Modern Methods in Heterogenous Catalysis Research:

Structure Determination by Neutron Diffraction

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History of neutron diffraction

1932 Chadwick discovers the neutron

1936 Mitchell & Powers confirm wave property of neutron

1945 first nuclear reactor: Oak Ridge

1946 Shull & Wollan: first neutron diffraction experiment

1969 Rietveld: Neutron powder diffraction refinement

1994 Nobel prize for Shull and Brockhouse

„for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter..."

Clifford Shull (1915 – 2001)

Properties of the neutron

Mass	$1.674928(1) \cdot 10^{-27}$ kg
Radius	~ 0.7 fm
Lifetime (free particel)	887 ± 2 sec (~ 15 min)
Spin	½
Charge	0
Magnetic moment	$-9.6491783(18) \cdot 10^{-27}$ J T^{-1}
	$-1.913\ \mu_N$ (nuclear magneton)
Quark structure	udd

Properties of the neutron

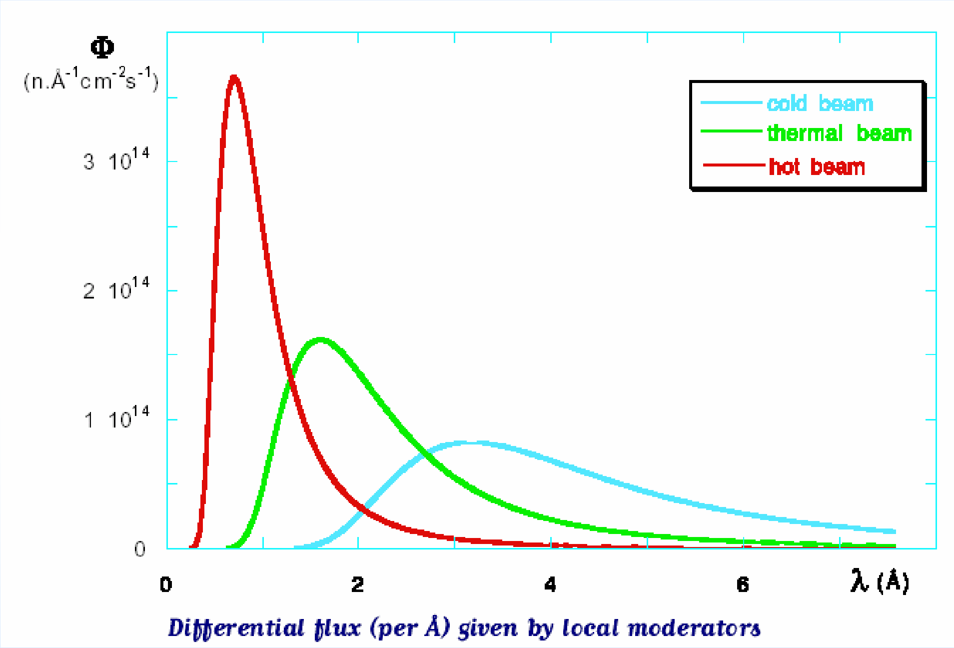
deBroglie wavelength

$$\lambda = \frac{h}{mv}$$

as gas: Maxwell-Boltzmann distribution

$$E = \frac{1}{2}\,mv^2 = \frac{3}{2}\,kT$$

$$\lambda^2 = \frac{h^2}{3mkT}$$



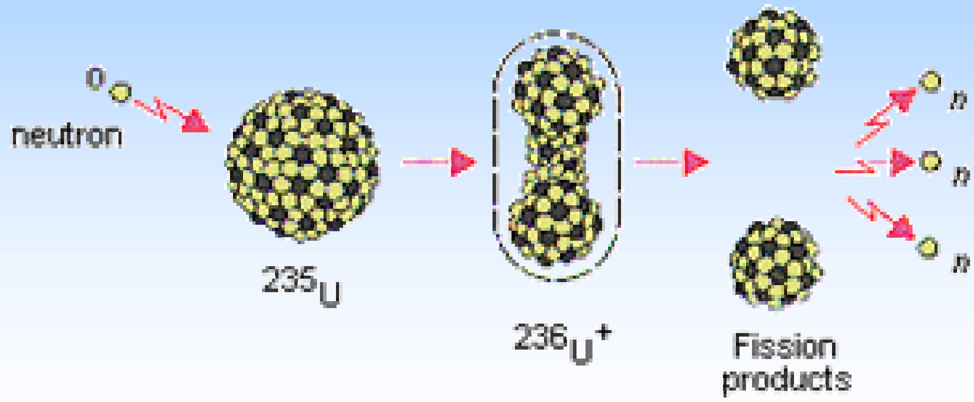
273 K (thermal neutrons) $\longrightarrow$ 1.55A

can be used for diffraction experiments

Neutron sources

nuclear fission:

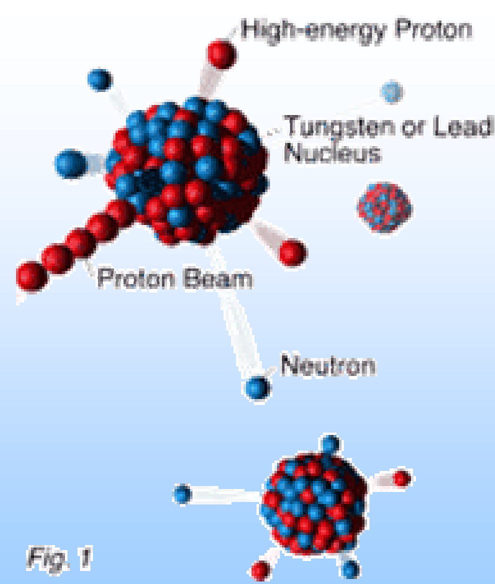
n + ^{235}U → n + n + smaller nuclei



spallation:

protons injected onto heavy element target

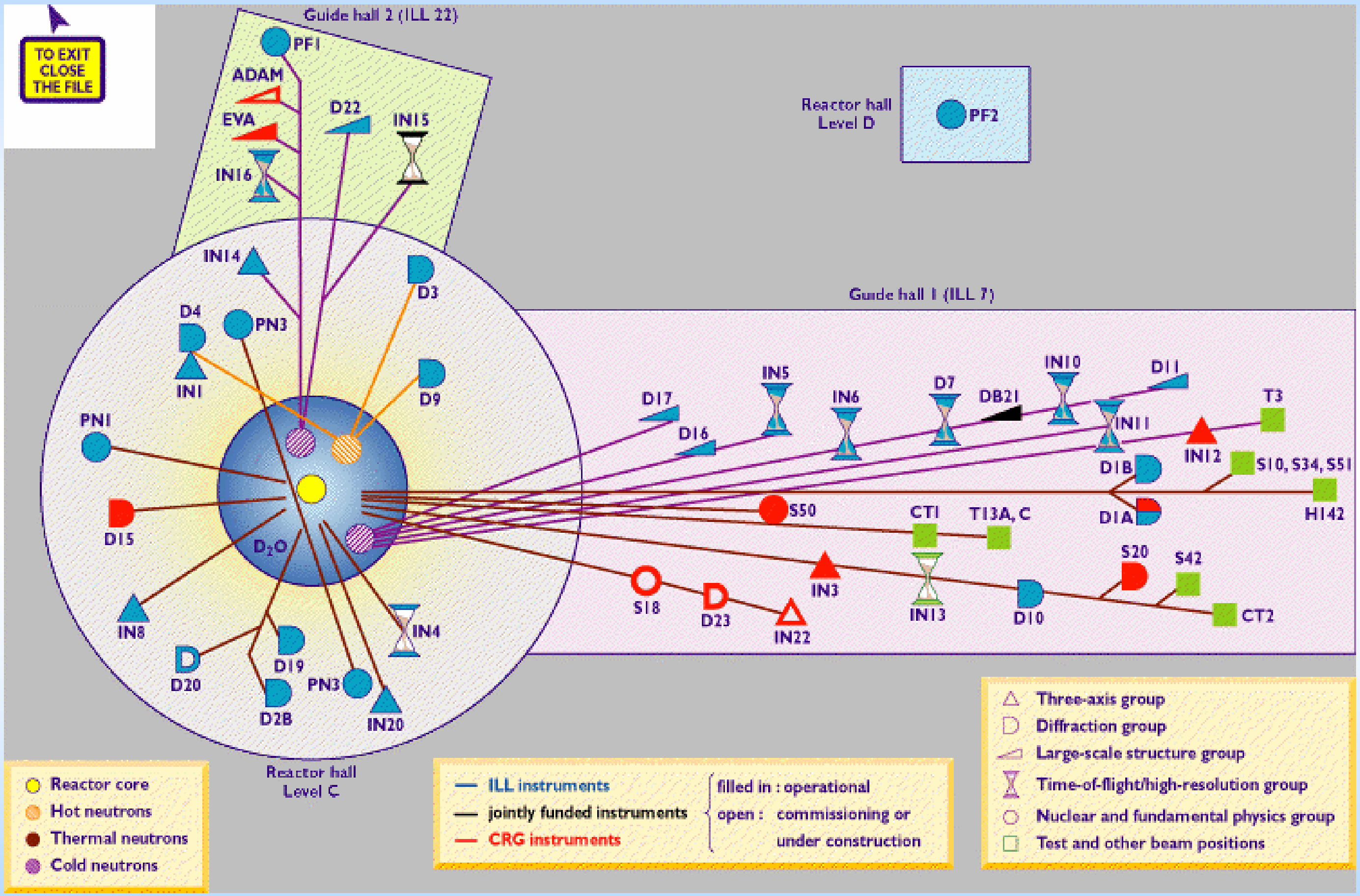
yields 20 - 30 neutrons per proton



Nuclear fission as neutron source

High flux reactor of ILL, Grenoble

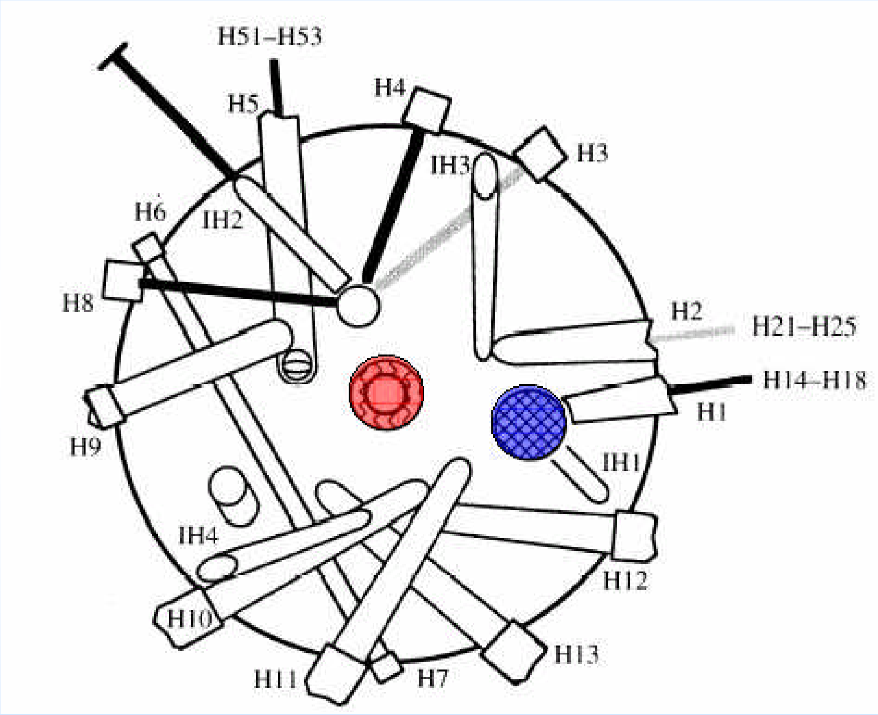
Nuclear fission as neutron source



Experimental hall of ILL/Grenonle

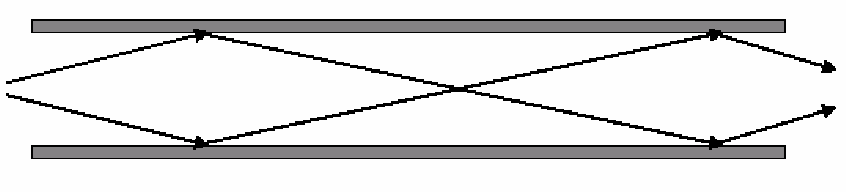
Nuclear fission as neutron source

after emission neutrons have energies of several MeV, slowed down to thermal energy (room temperature) at a moderator: light or heavy water, graphite



total reflection of neutrons:

neutrons extracted from the moderator by beam tubes or by neutron guides to the experiment

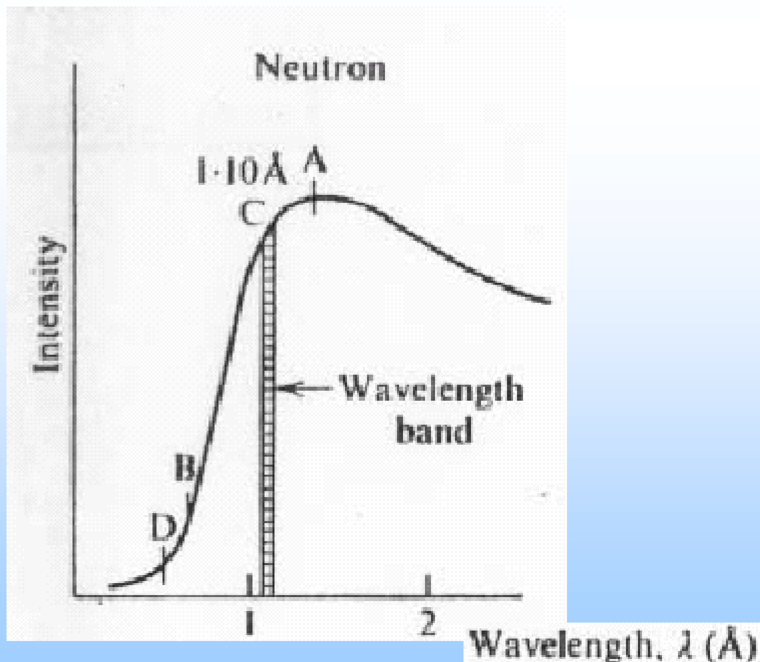


Nuclear fission as neutron source

diffraction experiments:

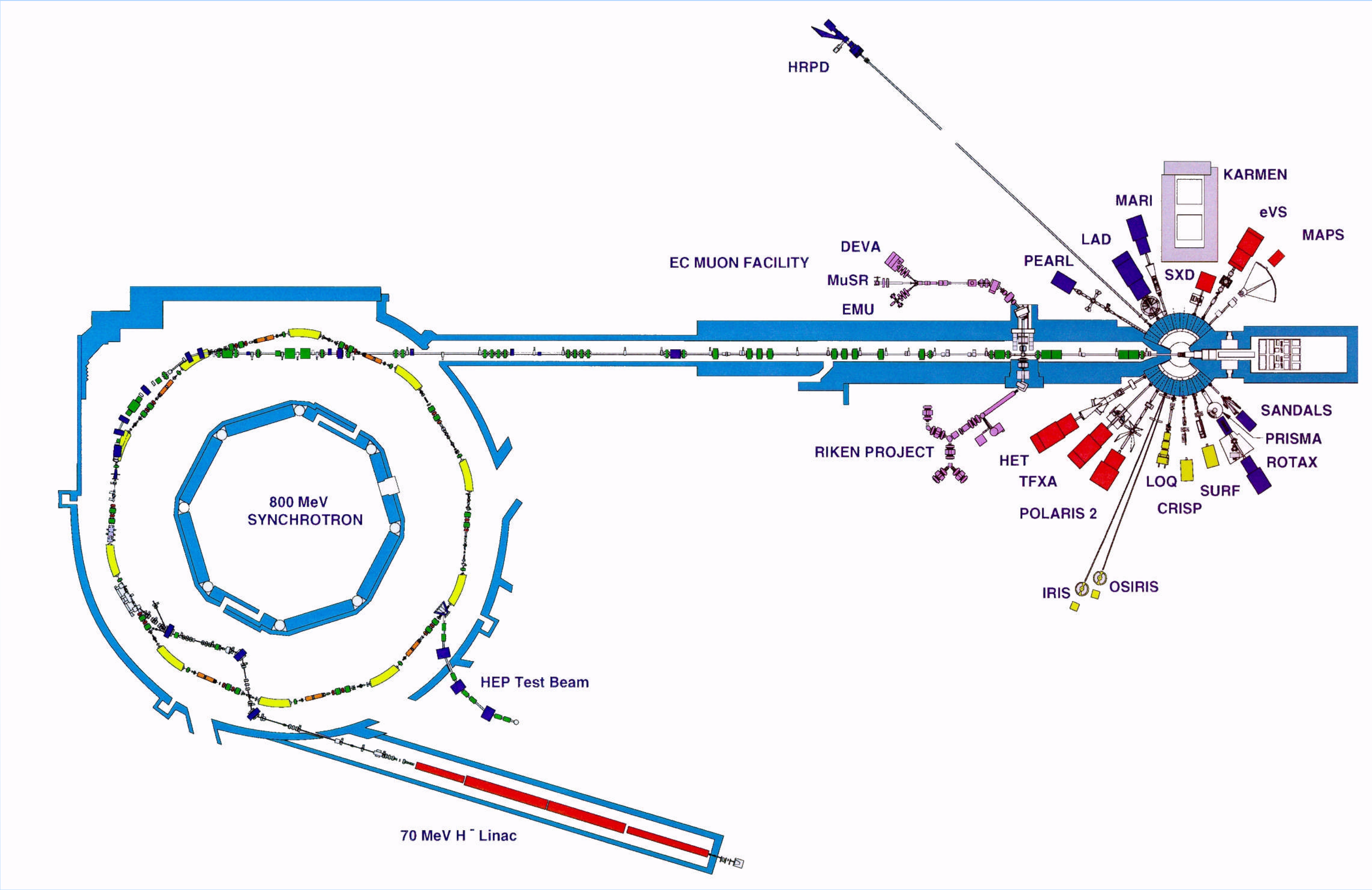
continous source, single wavelength is extracted from
the Maxwellian distribution by a monochromator crystal

constant wavelength diffraction, angle dispersive



Experimental hall of HMI/Berlin

Spallation as neutron source



ISIS, Rutherford Appleton Laboratory, Chilton/UK

Spallation as neutron source

pulsed neutrons → time-of-flight (TOF) experiments

one scattering angle, usually at angles 2θ > 90°

neutrons sort itselves accordig to their velocity und wavelength, therefore time of flight T is proportional to the wavelength:

$$\mathbf{T} = \frac{l\,Lm}{h}$$

L total flight path

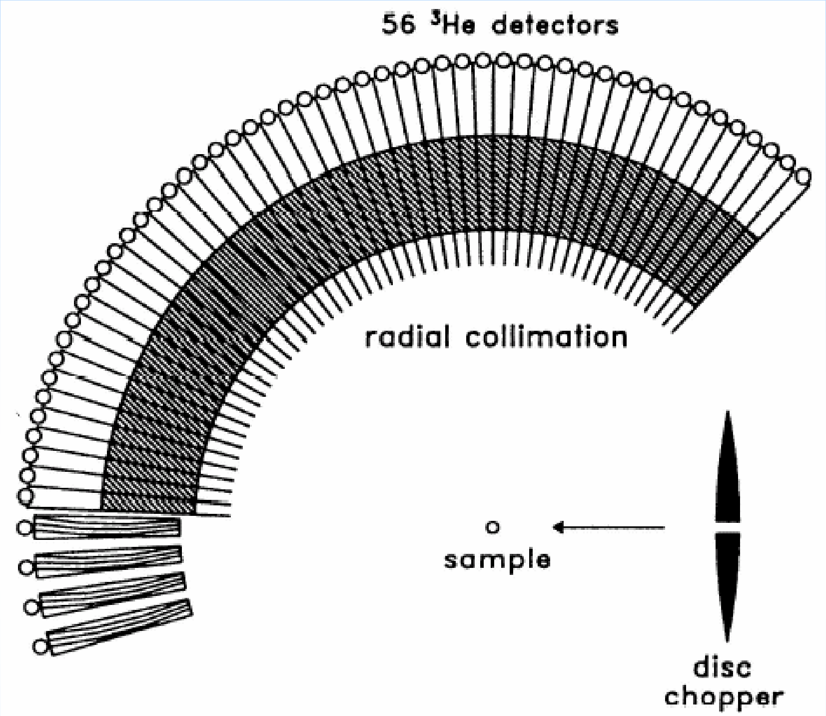
Neutron reactors

ILL	Institut Laue-Langevin	Grenoble /F	1971
BENSC	Hahn-Meitner-Institut	Berlin /D	1992
FRG-1	Forschungszentrum Geesthacht	near Hamburg /D	1958
FRM-II	TU München	Garching /D	2004
LLB	Laboratoire Léon Brillouin	Gif-sur-Yvette /F	1980
HFIR	Oak Ridge National Laboratory	Oak Ridge /USA	

Spallation Sources

ISIS	Rutherford Appleton Laboratory	Oxford /UK	1985
SINQ	Paul Scherrer Institut	Villigen /CH	1996
LANSCE	Los Alamos National Laboratory	Los Alamos /USA	
IPNS	Argonne National Laboratory	Argonne /USA	
KENS	High Energy	Tsukuba /Jpn.	

Detection of neutrons



proportional counter:

$^{10}BF_3$ gas tube: $^{1}n + {}^{10}B \rightarrow {}^{7}Li + {}^{4}He + \gamma$

^{3}He gas tube: $^{1}n + {}^{3}He \rightarrow {}^{3}H + {}^{1}H + \gamma$

scintillator or NIP (neutron imaging plate)

converter: $^{1}n + {}^{6}Li \rightarrow ({}^{7}Li) \rightarrow {}^{3}He + {}^{4}He + \gamma$

Neutron (non-magnetic) diffraction

Intensity I_{hkl}

$$I_{hkl} = \left|F_{hkl}\right|^2 \cdot LP \cdot A$$

LP Lorentz-polarisation factor

A absorption

X-ray structure factor F_{hkl}

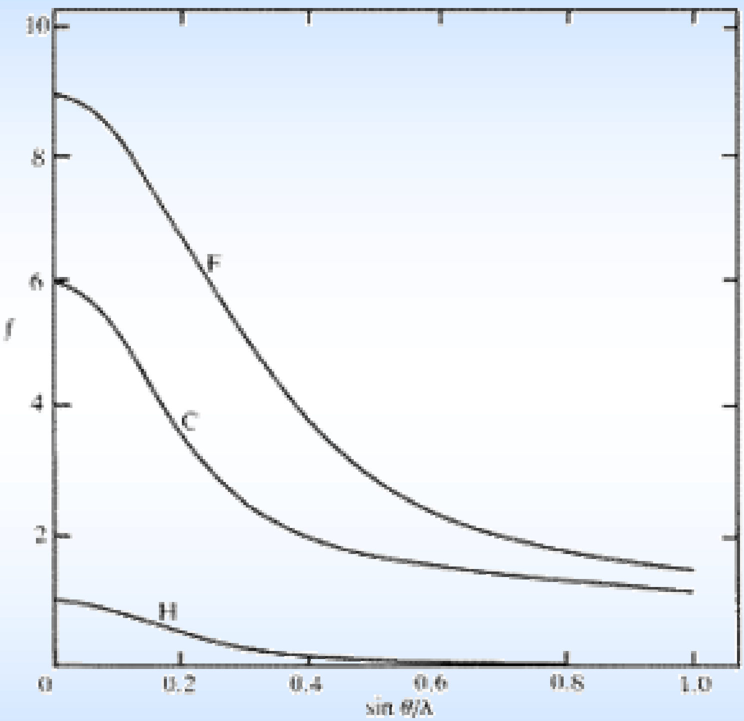
$$F_{(h,k,l)} = \sum_{j=1}^{atoms} f_{(j)} \exp\left[2\pi \cdot i(hx_{(j)} + ky_{(j)} + lz_{(j)})\right]$$

neutron structure factor F_{hkl}

$$F_{hkl} = \sum_j b_j e^{-W_j} e^{2\pi i(hx_j + ky_j + lz_j)}$$

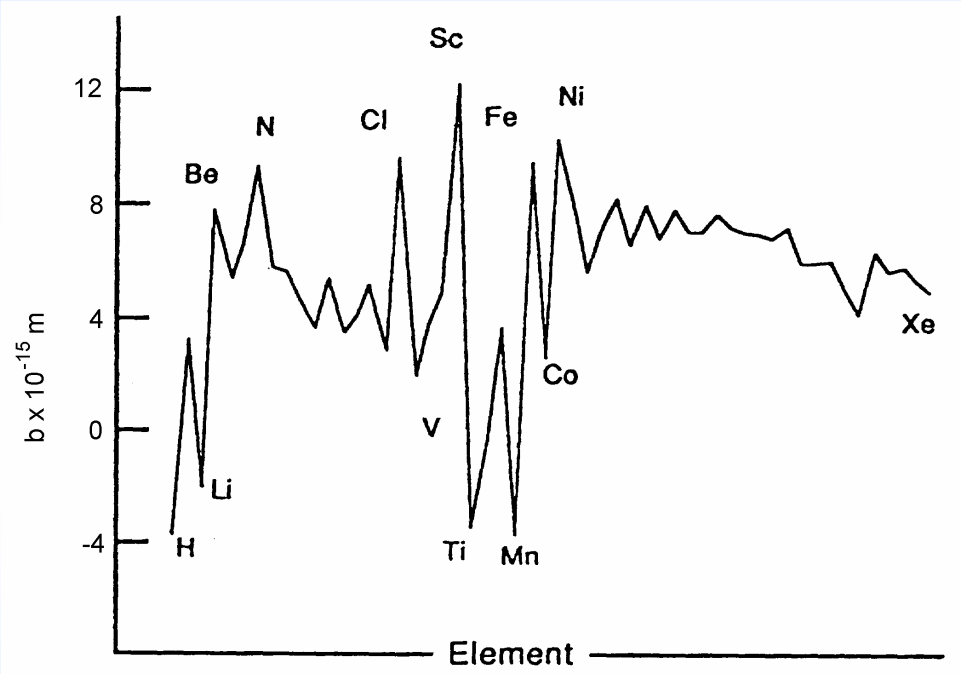
Neutron (non-magnetic) diffraction

Interaction of X-rays with electrons



Atomic form factors *f* for X-ray diffraction

Interaction of neutrons with nuclei



Scattering lengths *b* for neutron diffraction

Scattering length *b*

Properties	**Consequences**
- interaction with the nucleus (very small compared to neutron wavelength)	no decrease of intensity with 2θ temperature factors more accurate
- scattering length independent of atomic number	neighbouring elements can be distinguished
- b in the same order of magnitude	light elements can be detected besides heavy elements
- b independent of wavelength	
- every isotope has its own b	
- dimension of b: 1 fm = 10^{-15} m	
- b positive or negative	
- scattering power much smaller than X-rays	larger sample necessary

Absorption cross sections σ_{abs}

Absorption: usually small sample environment (furnace,...) no problem

but: resonance absorber: high absorption

(^{3}He, ^{6}Li, ^{10}B, ^{113}Cd, ^{149}Sm, ^{157}Gd) used as absorber, avoided in diffraction

dependent on cross section σ_{abs}

dimension of σ : 1 barn = 10^{-24} cm^2

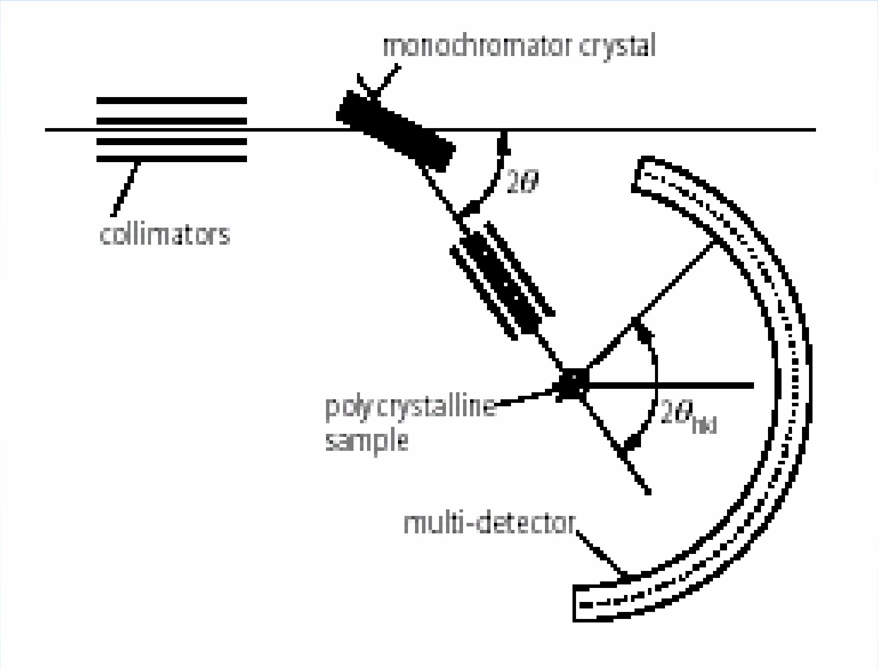
Scattering lengths *b* for neutron diffraction

ZSymbA	p or $T_{1/2}$	I	b_c	b_+	b_-	c	σ_{coh}	σ_{inc}	σ_{scatt}	σ_{abs}
0-N-1	**10.3 MIN**	**1/2**	**-37.0(6)**	**0**	**-37.0(6)**		**43.01(2)**		**43.01(2)**	**0**
1-H			**-3.7409(11)**				**1.7568(10)**	**80.26(6)**	**82.02(6)**	**0.3326(7)**
1-H-1	99.985	1/2	-3.7423(12)	10.817(5)	-47.420(14)	+/-	1.7583(10)	80.27(6)	82.03(6)	0.3326(7)
1-H-2	0.0149	1	6.674(6)	9.53(3)	0.975(60)		5.592(7)	2.05(3)	7.64(3)	0.000519(7)
1-H-3	12.26 Y	1/2	4.792(27)	4.18(15)	6.56(37)		2.89(3)	0.14(4)	3.03(5)	< 6.0E-6
2-He			**3.26(3)**				**1.34(2)**	**0**	**1.34(2)**	**0.00747(1)**
2-He-3	0.00013	1/2	5.74(7)	4.7(5)	8.8(1.4)	E	4.42(10)	1.6(4)	6.0(4)	5333.0(7.0)
2-He-4	0.99987	0	3.26(3)				1.34(2)	0	1.34(2)	0
3-Li			**-1.90(3)**				**0.454(10)**	**0.92(3)**	**1.37(3)**	**70.5(3)**
3-Li-6	7.5	1	2.0(1)	0.67(14)	4.67(17)	+/-	0.51(5)	0.46(5)	0.97(7)	940.0(4.0)
3-Li-7	92.5	3/2	-2.22(2)	-4.15(6)	1.00(8)	+/-	0.619(11)	0.78(3)	1.40(3)	0.0454(3)
4-Be-9	**100**	**3/2**	**7.79(1)**				**7.63(2)**	**0.0018(9)**	**7.63(2)**	**0.0076(8)**
5-B			**5.30(4)**				**3.54(5)**	**1.70(12)**	**5.24(11)**	**767.0(8.0)**
5-B-10	19.4	3	-0.2(4)	-4.2(4)	5.2(4)		0.144(6)	3.0(4)	3.1(4)	3835.0(9.0)
5-B-11	80.2	3/2	6.65(4)	5.6(3)	8.3(3)		5.56(7)	0.21(7)	5.77(10)	0.0055(33)
6-C			**6.6484(13)**				**5.551(2)**	**0.001(4)**	**5.551(3)**	**0.00350(7)**
6-C-12	98.89	0	6.6535(14)				5.559(3)	0	5.559(3)	0.00353(7)
6-C-13	1.11	1/2	6.19(9)	5.6(5)	6.2(5)	+/-	4.81(14)	0.034(11)	4.84(14)	0.00137(4)

http://www.ati.ac.at/~neutropt/scattering/table.html

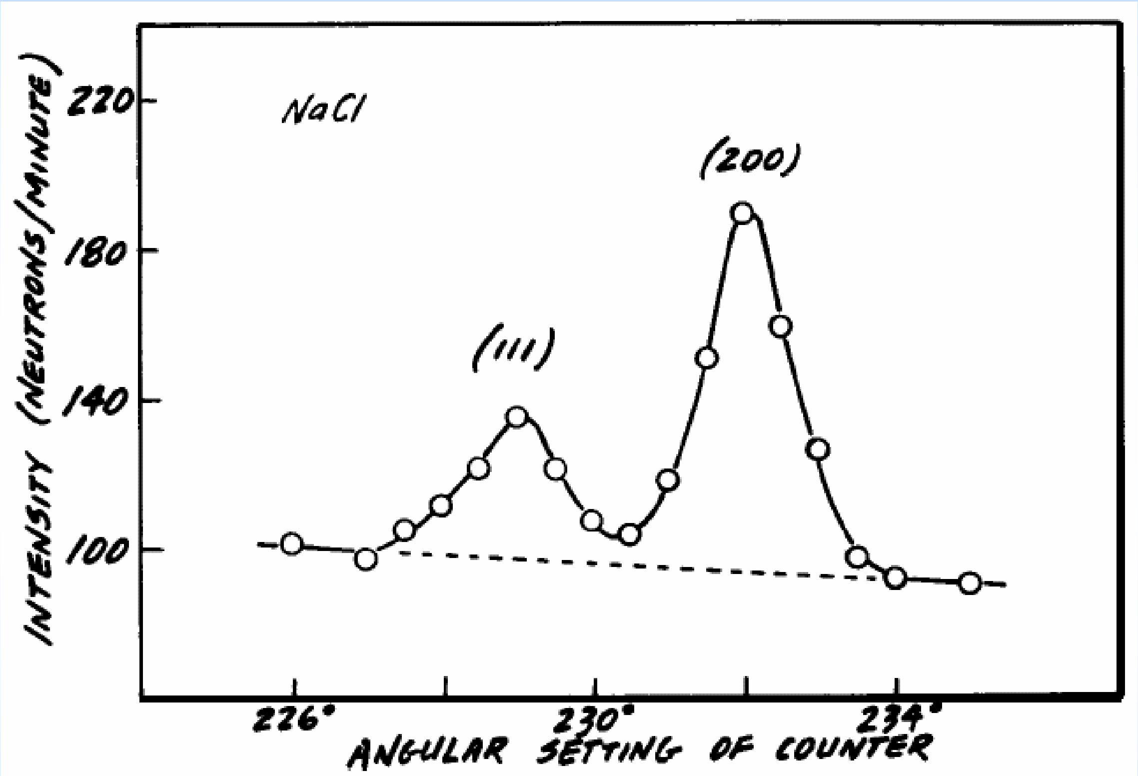
Neutron powder diffraction

Vanadium sample cans



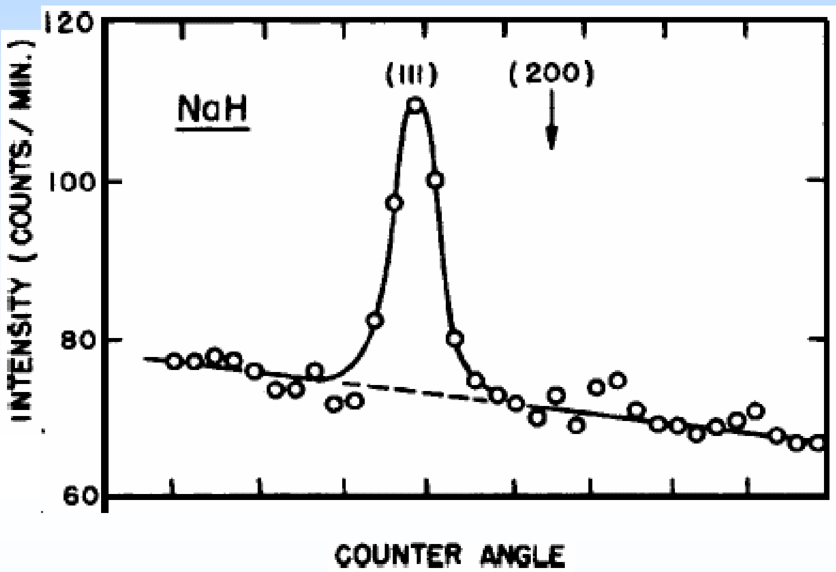
neutron powder diffraction

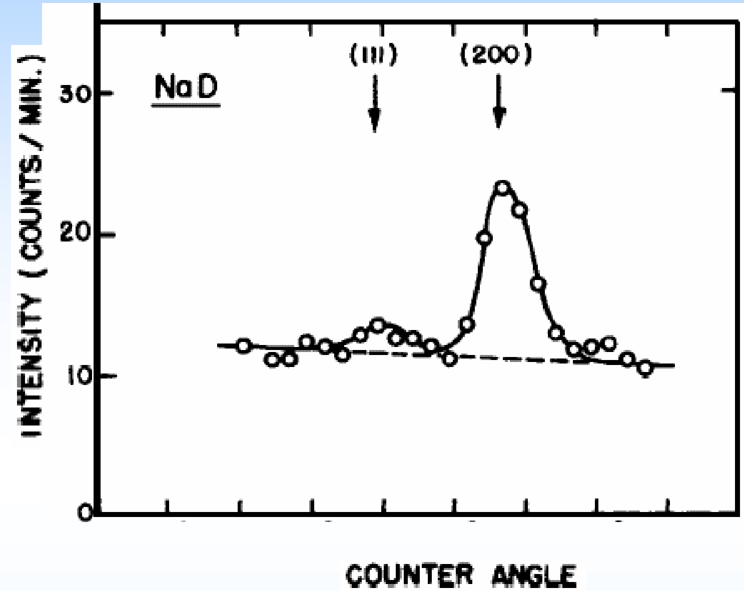
Neutron powder diffraction



Portion of the first powder diffraction pattern of NaCl taken at Oak Ridge by Shull and Wollan

Localization of light elements: hydrogen (deuterium)





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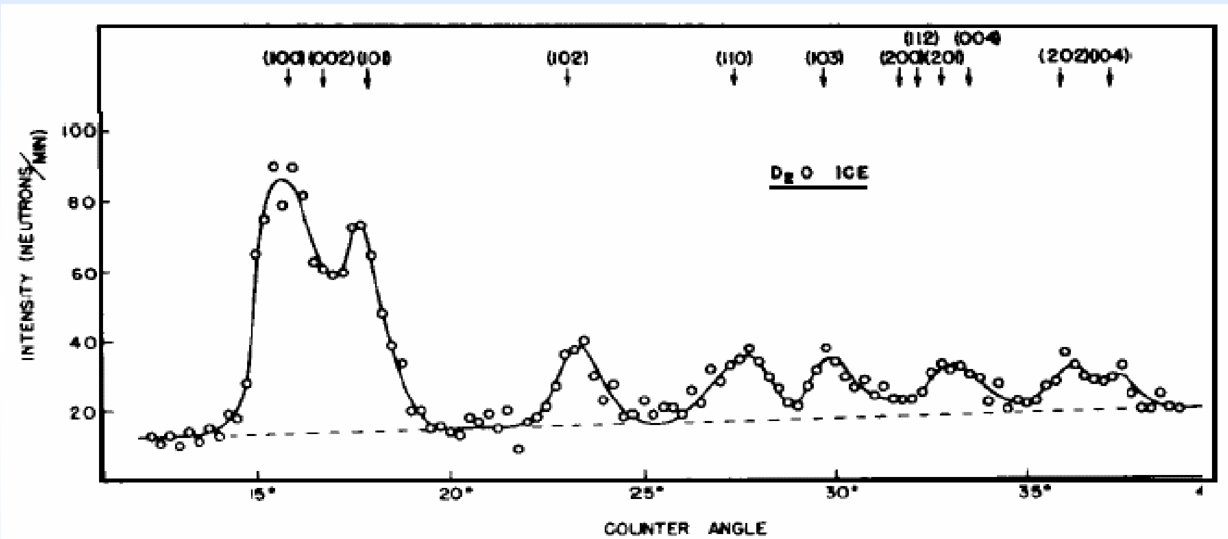
after C.G. Shull, E.O. Wollan, G.A. Morton, and W.L. Davidson, *Phys. Rev.* **73**, 482 – 487 (1948)

Localization of light elements: deuterium



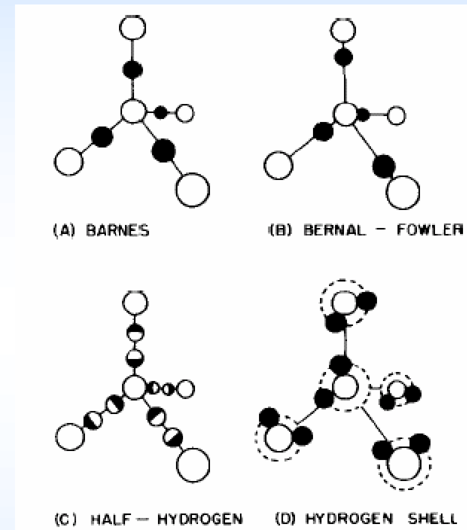
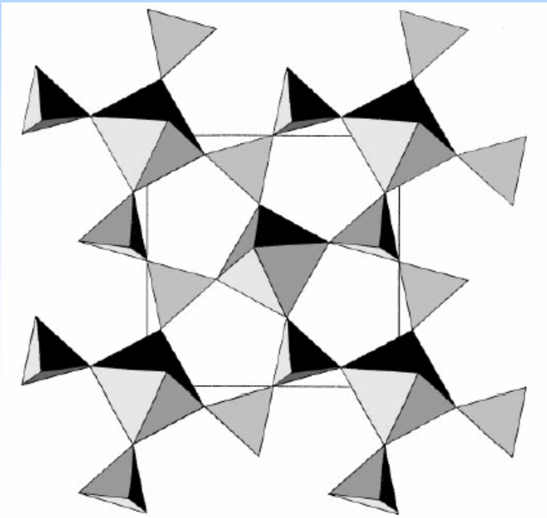
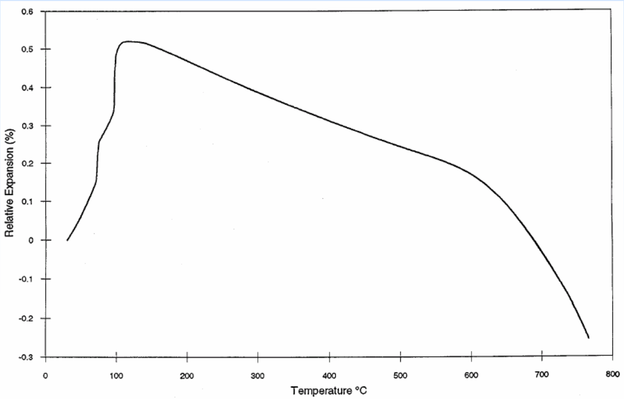


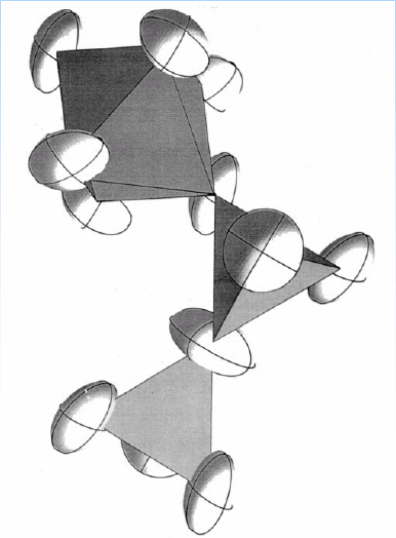
Fig. 6: Pattern Taken for a Sample of Powdered D_2O Ice.

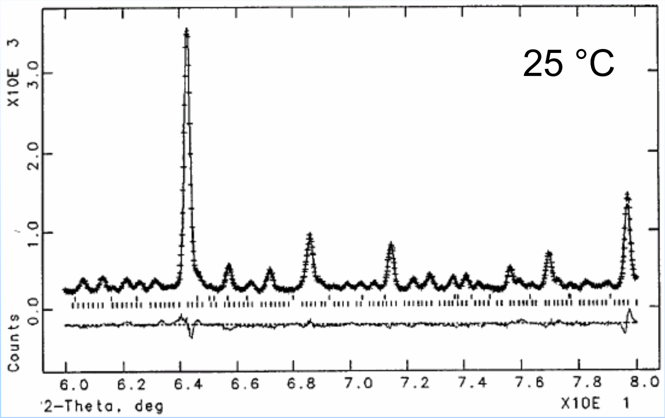
after E.O. Wollan, W.L. Davidson, and C.G. Shull, *Phys. Rev.* **75**, 1348 – 1352 (1949)

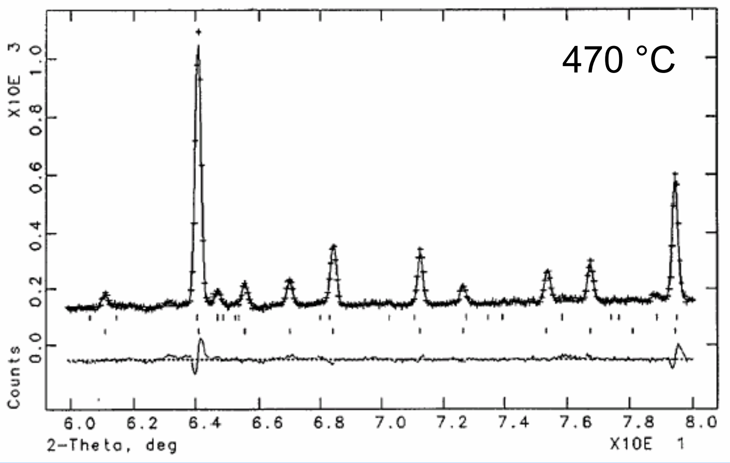
Localization of light elements: oxygen in ZrV_2O_7











after N. Khosrovani, A.W. Sleight, and T. Vogt, *J. Solid State Chem.* **123**, 355 – 360 (1997)

Differentiation between neighbouring elements

$Cu_8[P_{12}N_{18}O_6]Cl_2$ sodalite

N/O ordered or not?

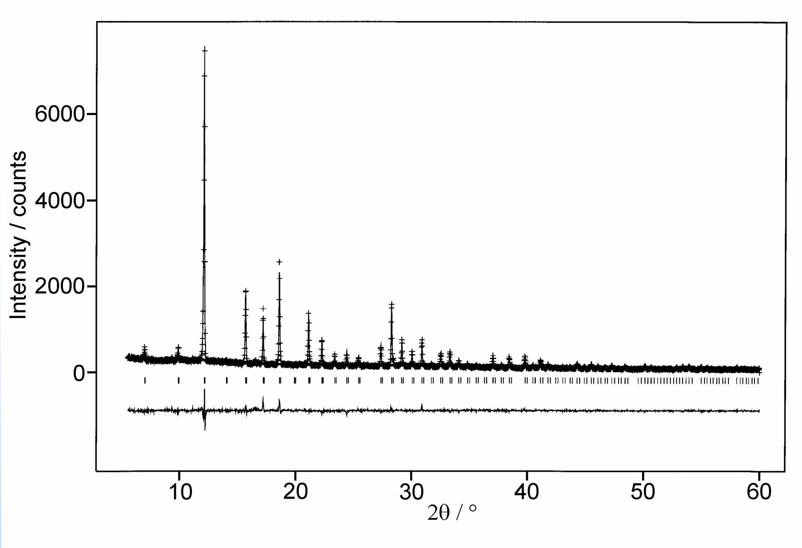
ZSymbA	p or $T_{1/2}$	I	b_c	b_+	b_-	c	σ_{coh}	σ_{inc}	σ_{scatt}	σ_{abs}
7-N			**9.36(2)**				**11.01(5)**	**0.50(12)**	**11.51(11)**	**1.90(3)**
7-N-14	99.635	1	9.37(2)	10.7(2)	6.2(3)		11.03(5)	0.50(12)	11.53(11)	1.91(3)
7-N-15	0.365	1/2	6.44(3)	6.77(10)	6.21(10)		5.21(5)	0.00005(10)	5.21(5)	0.000024(8)
8-O			**5.805(4)**				**4.232(6)**	**0.000(8)**	**4.232(6)**	**0.00019(2)**
8-O-16	99.75	0	5.805(5)				4.232(6)	0	4.232(6)	0.00010(2)
8-O-17	0.039	5/2	5.6(5)	5.52(20)	5.17(20)		4.20(22)	0.004(3)	4.20(22	0.236(10)
8-O-18	0.208	0	5.84(7)				4.29(10)	0	4.29(10)	0.00016(1)

after N. Stock, E. Irran, and W. Schnick, *Chem. Eur. J.* **4**, 1822 (1998)

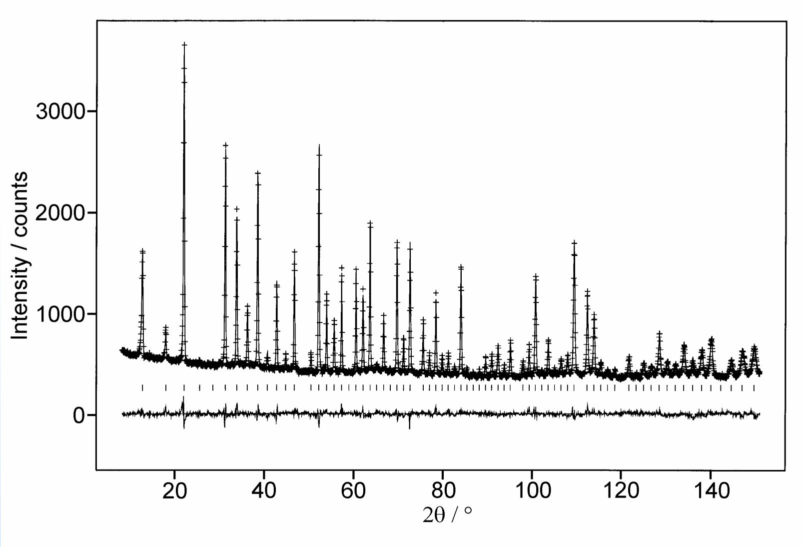
Differentiation between neighbouring elements

Rietveld refinement of neutron powder data D2B at ILL/Grenoble:

N/O statistically distributed



X-ray powder diffraction pattern



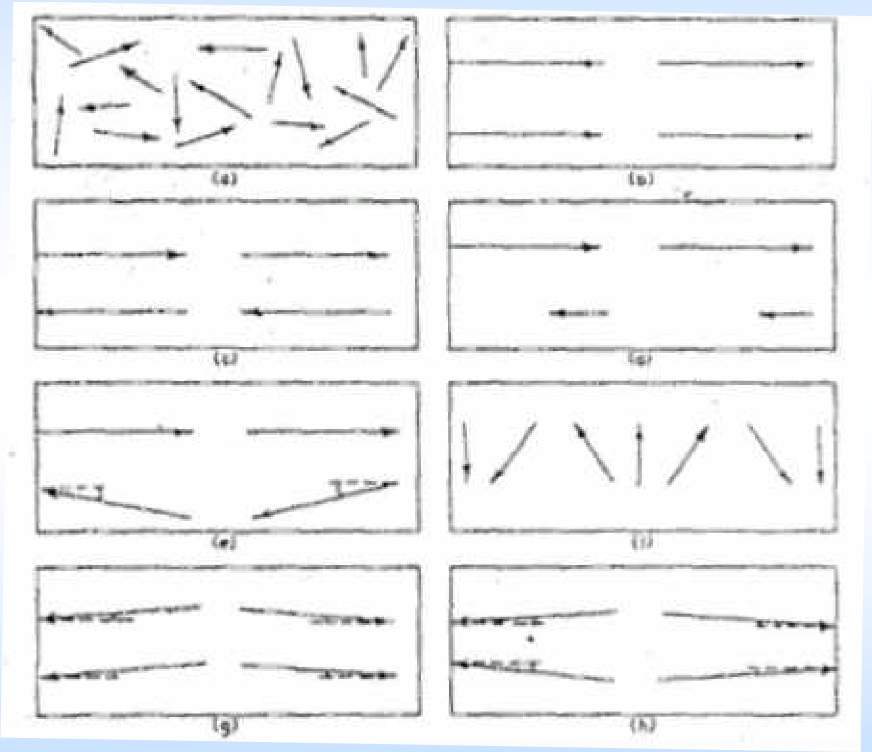
Neutron powder diffraction pattern

Neutron magnetic diffraction

interaction with electrons of the atomic shell
magnetic form factor is angle dependent

results:
- magnetic ordering
- orientation of the electron spins
  (experiments with polarized neutrons)
- valence distribution (magnetic momentum)

Ordering of the spins



spins:

a) disordered: paramagnetic

b) parallel: ferromagnetic

c) antiparallel: Néel type antiferromagnetic

d) uncompensated: Néel type ferrimagnetic

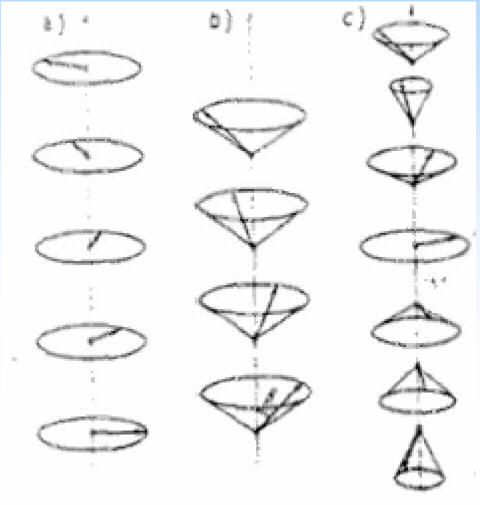
e) triangular antiparallel: ferrimagnetic

f) helical spiral: compensated antiferromagnetic
or uncompensated ferrimagnetic

g) canted: weak ferromagnetic

h) canted: compensated antiferromagnetic

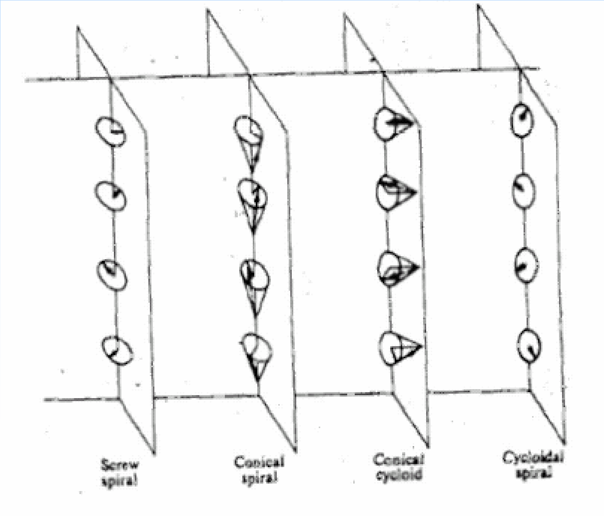
Magnetic ordering in ferromagnets

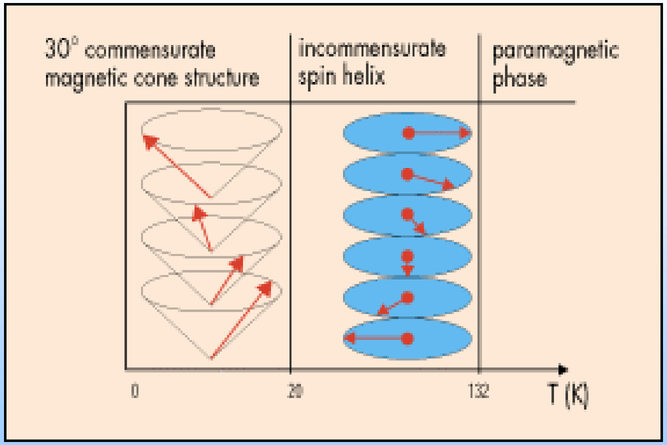


a) simple spiral

b) conical spiral

c) complex spiral





Schematic phase diagram of bulk Holmium

Magnetic ordering in the antiferromagnet MnO

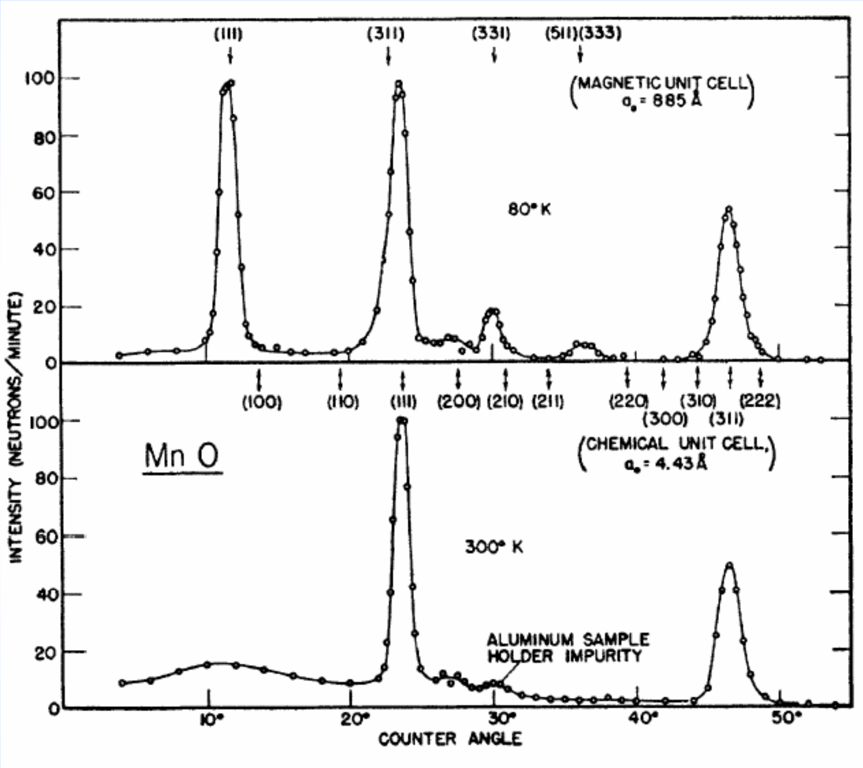
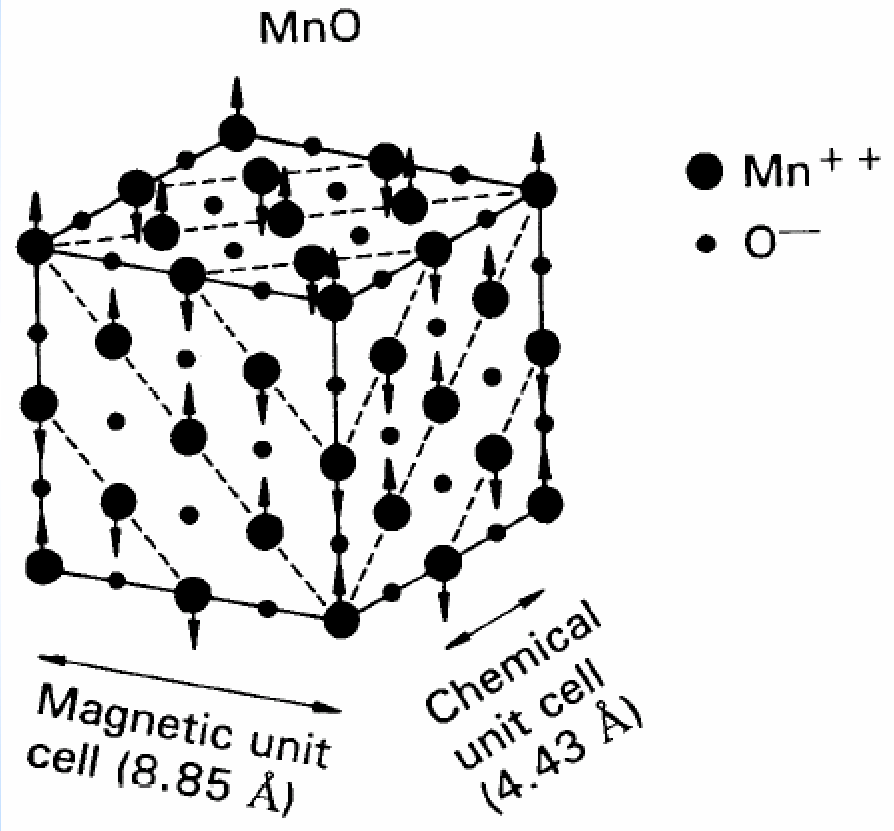


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.



after C.G. Shull and J. S. Smart, *Phys. Rev*. **76**, 1256 - 1256 (1949)

Magnetic ordering in the antiferromagnet MnF_2

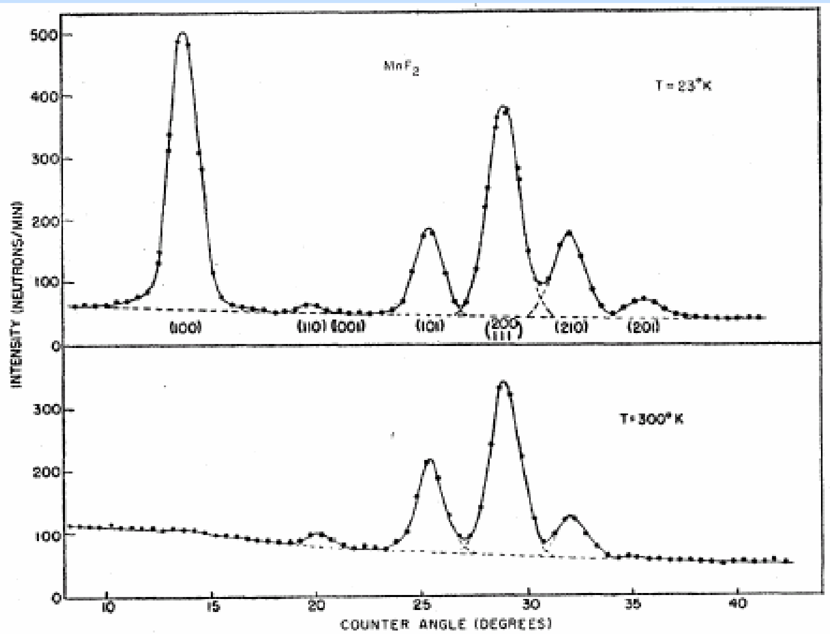


FIG. 1. Neutron diffraction patterns for MnF_2 in the paramagnetic state (295°K) and in the antiferromagnetic state (23°K). The unit cells for antiferromagnetic and nuclear scattering are of the same size.

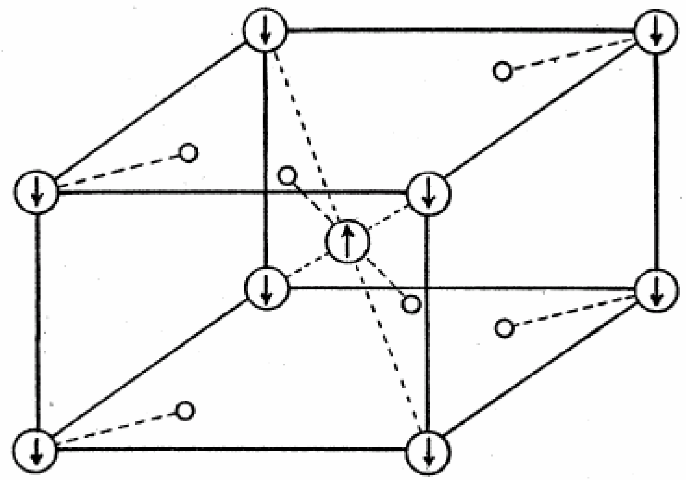
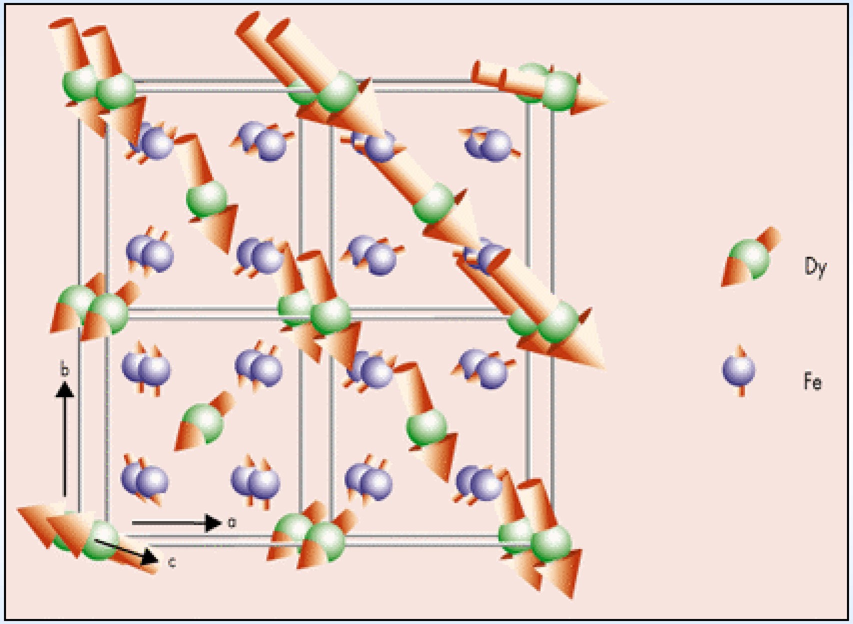
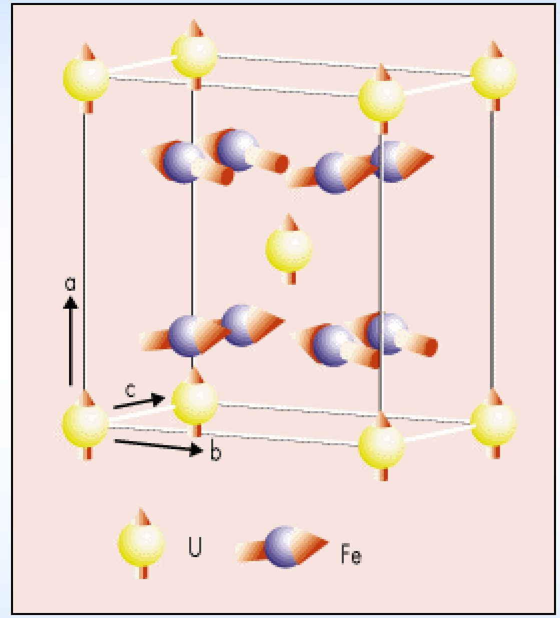


FIG. 4. Magnetic structure of MnF_2 showing the order and orientation of the Mn^{++} magnetic moments. The small circles correspond to fluorine sites.

after R. A. Erickson, *Phys. Rev*. **90**, 779 – 785 (1953)

Magnetic diffraction with polarised neutrons





$DyFe_4Al_8$
complex cycloidal magnetic configuration

UFe_4Al_8
U: weak ferromagnetism
Fe: almost antiferromagnetic

J.A. Paixao, P.J. Brown, B. Lebech, and G.H. Lander in: *Exploring Matter with neutrons*, ILL, 2000.

Conclusion

Neutron diffraction

- is complementary to X-ray diffraction
- allows us to detect light elements besides heavy elements
- neighbouring elements can be distinguished
- reliable temperature factors
- magnetic ordering determined