LECTURE 6: NEUTRON DIFFRACTION

- **Production of neutrons: fission and spallation**
- **ND versus XRD: many similarities but several important differences!**
- **Magnetic structure determination**

Neutron research facilities worldwide

NEUTRON FACILITIES WE HAVE BEEN USING

EUROPE

- Neutron Research Laboratory (NFL), Studsvik, SWEDEN (shut down)
- Petersburg Nuclear Physics Institute, Gatchina, RUSSIA
- Joint Institute for Nuclear Research (FLNP/JINR), Dubna, RUSSIA
- Institute for Energy Technology (IFE), Kjeller, NORWAY
- Institut Laue-Langevin (ILL), Grenoble, FRANCE
- Pulsed Neutron Source (ISIS), Oxford, UK (most recently)

USA

- Argonne National Laboratory (IPNS), USA (closed now)
- Oak Ridge National Laboratory, Spallation Neutron Source (SNS), USA (most recently)

JAPAN

- Japan Atomic Energy Research Institute (JAERI), Tokai, JAPAN

AUSTRALIA

- Bragg Institute (ANSTO), Sydney, AUSTRALIA (most recently)

The ESRF* & ILL* With Grenoble & the Beldonne Mountains

*ESRF = European Synchrotron Radiation Facility; ILL = Institut Laue-Langevin

Some historical steps

1932 Chadwick: neutrons

1936 Diffraction of neutrons

1944 Fission nuclear reactors → progress in ND methods (Brockhouse & Shull, Nobel 1994)

The Neutron has Both Particle-Like and Wave-Like Properties

- Mass: $m_n = 1.675 \times 10^{-27}$ kg
- Charge = 0; Spin = ½
- Magnetic dipole moment: $\mu_n = -1.913\ \mu_N$
- Nuclear magneton: $\mu_N = eh/4\pi m_p = 5.051 \times 10^{-27}$ J T^{-1}
- Velocity (v), kinetic energy (E), wavevector (k), wavelength (λ), temperature (T).
- $E = m_n v^2/2 = k_B T = (hk/2\pi)^2/2m_n$; $k = 2\pi/\lambda = m_n v/(h/2\pi)$

So-called "thermal" neutrons have the proper energy/wavelength for crystal structure determination through diffraction

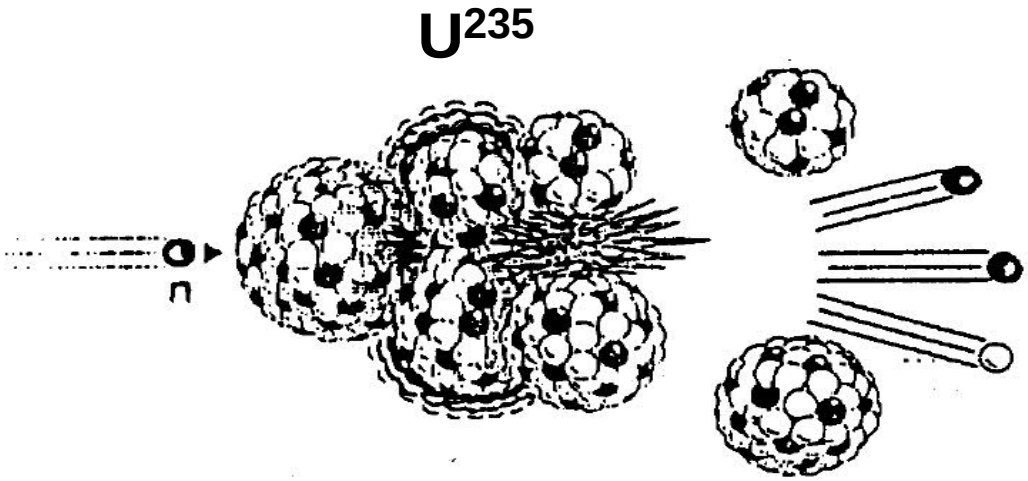
	Energy (meV)	Temp (K)	Wavelength (nm)
Cold	0.1 – 10	1 – 120	0.4 – 3
Thermal	5 – 100	60 – 1000	0.1 – 0.4
Hot	100 – 500	1000 – 6000	0.04 – 0.1

λ (nm) = 395.6 / v (m/s)

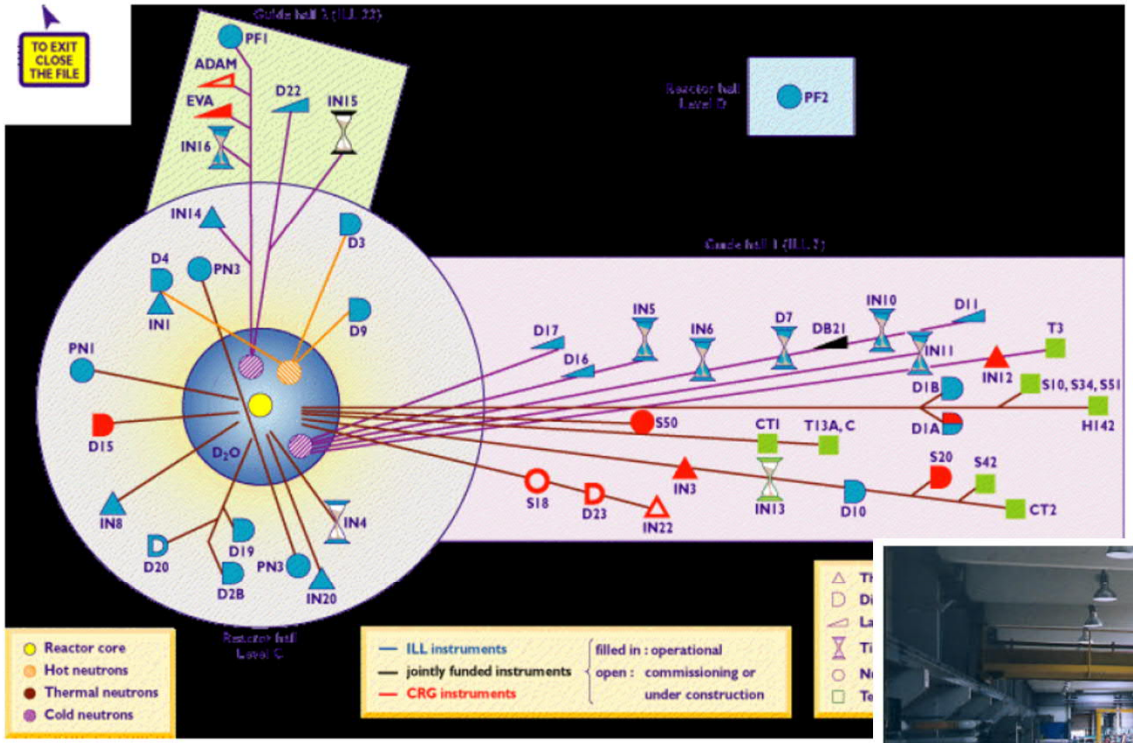
E (meV) = 0.02072 k^2 (k in nm^{-1})

PRODUCTION OF NEUTRONS: Nuclear reaction

- typical fission reaction: $^{235}U + n_{therm} \rightarrow A + B + 2.3\ n$
- the neutrons produced are slowered/moderated (e.g. with H_2O), after which they continue the fission reaction → chain reaction
- typical research reactors: 10 - 100 MW (e.g. Grenoble 57 MW)
- energy distribution of the neutron flux depends on the temperature of the moderator employed
- research reactors can not be used for energy production and *vice versa*



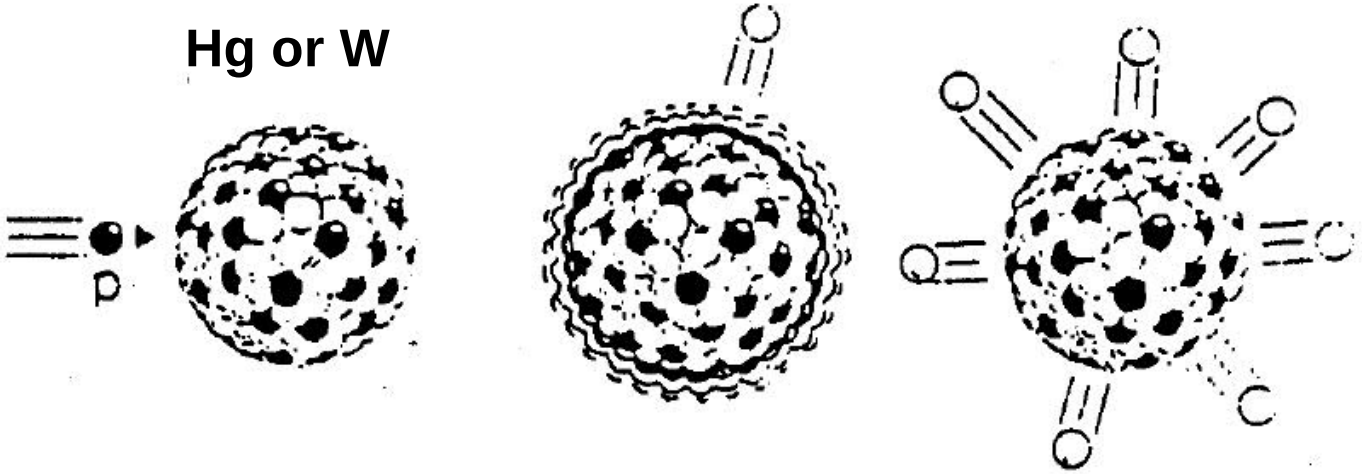
Neutron Sources Provide Neutrons for Many Spectrometers: Schematic Plan of the ILL Facility



- **Fission (= reactor) source**
- **Located in Grenoble**

PRODUCTION OF NEUTRONS: Spallation

- heavy metal (Hg, W) nuclei bombarded with high-energy protons (E_p = 800 MeV)
- protons from particle accelerators
- typical reaction: Hg + p → spallation product + x n
- x depends on E_p and the heavy metal employed
- for example: ^{238}U and E_p = 800 MeV, x = 28
- pulsed proton accelerator → pulsed neutron flux → **time-of-flight measurement**



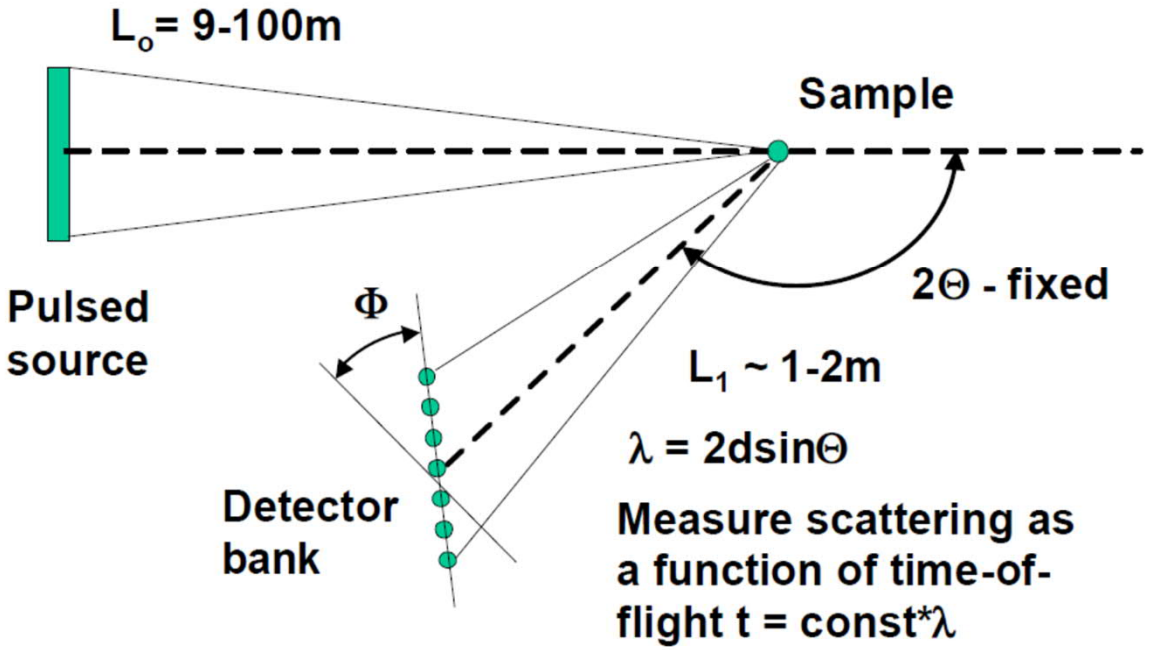
Science & Technology Facilities Council
ISIS

- **Spallation source**
- **Located in Oxfordshire, UK**
- **Isis is the local name for the River Thames**

TIME-of-FLIGHT DETECTOR

- Mandatory with spallation sources
- Detector is fixed at a certain 2θ value
- De Broglie relationship + Braggs law:
- $\lambda = h/m_n v_n = 2d_{hkl}\sin\theta$
- Time of flight becomes: $t = 2d_{hkl}L(m_n/h)\sin\theta$
- Time of flight depends on d_{hkl} if all other parameters are fixed

Neutron Powder Diffraction using Time-of-Flight

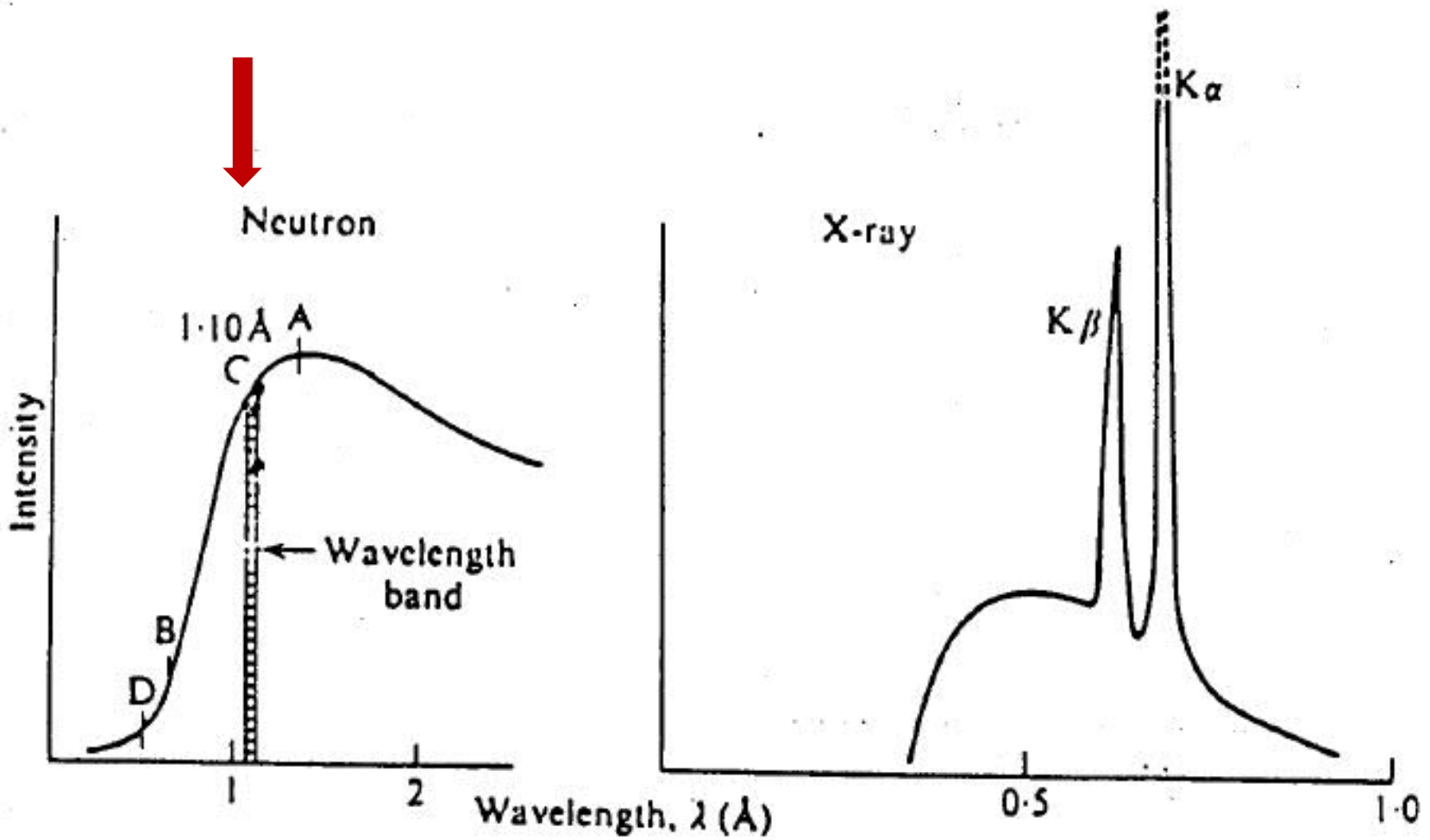


NEUTRON (powder) DIFFRACTION (ND)

- Elastic (= no energy lost) neutron scattering

- Production of neutrons: (i) nuclear reactor
  (ii) spallation source
- Wavelength of so-called ”thermal neutrons” 1 ~ 10 Å
  → crystal structure determination
- Wavelength of neutron flux is less accurate than that of characteristic x-ray radiation → Lattice parameters are determined less accurately from ND than from XRD
- Neutron scattering weaker than x-ray scattering
  → Large sample amounts needed
- Neutron scattering does not depend on the reflection angle (x-ray scattering does)
- Neutron flux scatters from atomic nuclei → Scattering factor does not depend on electron density (atomic number)
  → Light and heavy atoms may be equally visible for neutons

Challenge to separate a narrow wavelength range

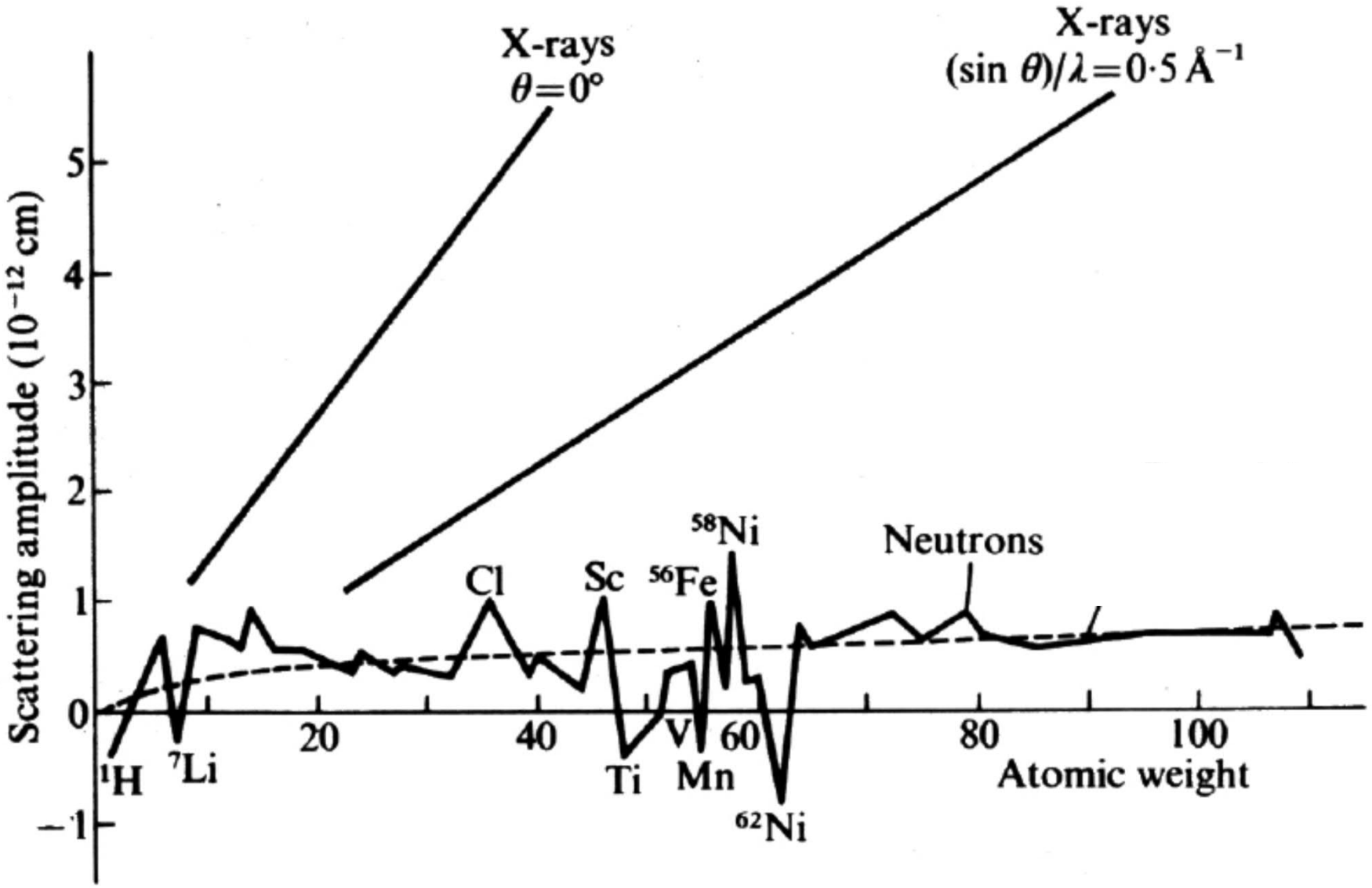


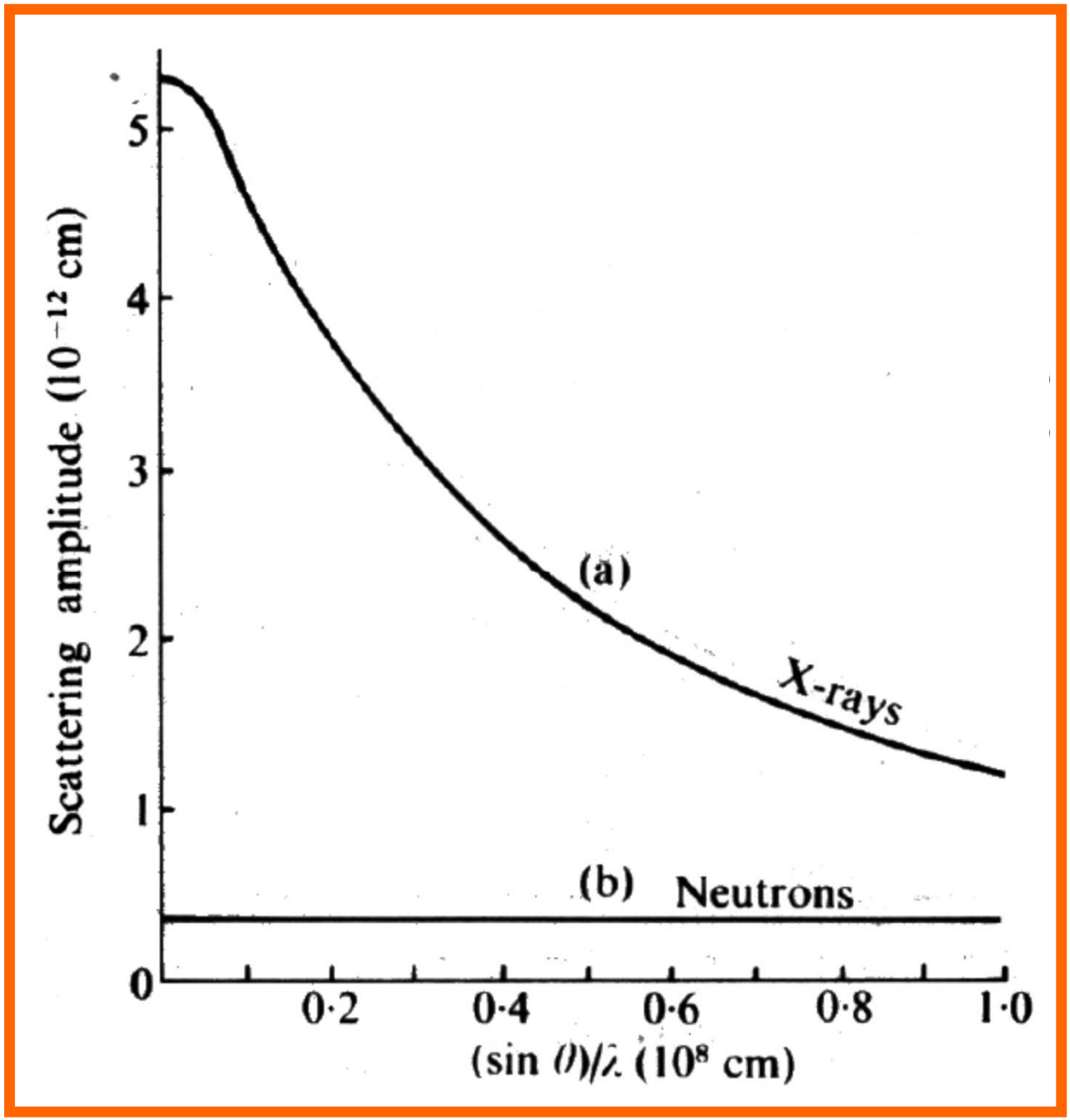
Neutrons scatter from an atomic nuclei

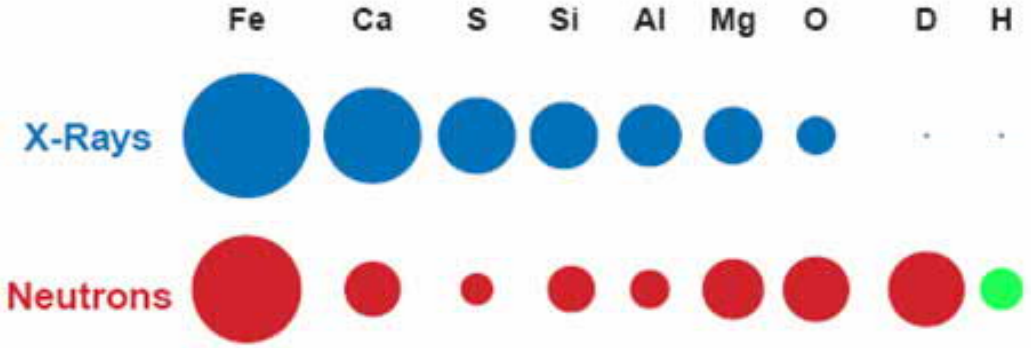
- **Scattering strength does not depend on atomic number**
  - → **positions of light elements (e.g. H and O) can be determined with the same accuracy as those of heavy elements**
  - → **highly useful for example in studies on perovskite oxides**
  - → **sometimes solving an unknown structure is more difficult with ND than with XRD, since all the atoms are ”seen”**
- **No ”bonding effects” in atomic positions**
  - → **important when hydrogen-bonded structures are studied (ND reveals typically ~0.2 Å longer O-H bonds than XRD)**
- **Scattering strength may vary strongly among different isotopes of the same element**
  - → **”isotope substitution”**
- **Neutron scattering factor can be also negative !**

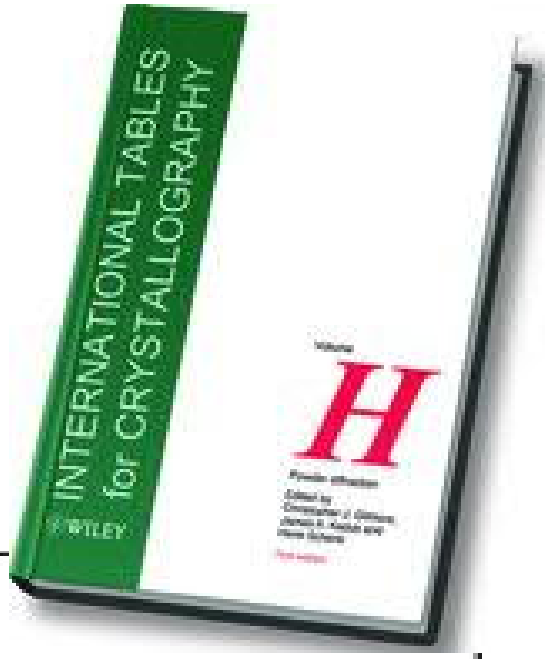
Scattering strength

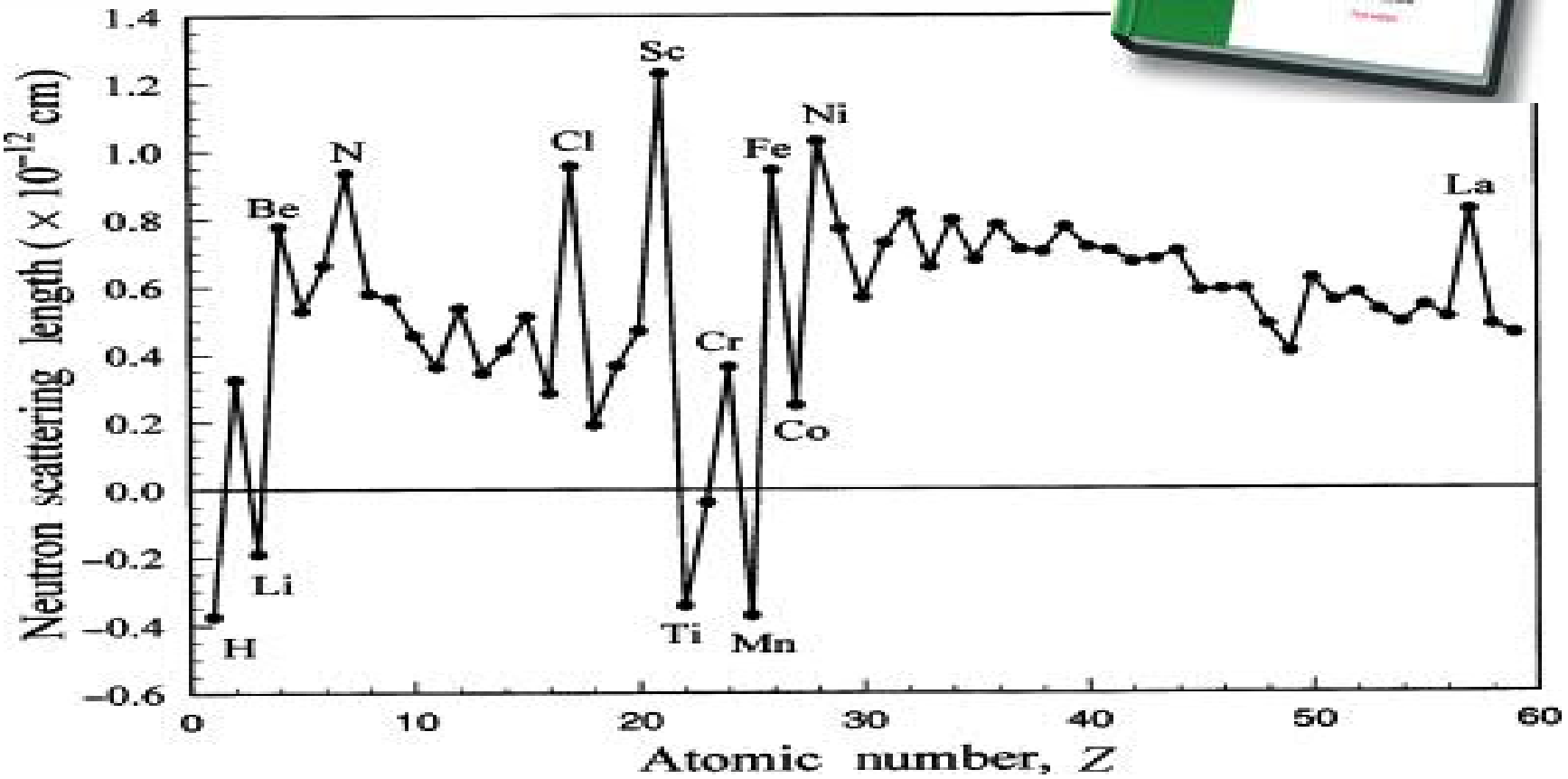
- Tells how strongly neutrons/ x-rays are scattered (= diffracted)
- OTHER TERMINOLOGIES: Scattering factor, Scattering length, Scattering amplitude, Scattering cross-section, Form factor

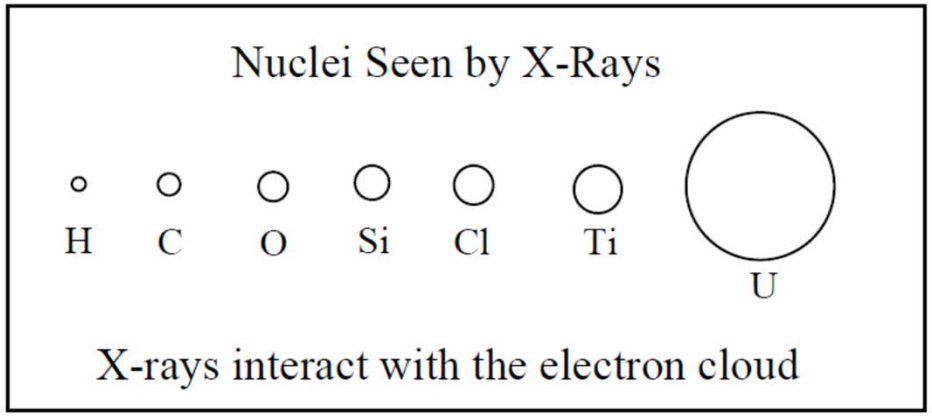

X-rays
θ=0°
X-rays
(sin θ)/λ=0·5 Å⁻¹
Scattering amplitude (10⁻¹² cm)
5
4
3
2
1
0
−1
Cl
Sc
⁵⁶Fe
⁵⁸Ni
Neutrons
¹H
⁷Li
20
40
Ti
V
Mn
60
⁶²Ni
80
100
Atomic weight

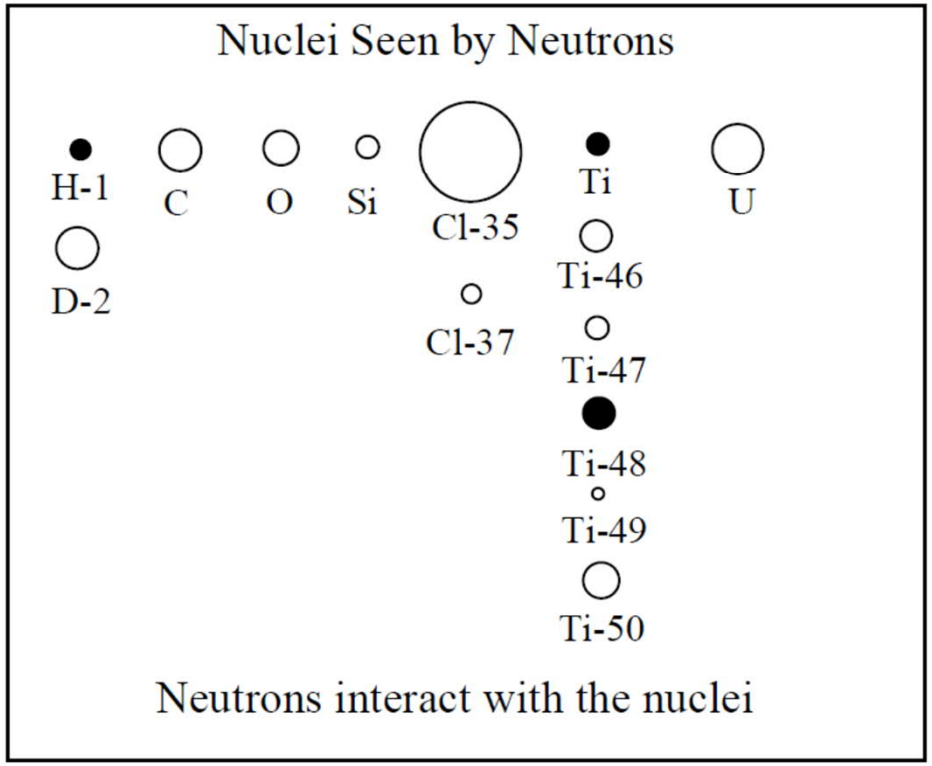

Scattering amplitude (10^{-12} cm)
5
4
3
2
1
0
(a)
X-rays
(b) Neutrons
0·2
0·4
0·6
0·8
1·0
(sin θ)/λ (10^8 cm)


Fe
Ca
S
Si
Al
Mg
O
D
H
X-Rays
Neutrons


INTERNATIONAL TABLES
for CRYSTALLOGRAPHY
H
WILEY


Neutron scattering length (× 10⁻¹² cm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
0
10
20
30
40
50
60
Atomic number, Z
H
Li
Be
N
Cl
Sc
Ti
Cr
Mn
Fe
Co
Ni
La


Nuclei Seen by X-Rays
H
C
O
Si
Cl
Ti
U
X-rays interact with the electron cloud

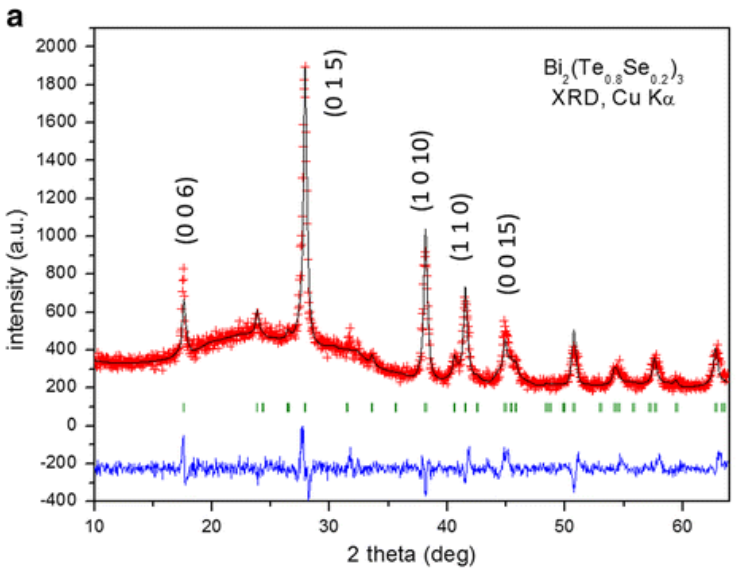

Nuclei Seen by Neutrons
H-1
D-2
C
O
Si
Cl-35
Cl-37
Ti
Ti-46
Ti-47
Ti-48
Ti-49
Ti-50
U
Neutrons interact with the nuclei

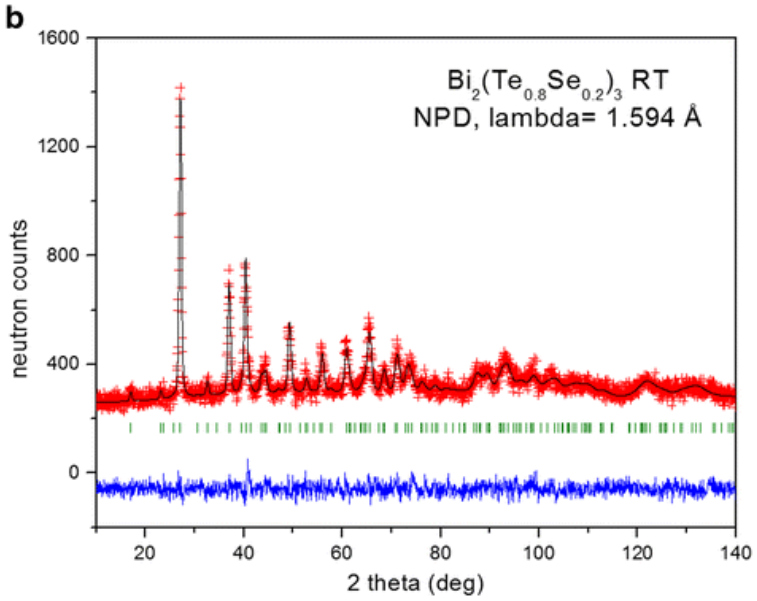
SAMPLES

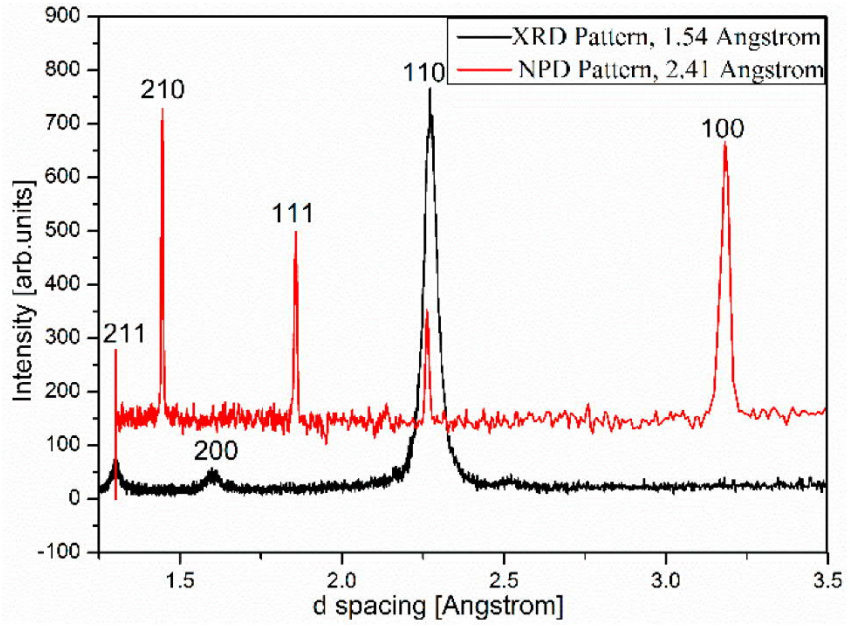
- single crystal (optimally roundish: XRD 0.1 ~ 0.3 mm, ND ~1 cm)
- **powder: XRD >10 mg , ND preferably >1 g**
- thin film: XRD, ED
- amorphous material: XRD, ND
- liquid: XRD (θ-θ geometria)
- gas (ED); electron diffraction is a very local method

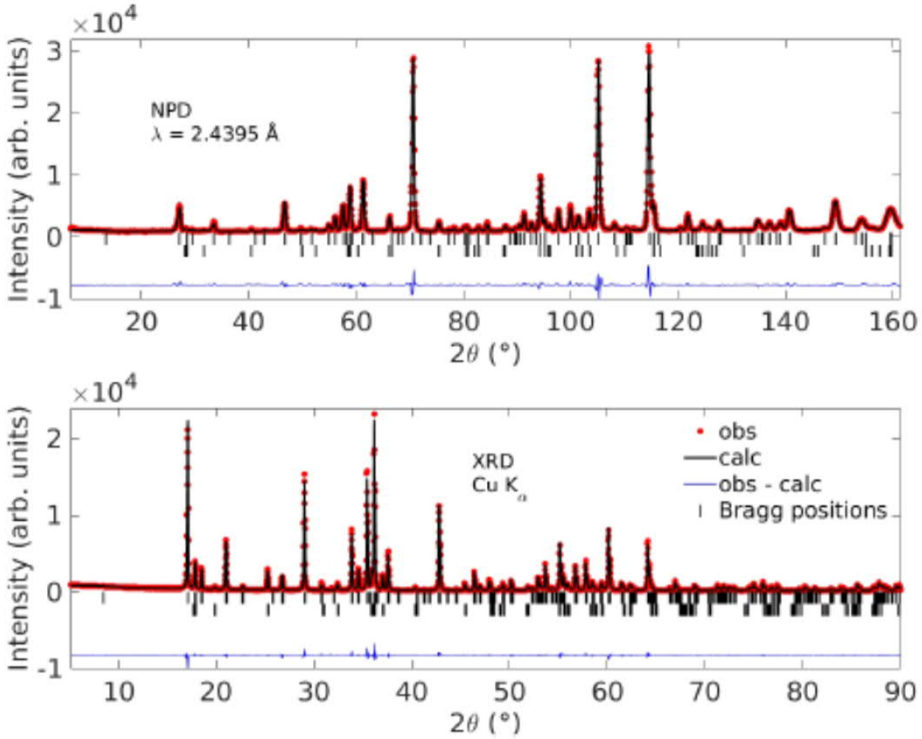
Vanadinium
SAMPLE HOLDERS
for ND

Why ND and XRD patterns for the same sample may look different ?







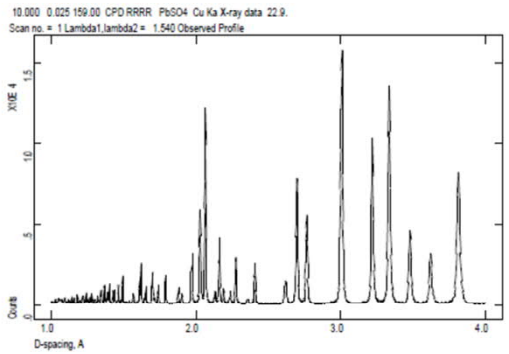


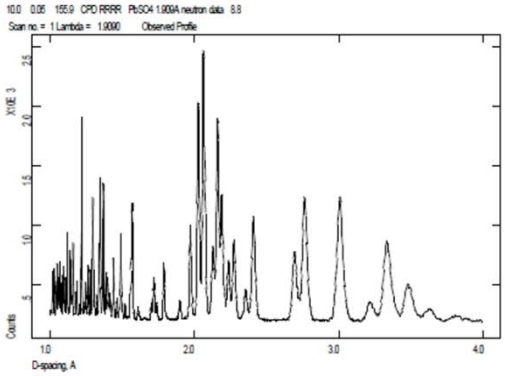
Why ND and XRD patterns for the same sample look different ?

- Different λ → To make them similar, plot in terms of d
- Different sample preparation → Different orientation of crystallites
- Scattering factor depends on angle in XRD, not in ND
- Different atomic/nucleic scattering factors → Different peak intensity ratios
- ND sees magnetic ordering too, XRD not

Compare X-ray & Neutron Powder Patterns

X-ray Diffraction - CuKa
Phillips PW1710
- **Higher resolution**
- **Intensity fall-off at small d spacings**
- **Better at resolving small lattice distortions**

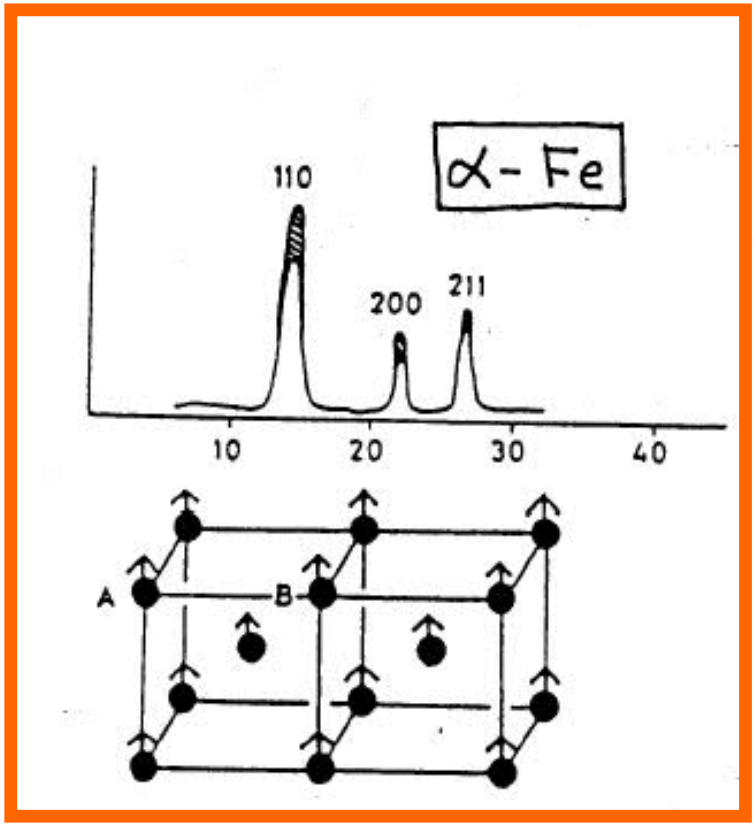


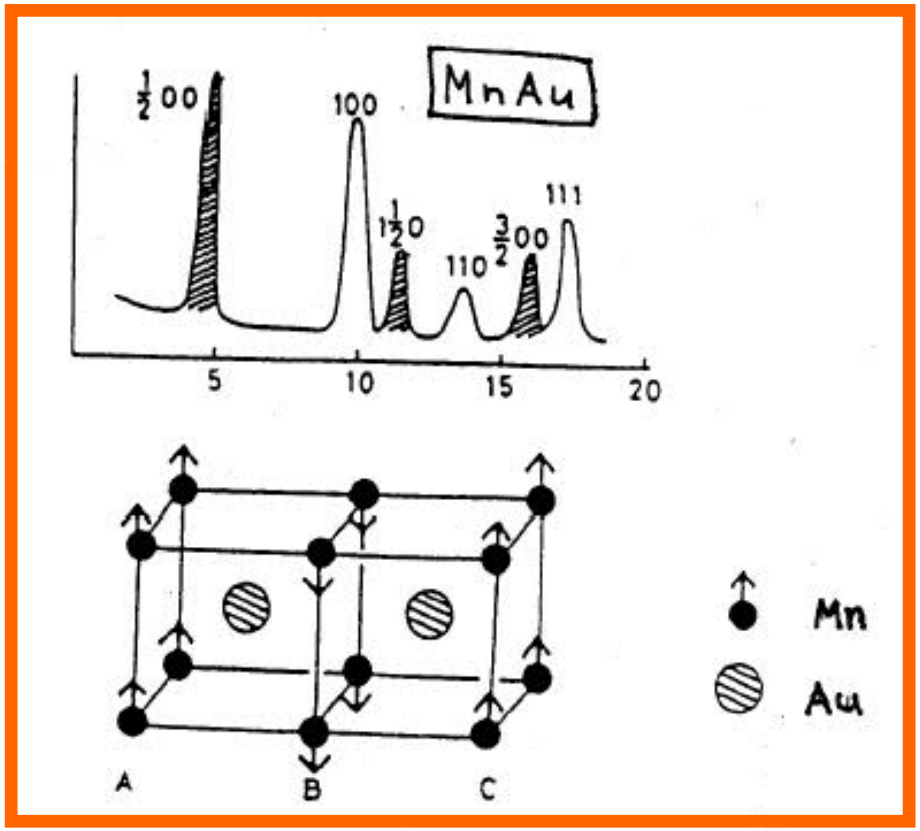


Neutron Diffraction - D1a, ILL
λ=1.909 Å
- **Lower resolution**
- **Much higher intensity at small d-spacings**
- **Better atomic positions/thermal parameters**

Neutrons possess magnetic moment

- Neutrons have magnetic moment, though no electric charge
- Stronger scattering from atoms with ordered spin → magnetic structure determination

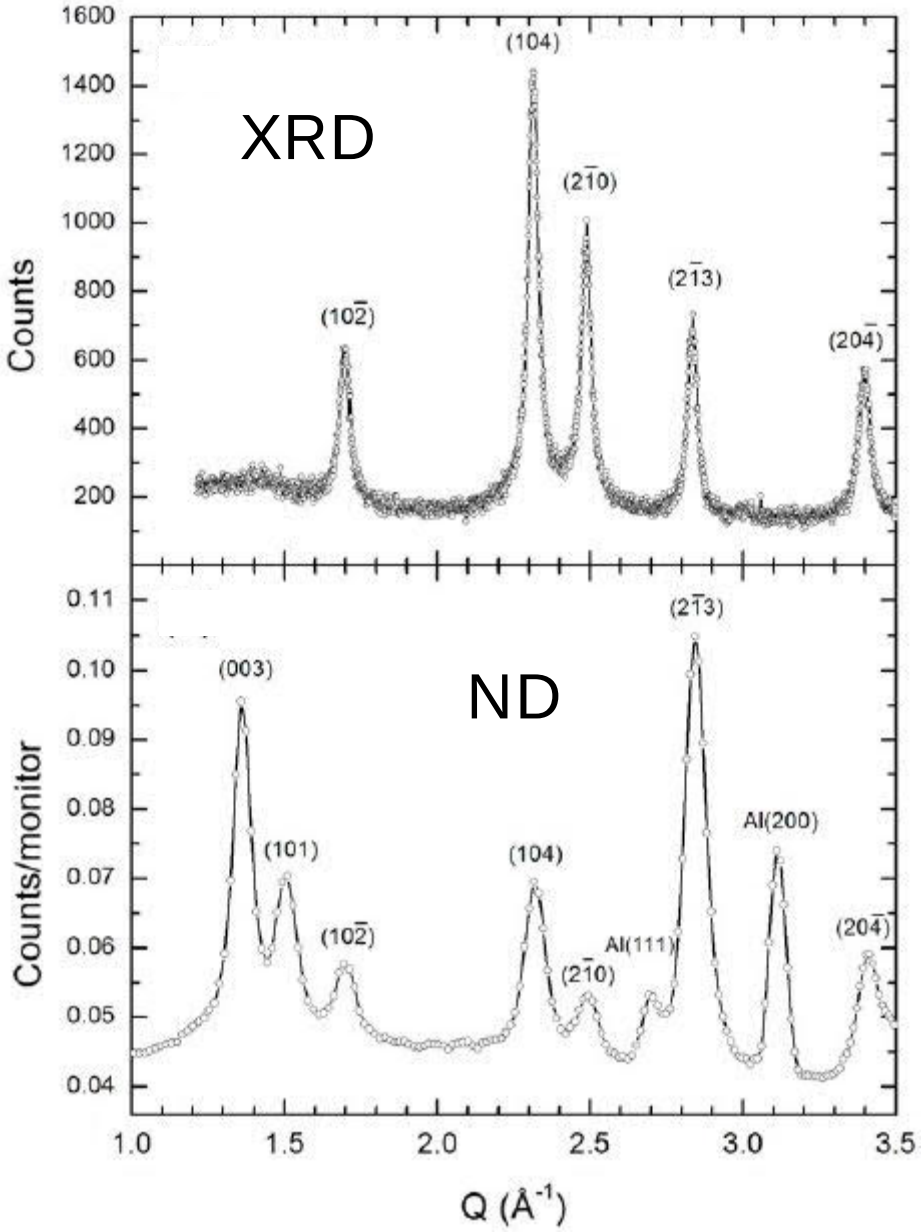




Ferromagnetic:
- changes in peak intensities

Antiferromagnetic:
- additional peaks

Antiferromagnetic hematite Fe_2O_3



Antiferromagnetic MnO ($T_N \approx 120$ K)

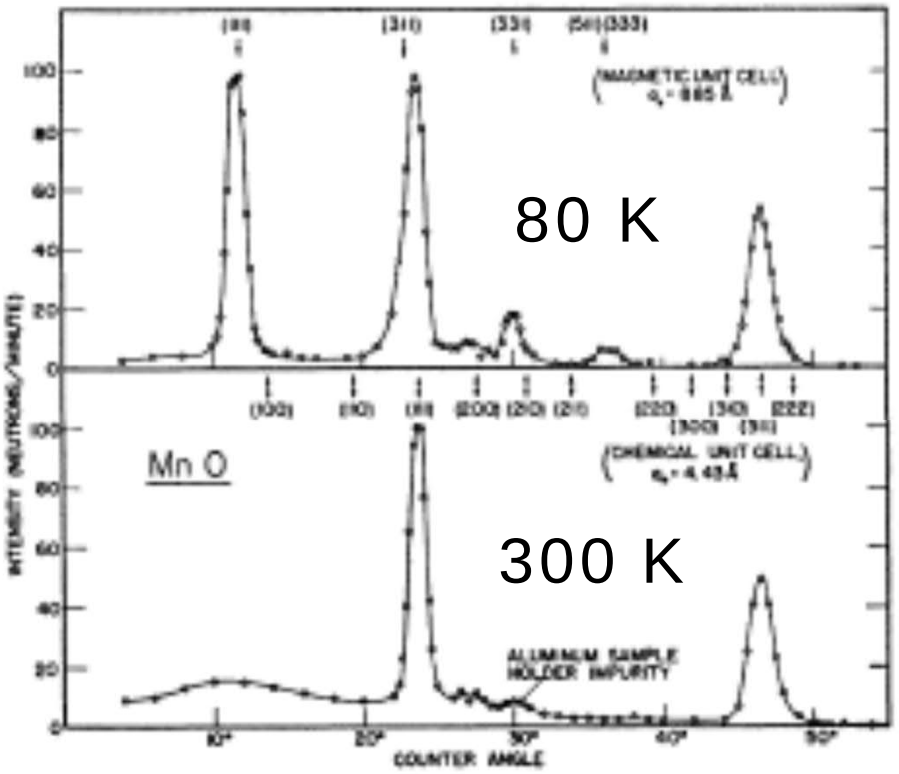
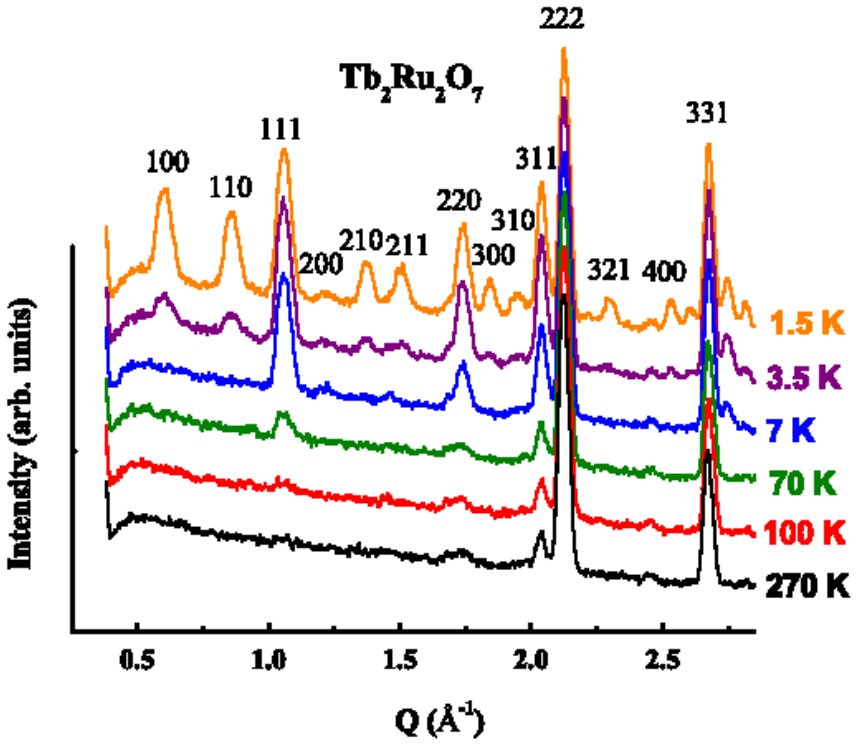
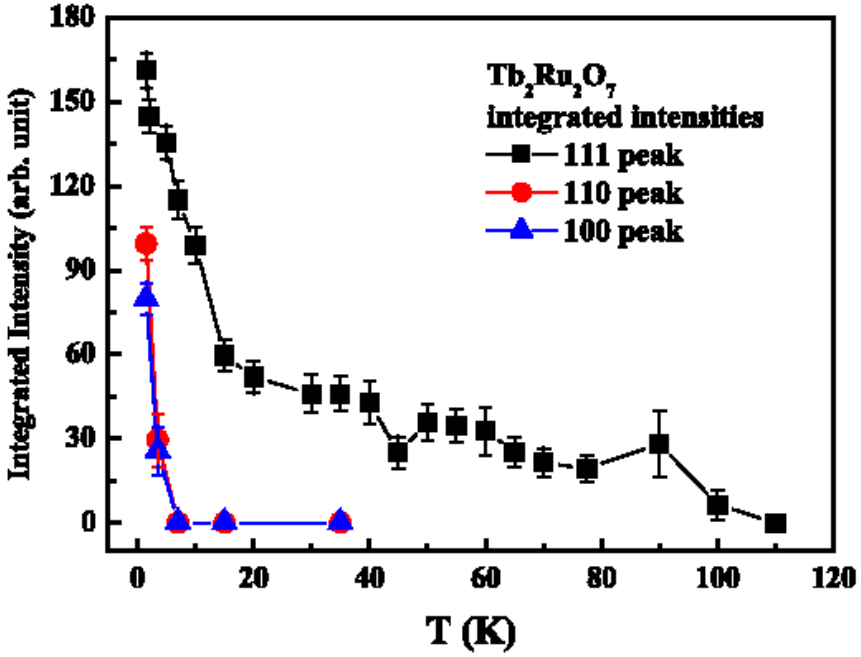


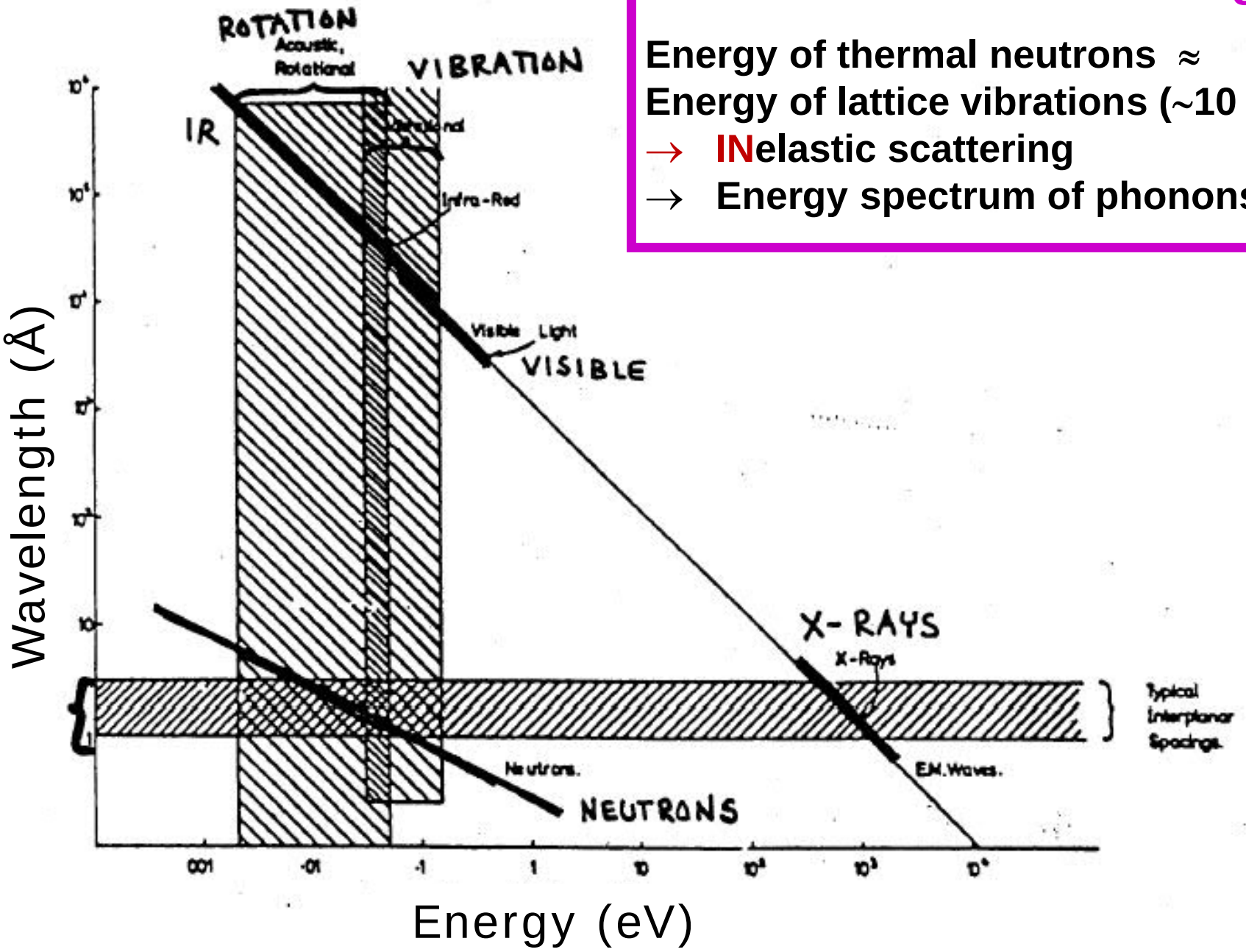
FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.


Tb2Ru2O7
100
110
111
200
210
211
220
300
310
311
222
321
400
331
1.5 K
3.5 K
7 K
70 K
100 K
270 K
Intensity (arb. units)
0.5
1.0
1.5
2.0
2.5
Q (Å-1)

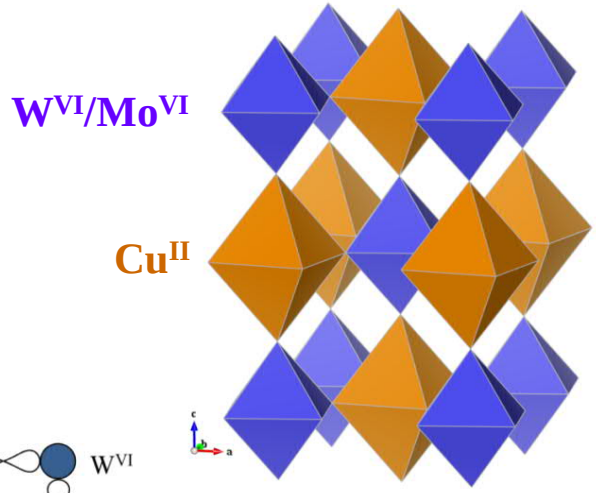

Tb2Ru2O7
integrated intensities
111 peak
110 peak
100 peak
Integrated Intensity (arb. unit)
180
150
120
90
60
30
0
0
20
40
60
80
100
120
T (K)

Inelastic neutron scattering

Energy of thermal neutrons ≈
Energy of lattice vibrations (~10 meV)
→ INelastic scattering
→ Energy spectrum of phonons

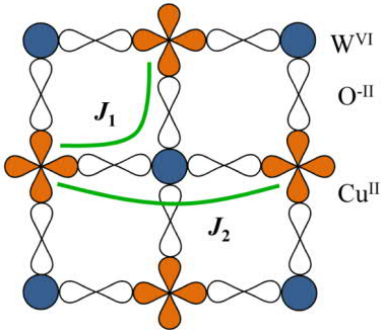


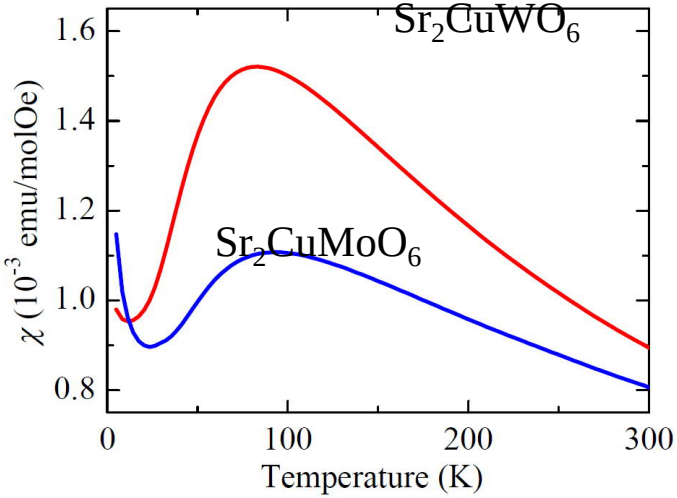
OUR OWN RESEARCH EXAMPLE



Double Perovskites $Sr_2Cu(W,Mo)O_6$

- ***B*-site ordered double perovskites**
- **Sr_2CuWO_6: synthesis in air**
- **Sr_2CuMoO_6: high-pressure synthesis (only very small sample amounts!)**
- **Cu^{II} : d^9 (Jahn-Teller) & magnetic (S = ½)**
- **WE COULD EXPECT:**
  - **Low-dimensional (2D) magnetism**
  - **Interesting quantum effects**
- **Magnetic measurements (SQUID): some magnetic transition around 25 K**
- **URGENT QUESTION: is it long-range magnetism (FM or AFM ?)**



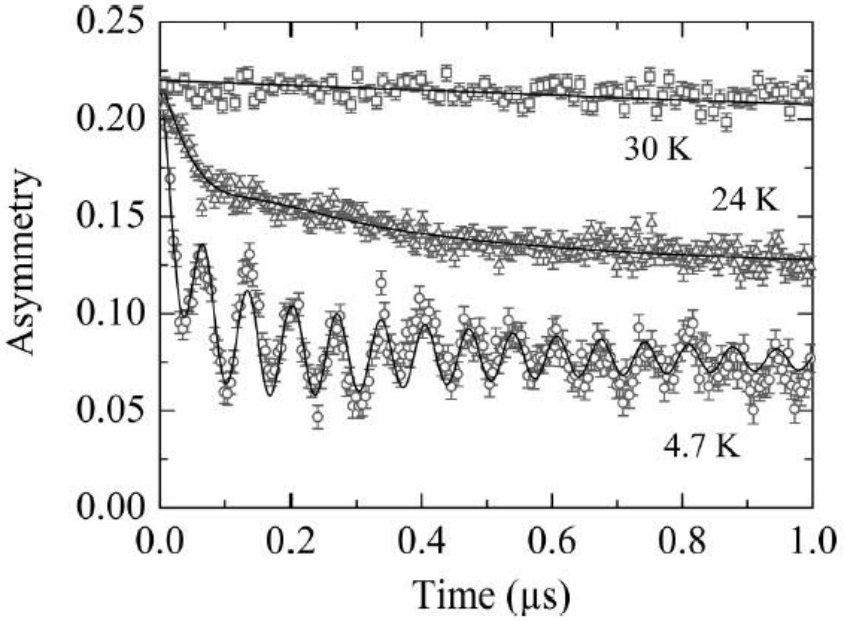


S. Vasala, J.-G. Cheng, H. Yamauchi, J.B. Goodenough & M. Karppinen, $Sr_2Cu(W_{1-x}Mo_x)O_6$: a quasi-two-dimensional magnetic system, *Chemistry of Materials* **24**, 2764 (2012).

Sr_2CuWO_6
(normal-pressure synthesized)

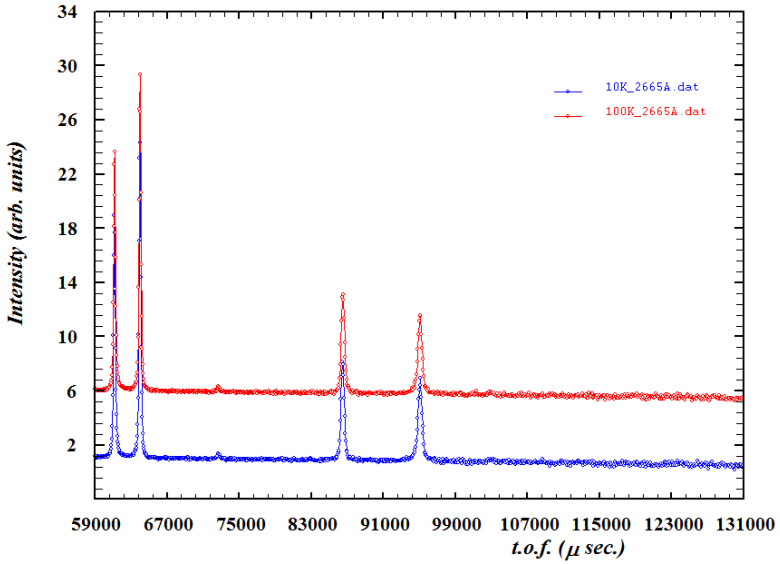
MUON SPIN EXPERIMENTS

- Paul Scherrer Institute, Switzerland
- Long-range order below 24 K !
- **QUESTION:** Can we confirm this with ND, and determine the magnetic structure



NEUTRON DIFFRACTION

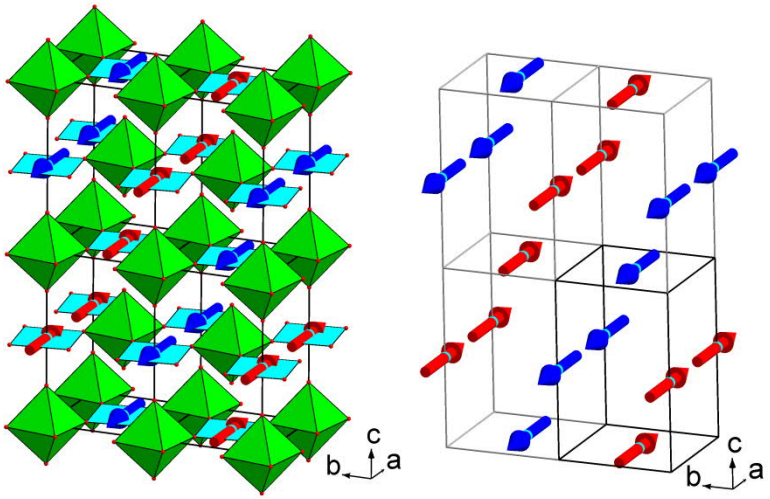
- POWGEN beamline, SPS, Oak Ridge National Laboratory, USA
- No additional magnetic reflections (10 K versus 100 K) seen, WHY ?
- Sample amount large (~5 g) but the expected magnetic moment small (< 0.5 μ_B)

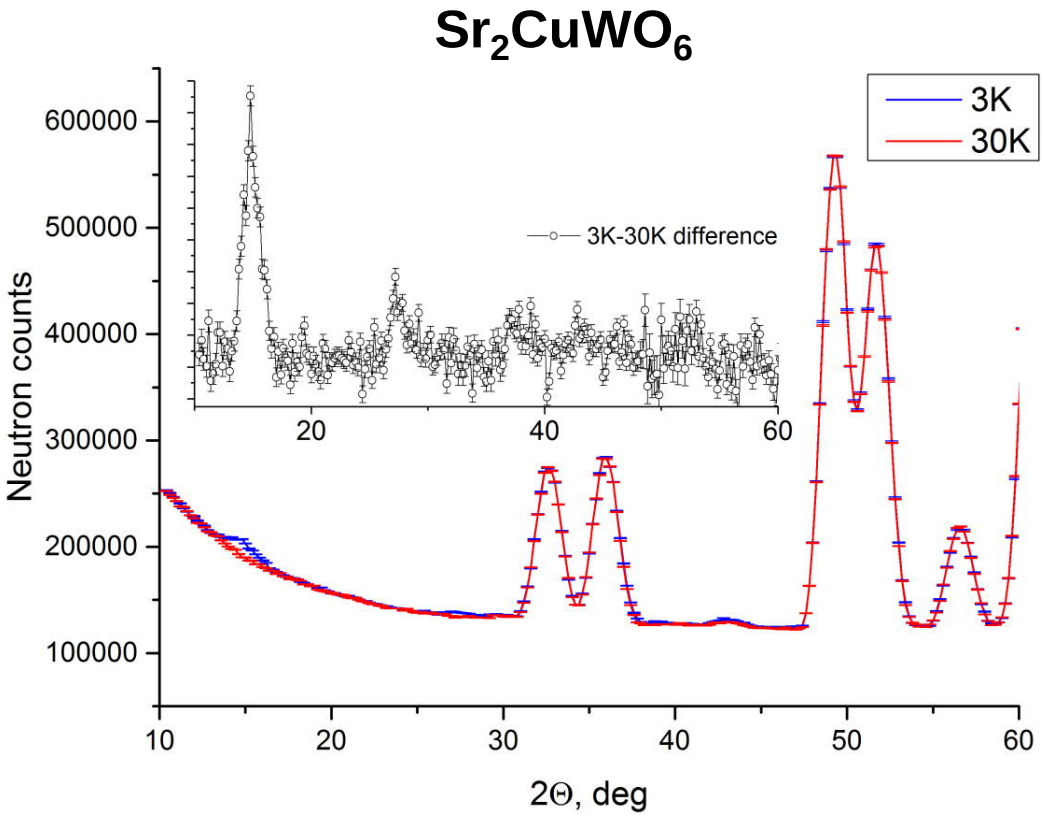


Vasala, Saadaoui, Morenzoni, Chmaissem, Chan, Chen, Hsu, Yamauchi & MKarppinen, Characterization of magnetic properties of Sr_2CuWO_6 and Sr_2CuMoO_6, *Physical Review B* **89**, 134419 (2014).

HIGH-FLUX NEUTRON DIFFRACTION

- High-flux triple-axis spectrometerTaipan, OPAL reactor, ANSTO, Australia
- Clear additional magnetic reflections (3 K versus 30 K)
- Type-II antiferromagnetic structure (in agreement with our electronic structure calculations)





S. Vasala, M. Avdeev, S. Danilkin, O. Chmaissem & M. Karppinen, Magnetic structure of Sr_2CuWO_6, *Journal of Physics; Condensed Matter* **26**, 496001 (2014).

NEXT STEPS …

- Magnetic structures of **high-pressure synthesized** $Sr_2Cu\mathit{B}O_6$: *B* = Mo, Ir, Te
- **Small sample** amount of 50 ~ 200 mg !
- **High-flux** and **huge-detector-area** WISH diffractometer, **ISIS**, Oxford, UK (optimized for detecting low magnetic intensity from small sample sizes)

S. Vasala, H. Yamauchi & M. Karppinen, Synthesis, crystal structure and magnetic properties of a new *B*-site ordered double perovskite Sr_2CuIrO_6, *Journal of Solid State Chemistry* **220**, 28-31 (2014).

H.C. Walker, O. Mustonen, S. Vasala, D.J. Voneshen, M.D. Le, D.T. Adroja & M. Karppinen, Spin wave excitations in the tetragonal double perovskite Sr_2CuWO_6, *Physical Review B* **94**, 064411 (2016).

O. Mustonen, S. Vasala, K.P. Schmidt, E. Sadrollahi, H. C. Walker, I. Terasaki, F.J. Litterst, E. Baggio-Saitovitch & M. Karppinen, Tuning the *S* = 1/2 square-lattice antiferromagnet $Sr_2Cu(Te_{1-x}W_x)O_6$ from Néel order to quantum disorder to columnar order, *Physical Review B* **98**, 064411 (2018).

O. Mustonen, S. Vasala, E. Sadrollahi, K.P. Schmidt, C. Baines, H.C. Walker, I. Terasaki, F.J. Litterst, E. Baggio-Saitovitch & M. Karppinen, Spin-liquid-like state in a spin-1/2 square-lattice antiferromagnet perovskite induced by d^{10}–d^0 cation mixing, *Nature Communications* **9**, 1085 (2018).

O. Mustonen, S. Vasala, H. Mutch, C.I. Thomas, G.B.G. Stenning, E. Baggio-Saitovitch, E.J. Cussen & M. Karppinen, Magnetic interactions in the *S* = 1/2 square-lattice antiferromagnets Ba_2CuTeO_6 and Ba_2CuWO_6: parent phases of a possible spin liquid, *Chemical Communications* **55**, 1132 (2019).

	X-rays	Neutrons	Electrons
Typical E / λ	12 keV / 1.0 Å	25 meV / 1.8 Å	50 kV / 0.05 Å
Scattering from	Electron cloud	Nuclei	Electric field (nucleus & electrons)
Detects	Electron density	Atomic positions	Atomic positions
Scattering strength	Strong, depends strongly on Z	Weak, no dependence on Z or angle	Very strong, depends on Z
Penetration	Good	Good	Bad
Sample amount	10 ~ 100 mg	0.1 ~ 10 g	"Local"
Magnetic structure	NOT possible	Possible	NOT possible
Wavelength	Well monochromatic	Not perfectly monochromatic	Extremely monochromatic