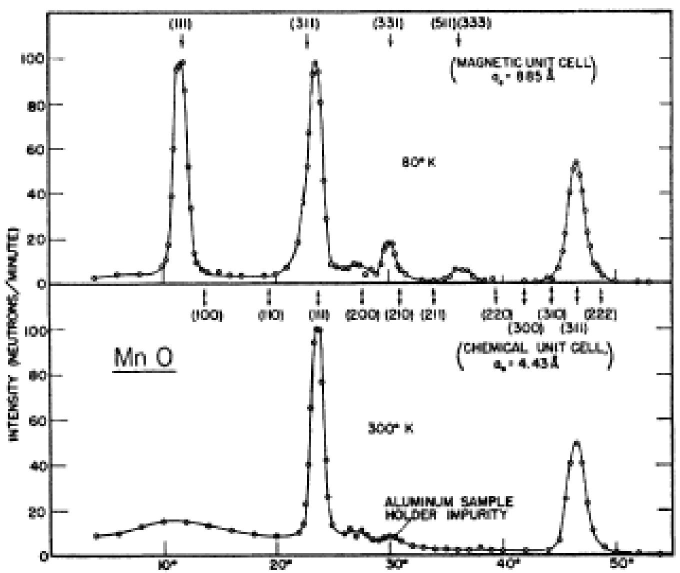
- See scattering where reciprocal lattice point lies on Ewald Sphere
- But, whither magnetism???

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

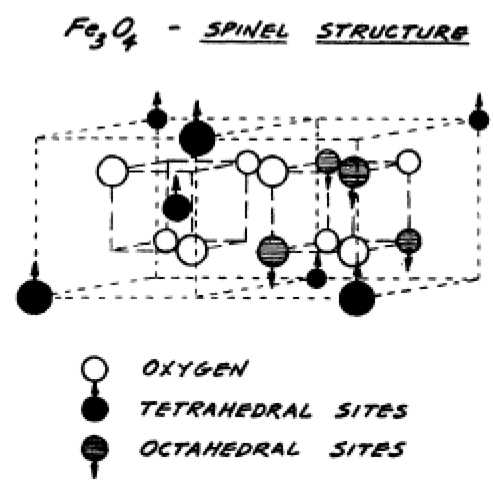
August 29, 1949



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

C. G. Shull, E. O. Wollan, and W. A. Strauser
Oak Ridge National Laboratory, Oak Ridge, Tennessee

December 8, 1950



howstuffworks

It's good to know

$$F(q) = \sum_i f(q) s_{\perp,i} \, e^{i q \cdot r_i}$$

$$I \propto |F|^2$$

sensitive to component of moment $\perp$ Q

orthorhombic cell

00L reflections?

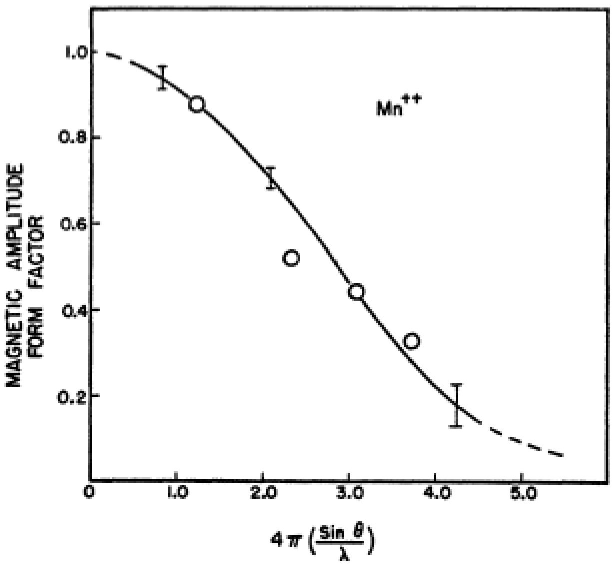
H00 reflections

K00 ?

PHYSICAL REVIEW VOLUME 83, NUMBER 2 JULY 15, 1951

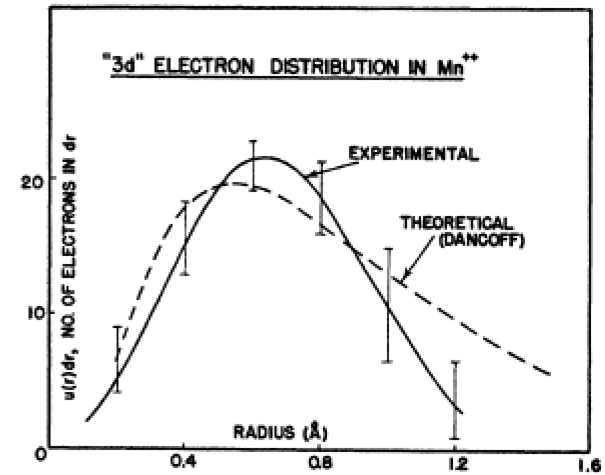
Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. Shull, W. A. Strauser, and E. O. Wollan
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received March 2, 1951)



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

$$u(r) = (2r/\pi)\int_0^\infty kf(k)\,\sin krdk$$



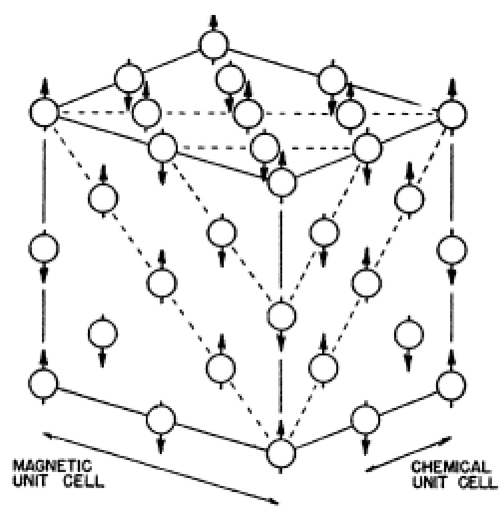
(a) The magnetic moments are aligned along arbitrary [100] directions, in other words, along the cube axes, as illustrated in Fig. 5. For this case it can be shown that q^2 (average) $= \frac{2}{3}$ for each of the four observed magnetic reflections in MnO.

(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.

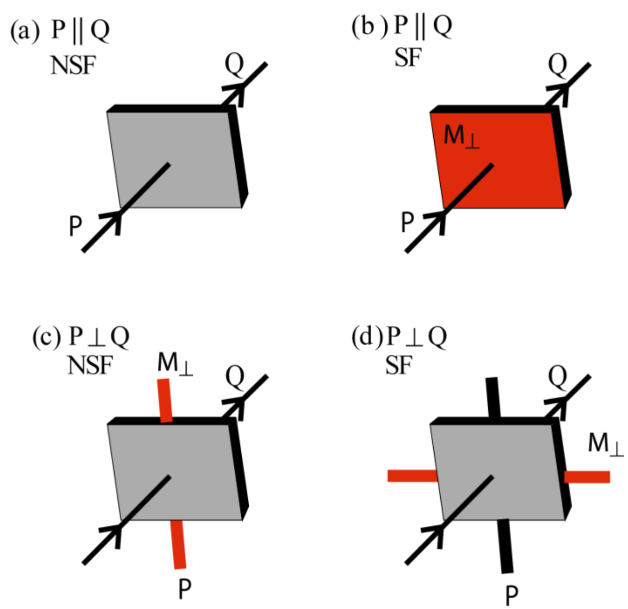
	Calculated for various oriented models (a)	(b)	(c)	Observed (neutrons/min)
(111)	1038	0	1560	1072
(311)	460	675	...	308
(331)	129	109	...	132
(511) (333)	54	24	...	70



PHYSICAL REVIEW VOLUME 84, NUMBER 5 DECEMBER 1, 1951

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)



PHYSICAL REVIEW VOLUME 100, NUMBER 2 OCTOBER 15, 1955

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

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

(Received May 9, 1955)

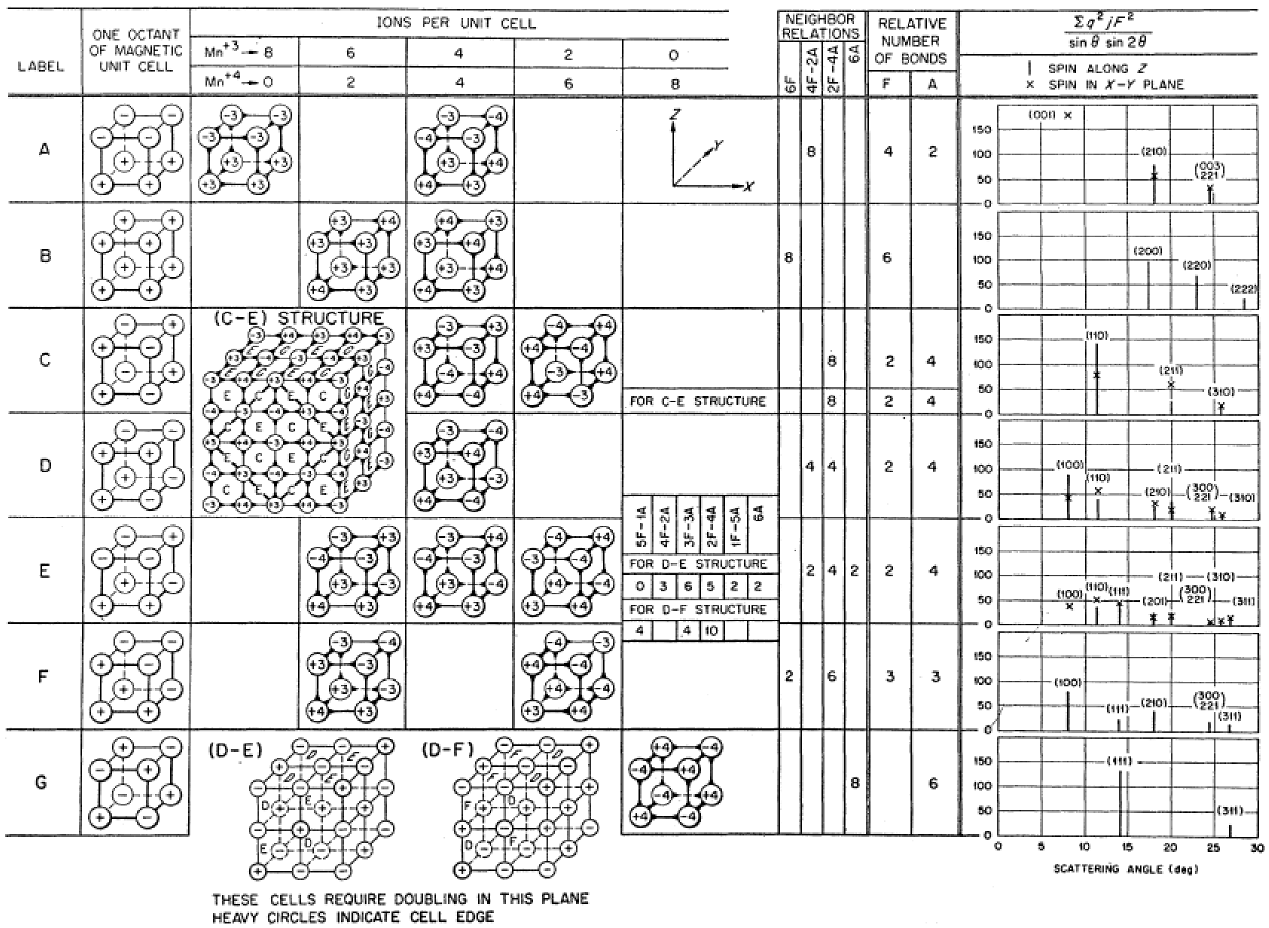
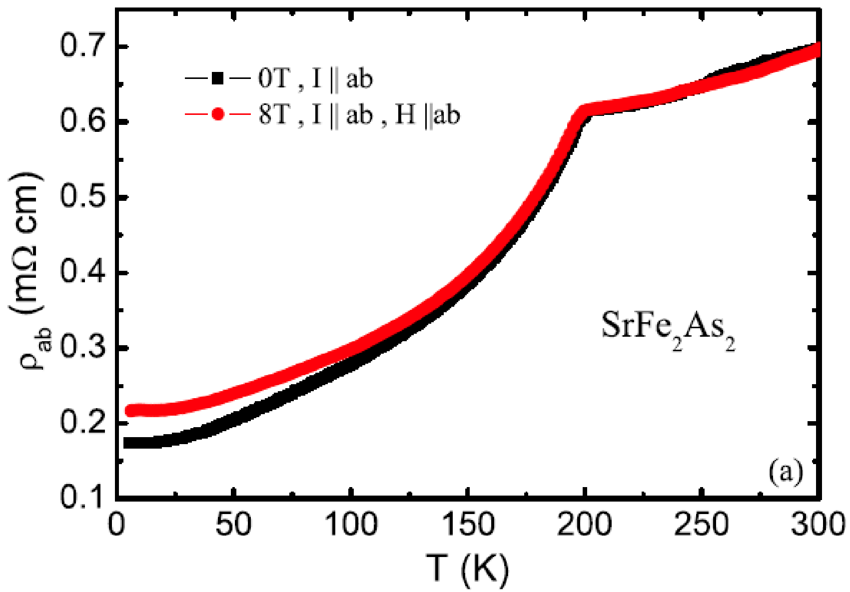


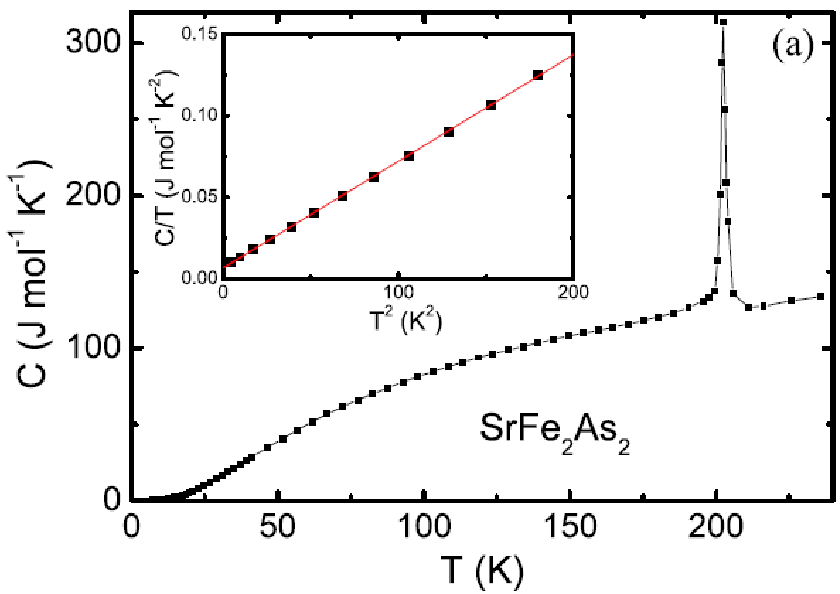
FIG. 18. Scheme of magnetic structures and related information. *A*, *B*, *C*, *G*, and (*C-E*) definitely observed and some evidence for *D* and *F*. Ion ordering schemes represent arrangements consistent with certain coupling criteria. Arrowheads are a schematic representation of Goodenough's semicovalent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

Intermission

How it starts?

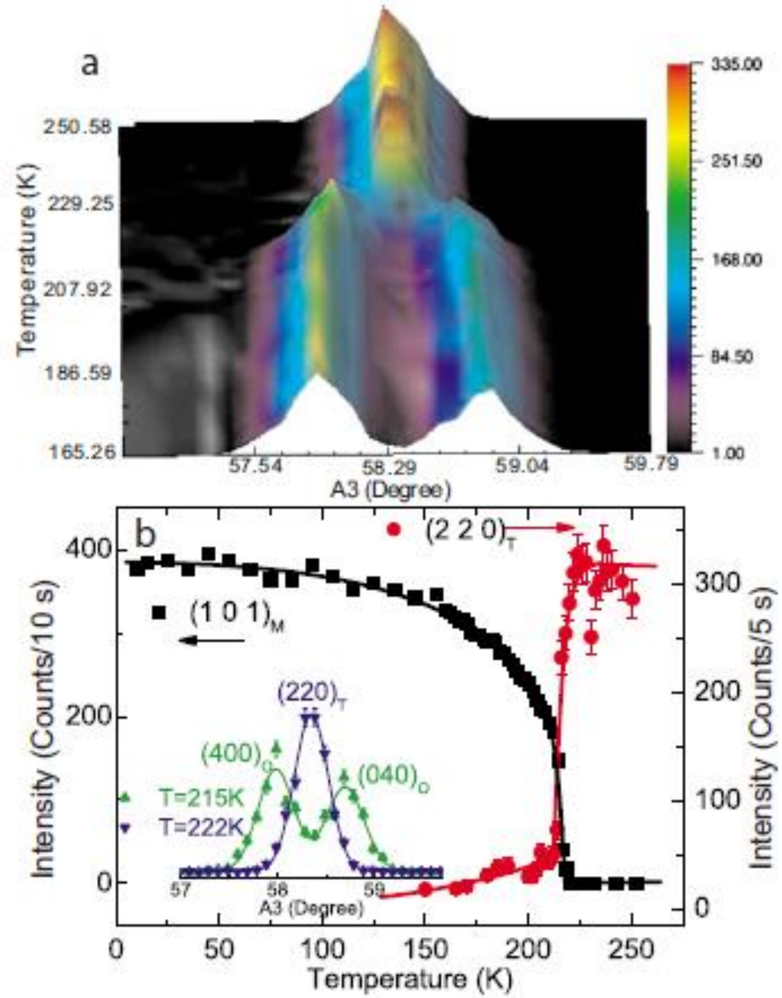
Bulk Data Comes In





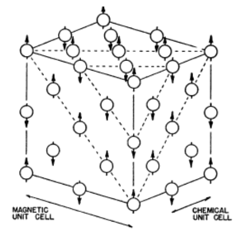
Physical Review B **78**, 22514 (2008)

Neutrons to the Rescue



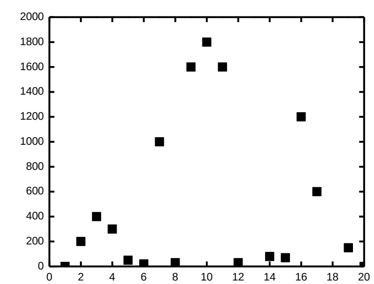
Physical Review B **78**, 140504 (2008)

Guess and Check (Refinement)

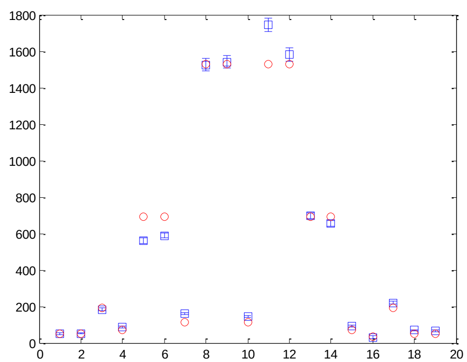


Update model

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

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

"R factors in Rietveld analysis: How good is good enough?", Brian Toby,Powder Diffraction 21, 67 (2006)

Optimization Approaches

Simulated Annealing

Marquardt-Levenberg

Genetic Algorithm

How I proceed

- Think about the problem
- Powder diffraction
- Think some more
- Try Representational Analysis (or Group theory)
- Single crystal diffraction
- Think a lot!!!
- Polarized diffraction
- Spherical polarimetry
- Think some more…

YMn_2O_5

PRL 96, 097601 (2006) PHYSICAL REVIEW LETTERS week ending 10 MARCH 2006

Ferroelectricity Induced by Acentric Spin-Density Waves in YMn_2O_5

L. C. Chapon,[1] P. G. Radaelli,[1,2] G. R. Blake,[1,3] S. Park,[4] and S.-W. Cheong[4]

Powder

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

Spiral Spin Structure in the Commensurate Magnetic Phase of Multiferroic RMn_2O_5

Hiroyuki KIMURA*, Satoru KOBAYASHI[1], Yoshikazu FUKUDA, Toshihiro OSAWA,
Youichi KAMADA, Yukio NODA, Isao KAGOMIYA[2], and Kay KOHN[3]

xtal

PHYSICAL REVIEW B 78, 245115 (2008)

Spiral spin structures and origin of the magnetoelectric coupling in YMn_2O_5

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

Xtal+spherical polarimetry

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

Incommensurate magnetic structure of YMn_2O_5: A stringent test of the multiferroic mechanism

Xtal+more representation analysis

P. G. Radaelli,[1,2] C. Vecchini,[1,3] L. C. Chapon,[1] P. J. Brown,[4] S. Park,[5] and S-W. Cheong[5]

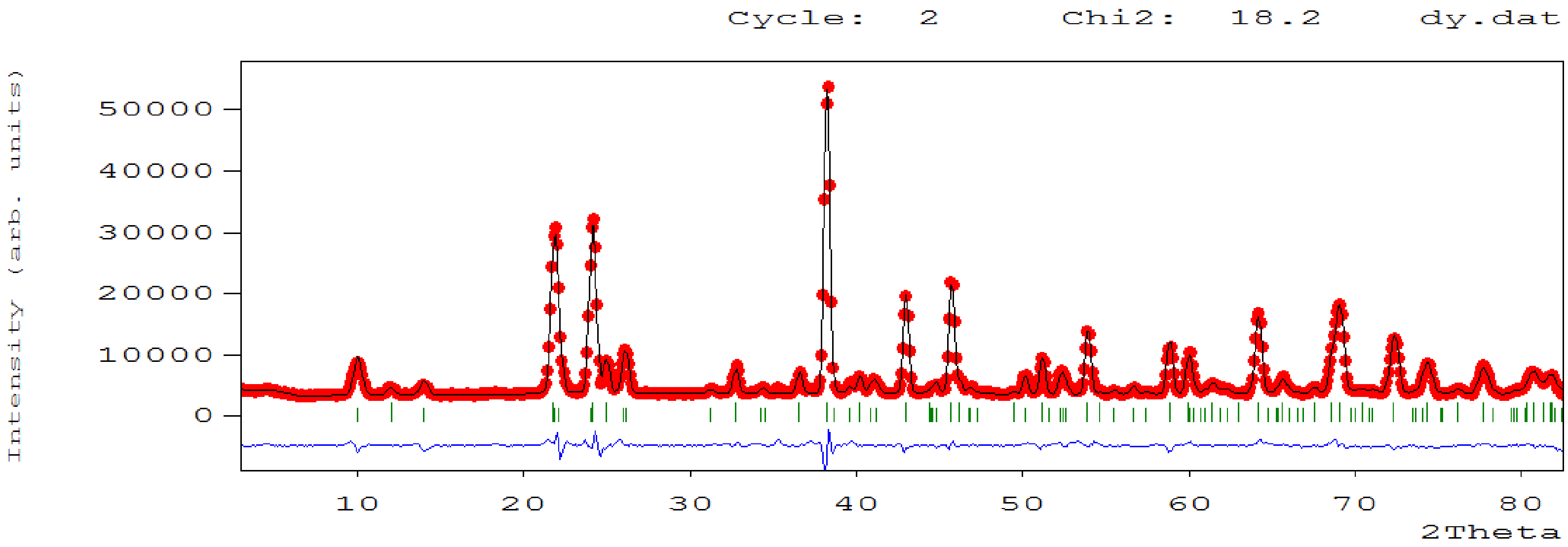
Powder Diffraction

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



Cycle: 2
Chi2: 18.2
dy.dat
Intensity (arb. units)
50000
40000
30000
20000
10000
0
10
20
30
40
50
60
70
80
2Theta

Single Crystal Diffraction

Advantages

- Can fully determine **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…

Questions?