SCHEDULE

	Date		Topic
1.	Tue	14.09.	Lec-1: Introduction
2.	Fri	17.09.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Fri	17.09.	EXERCISE 1
4.	Tue	21.09.	Lec-3: Crystal chemistry & BVS
5.	Fri	24.09.	Lec-4: Molecular Symmetry & Point Groups
6.	Fri	24.09.	EXERCISE 2
7.	Tue	28.10.	Lec-5: Crystallography & Space Groups
8.	Fri	01.10.	Lec-6: XRD & Reciprocal Lattice
9.	Fri	01.10.	EXERCISE 3
10.	Tue	05.10.	Lec-7: ND
11.	Fri	08.10.	Lec-8: Rietveld
12.	Fri	08.10	EXERCISE 4: Rietveld
13.	Tue	12.10.	Lec-9: Synchrotron rad. & XAS & RIXS
14.	Fri	15.10.	Lec-10: EXAFS & Mössbauer
15.	Fri	15.10.	EXERCISE 5
16.	Tue	19.10.	Seminars: XPS, ED, HRTEM, SEM, AFM
17.	Fri	22.10.	Lec-11: GI-XRD & XRR
18.	Fri	22.10.	EXERCISE 6: XRR

EXAM: Friday, Oct. 29th, 2021

LECTURE 7: 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 (todays example)**

USA

- Argonne National Laboratory (IPNS), USA (temporarily closed)
- **Oak Ridge National Laboratory, Spallation Neutron Source (SNS), USA (todays example)**

JAPAN

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

AUSTRALIA

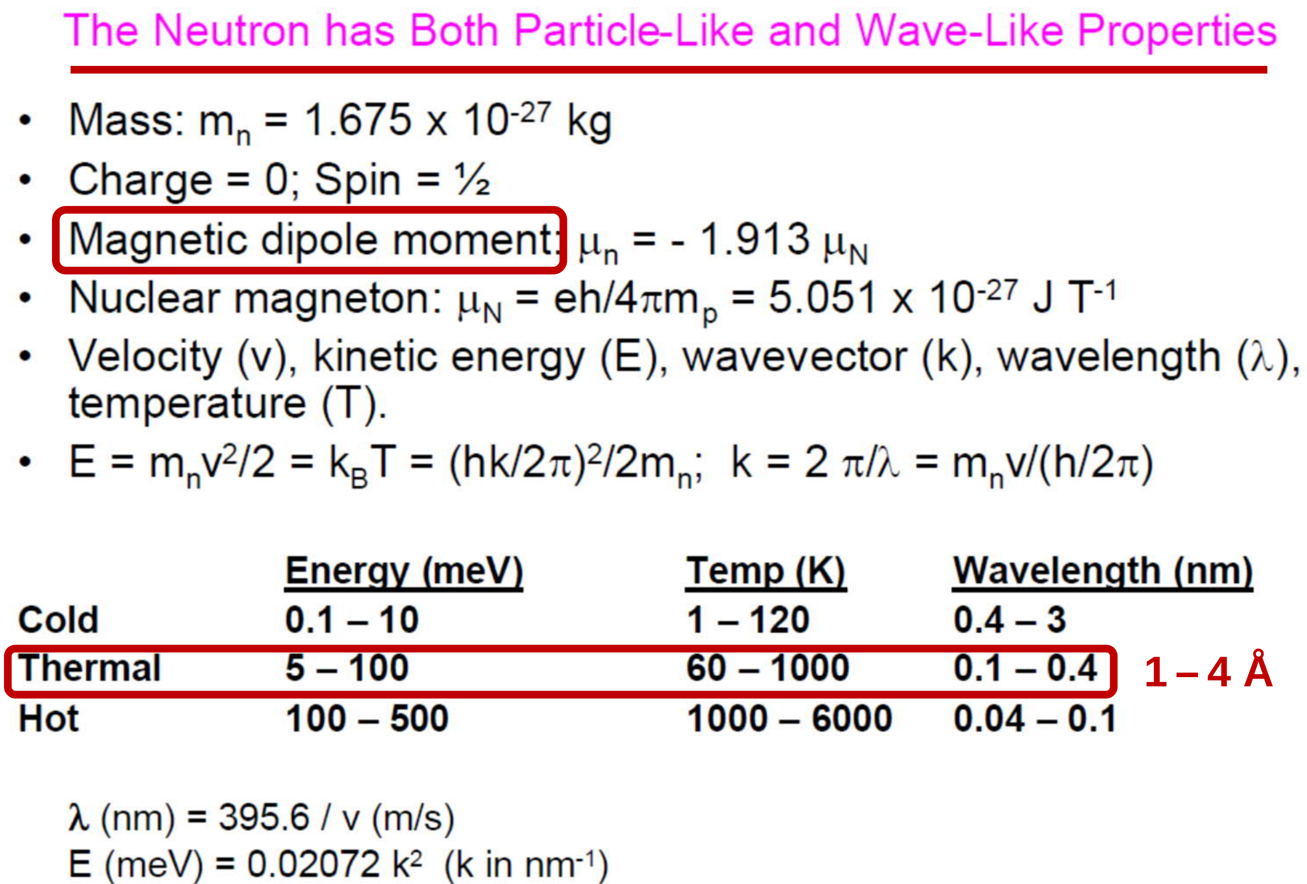
- Bragg Institute (ANSTO), Sydney, AUSTRALIA **(todays example)**

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).
- $E = m_n v^2/2 = k_B T = (hk/2\pi)^2/2m_n$; $k = 2\pi/\lambda = m_n v/(h/2\pi)$

"Thermal" neutrons have the proper energy & wavelength for crystal structure determination through diffraction

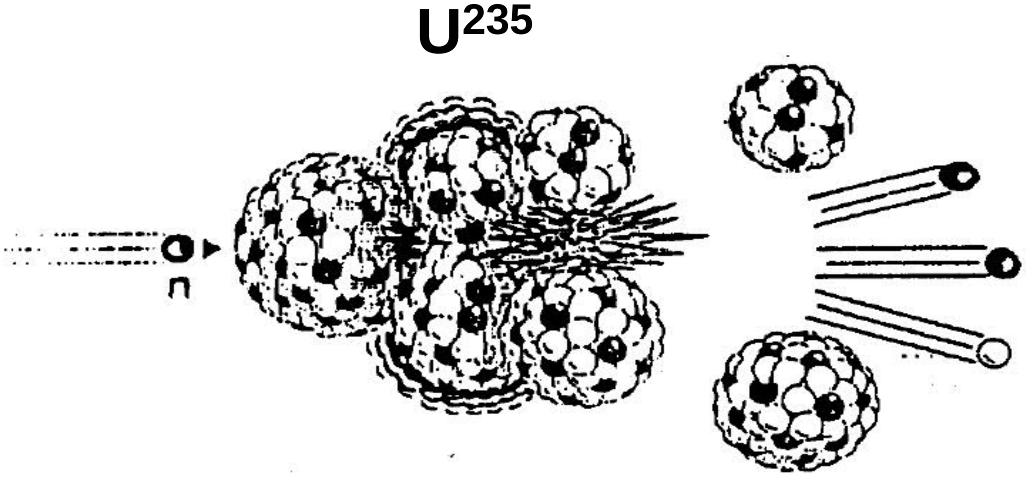
	Energy (meV)	Temp (K)	Wavelength (nm)
Cold	0.1 – 10	1 – 120	0.4 – 3
Thermal	5 – 100	60 – 1000	0.1 – 0.4
Hot	100 – 500	1000 – 6000	0.04 – 0.1

1 – 4 Å

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: $^{235}U + n_{therm} \rightarrow A + B + 2.3\ n$
- Thus produced neutrons 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)
- 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

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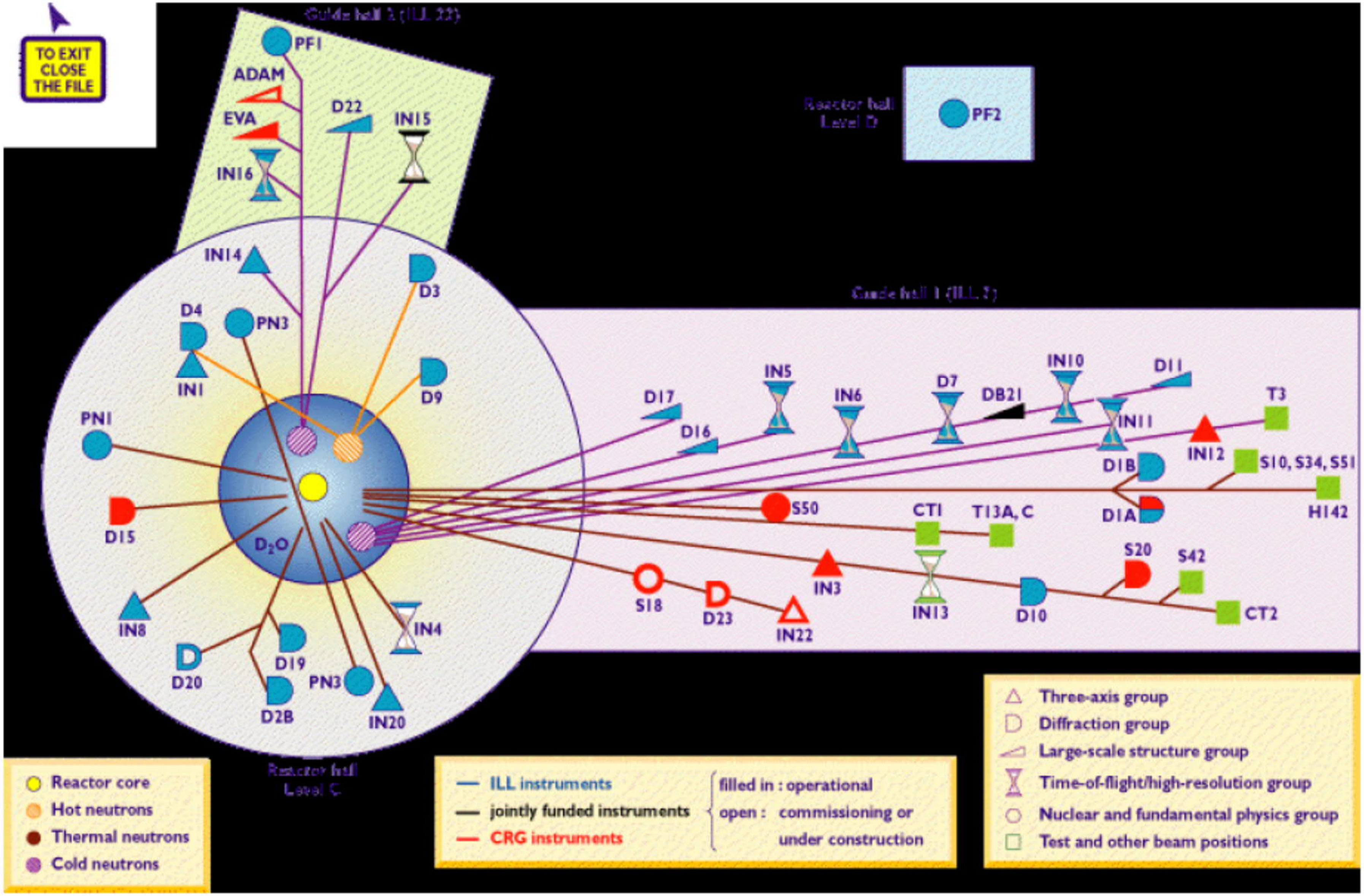
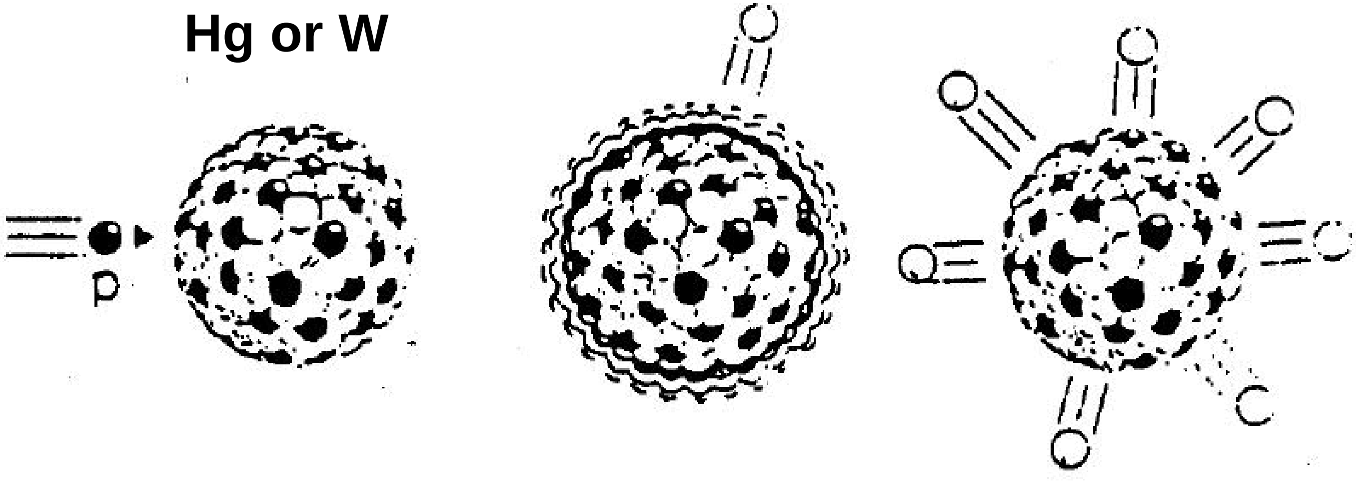


PRODUCTION OF NEUTRONS: Spallation

- Heavy metal (e.g. 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

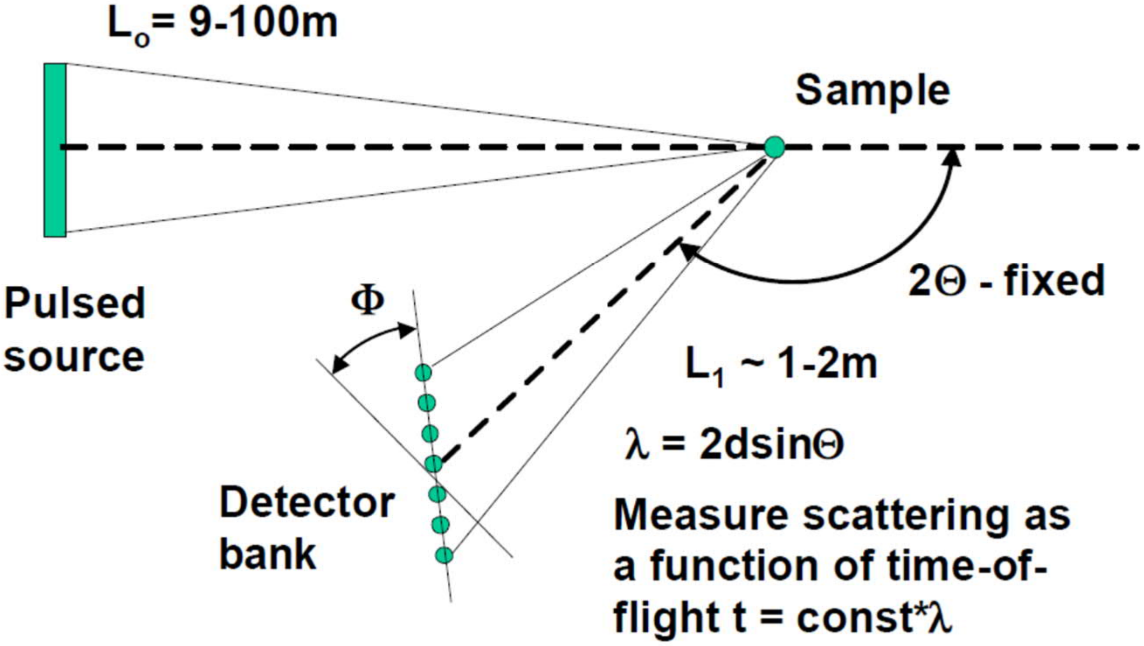
ISIS

- **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



$\lambda = 2d\sin\Theta$

Measure scattering as a function of time-of-flight t = const*λ

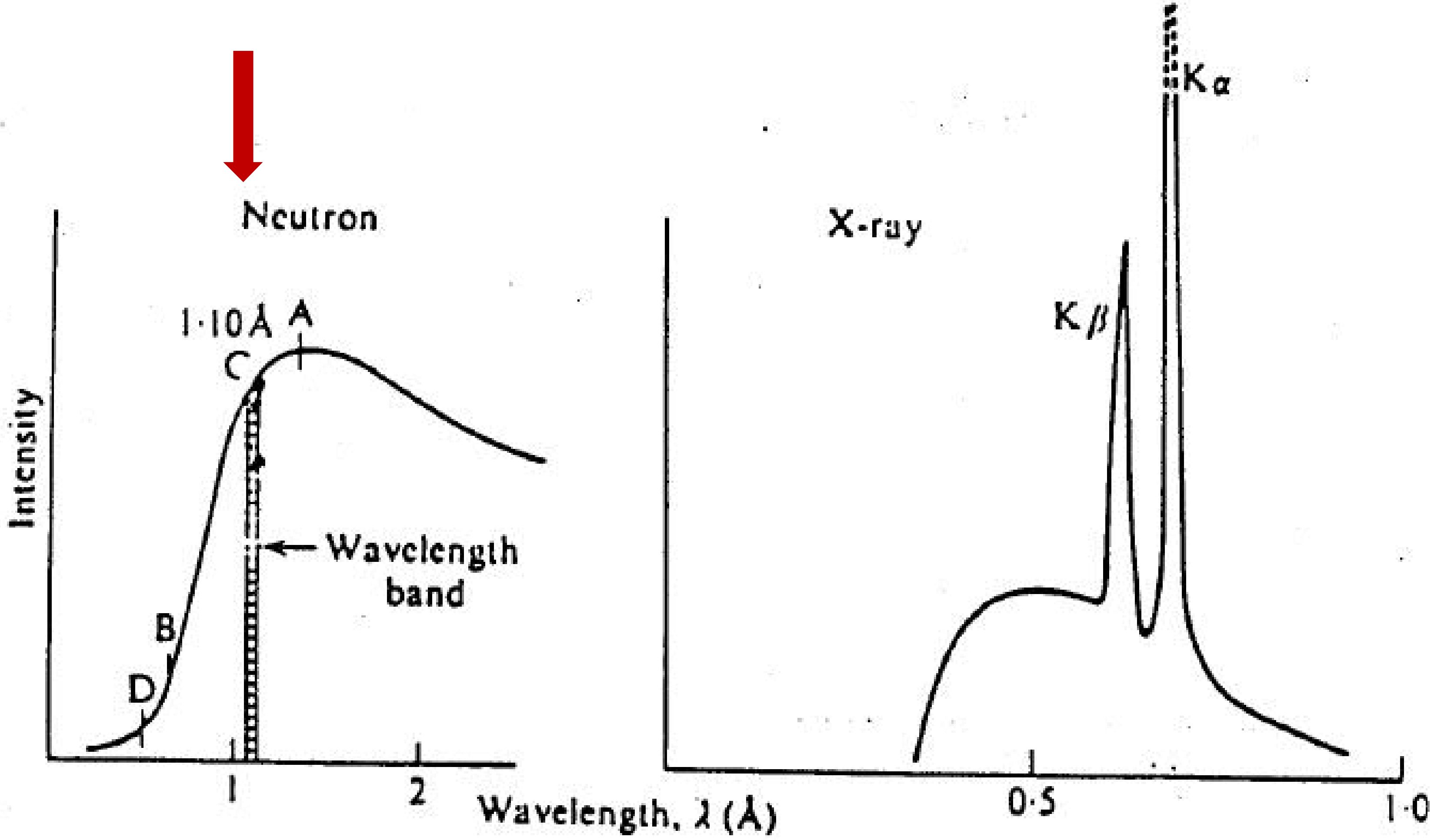
NEUTRON (powder) DIFFRACTION (ND)

- 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

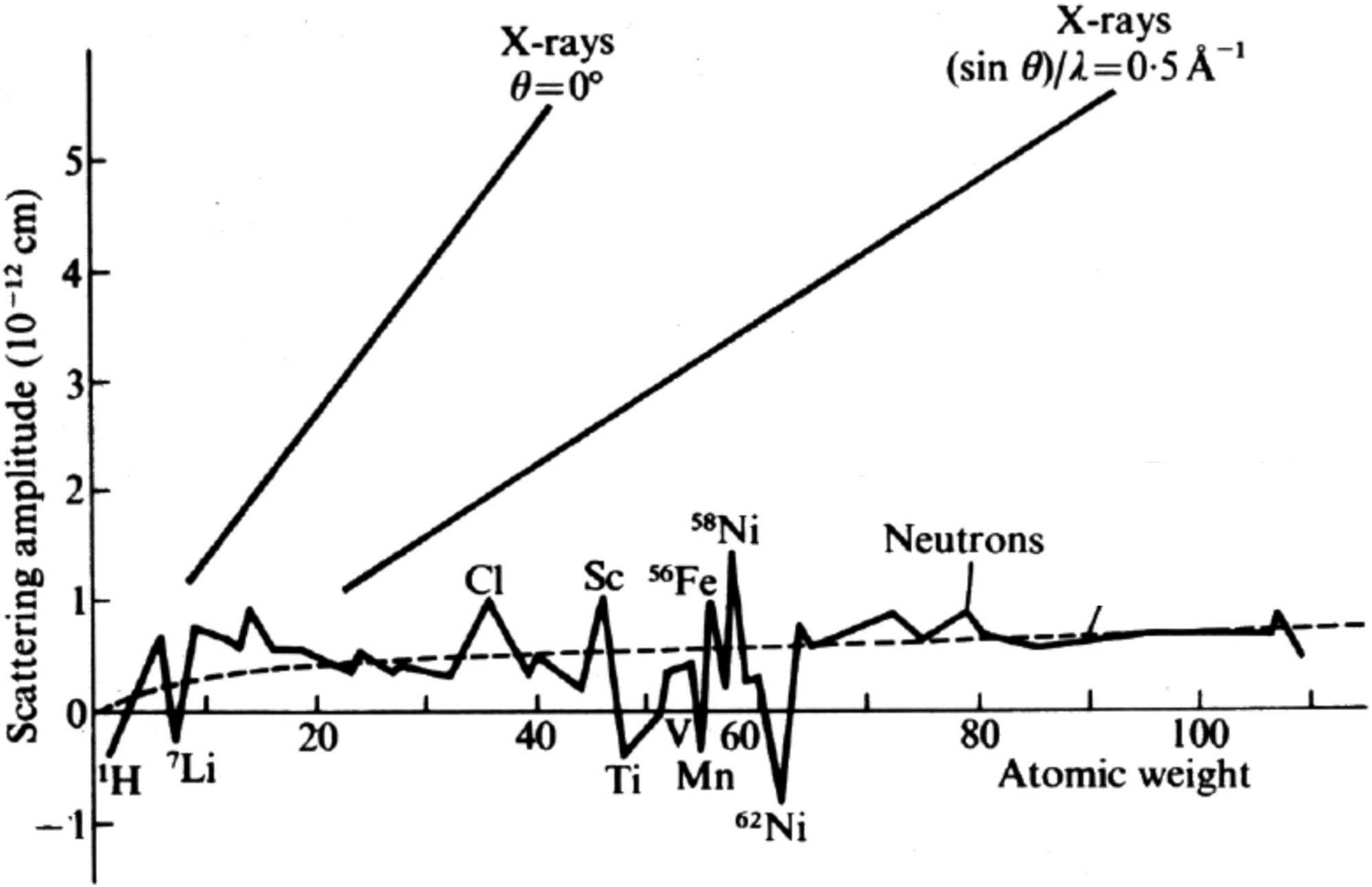


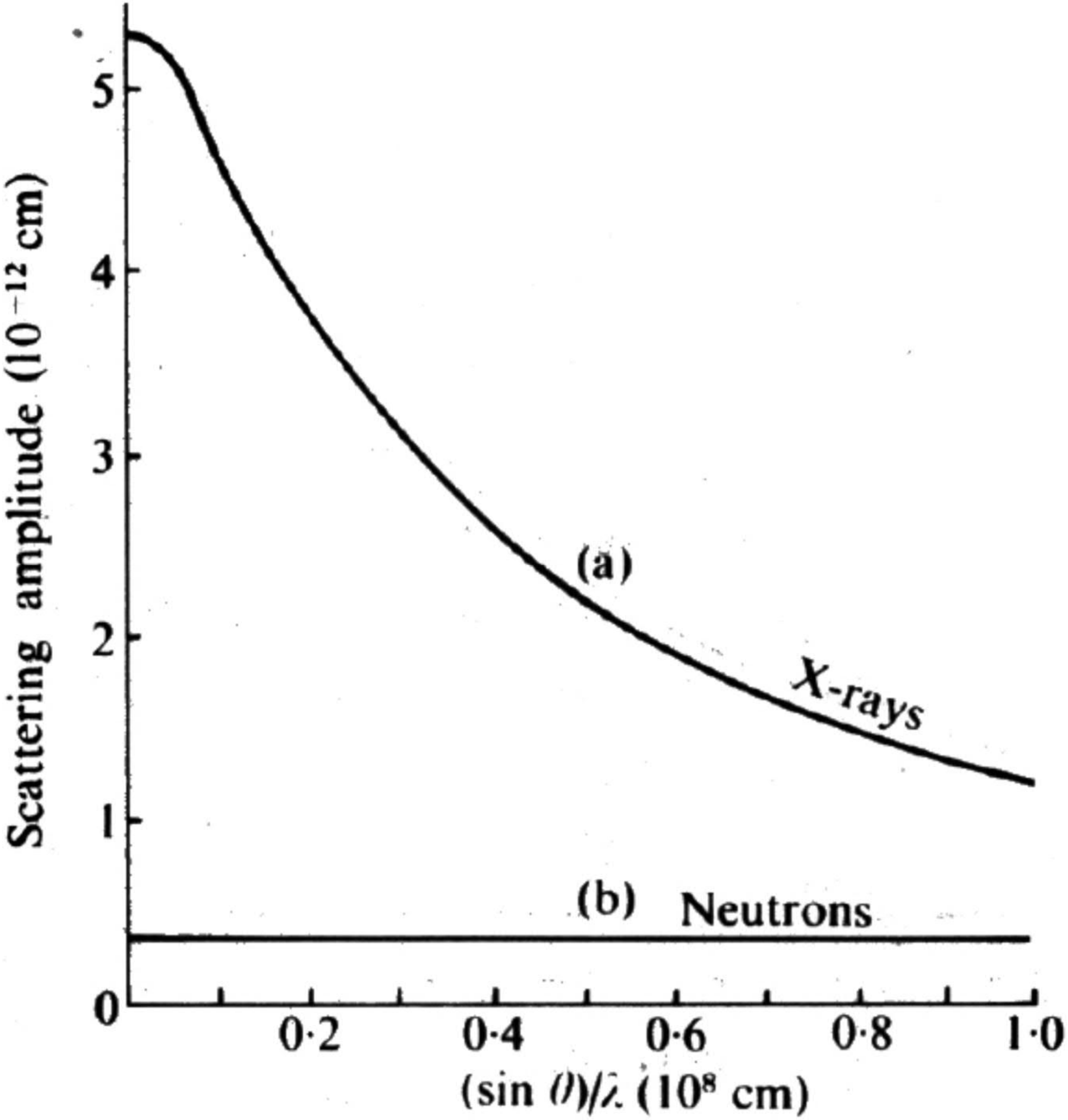
Neutrons scatter from an atomic nuclei

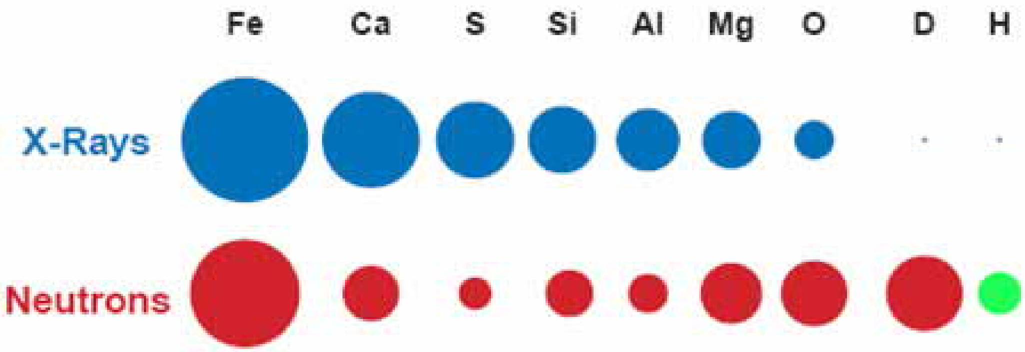
- Scattering strength does not depend on atomic number
  - → positions of light elements (e.g. H and O) can be determined with the same accuracy as those of heavy elements
  - → highly useful for example in studies on perovskite oxides
  - → sometimes solving an unknown structure is more difficult with 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
$\theta = 0°$
X-rays
$(\sin\theta)/\lambda = 0{\cdot}5$ Å^{-1}
Scattering amplitude (10^{-12} cm)
5
4
3
2
1
0
−1
Cl
Sc
^{56}Fe
^{58}Ni
Neutrons
^{1}H
^{7}Li
20
40
Ti
V
Mn
60
^{62}Ni
80
100
Atomic weight


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

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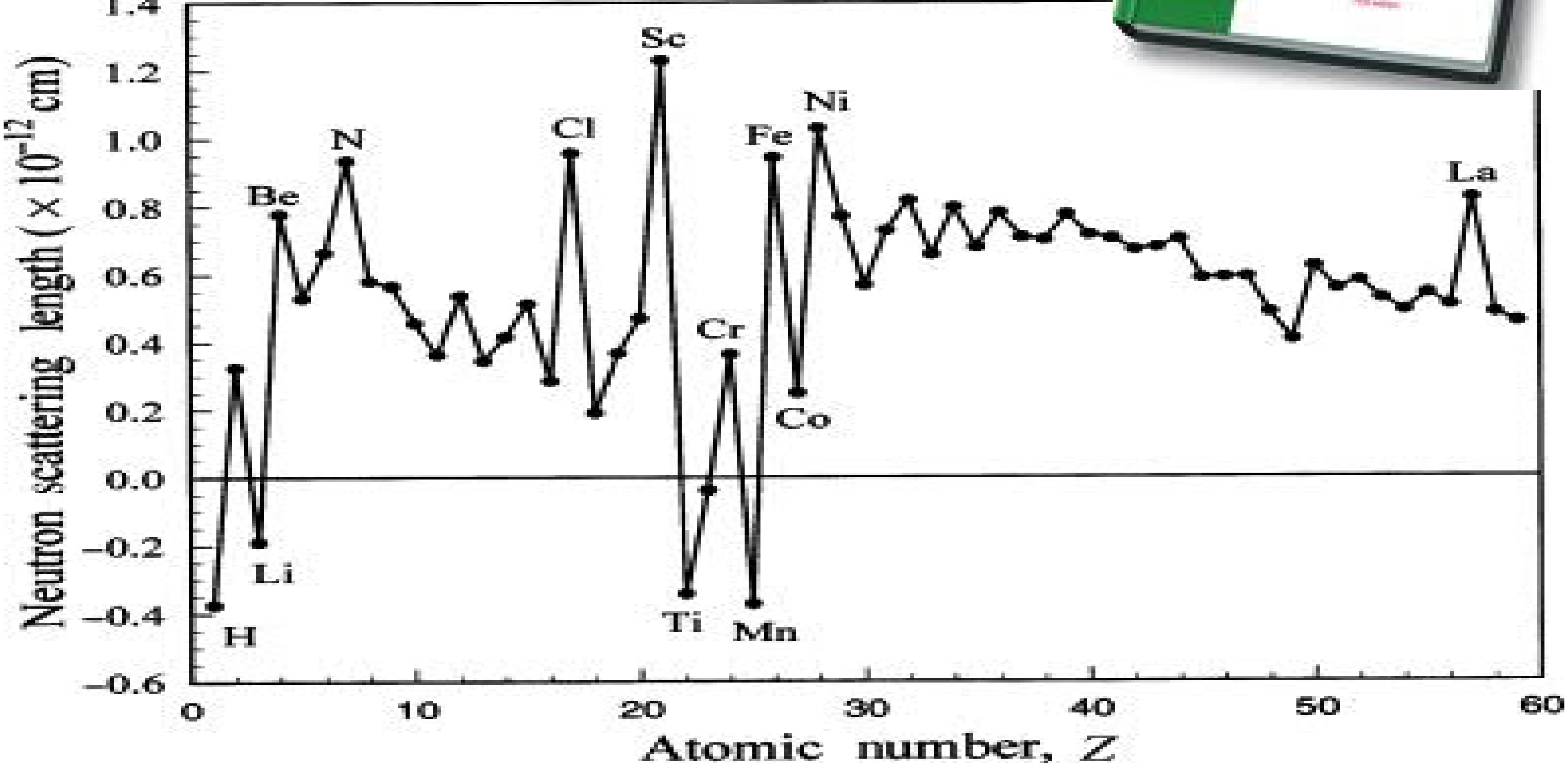
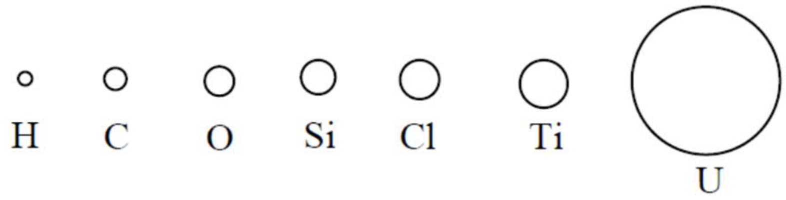
WILEY

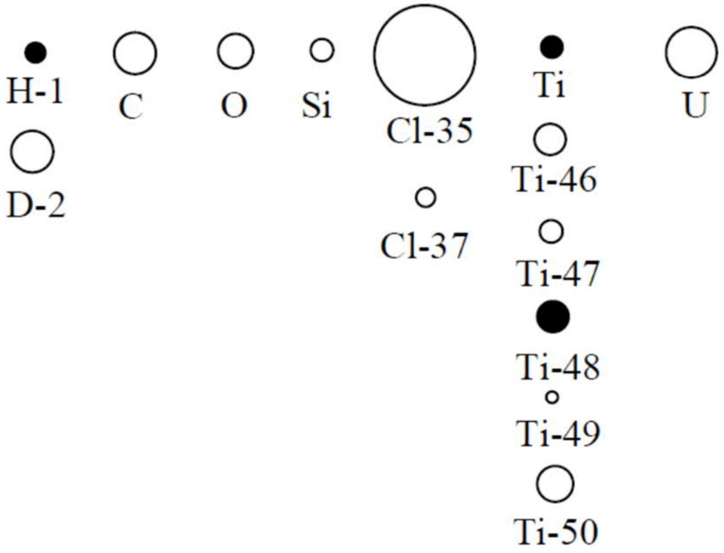


Nuclei Seen by X-Rays



X-rays interact with the electron cloud

Nuclei Seen by Neutrons



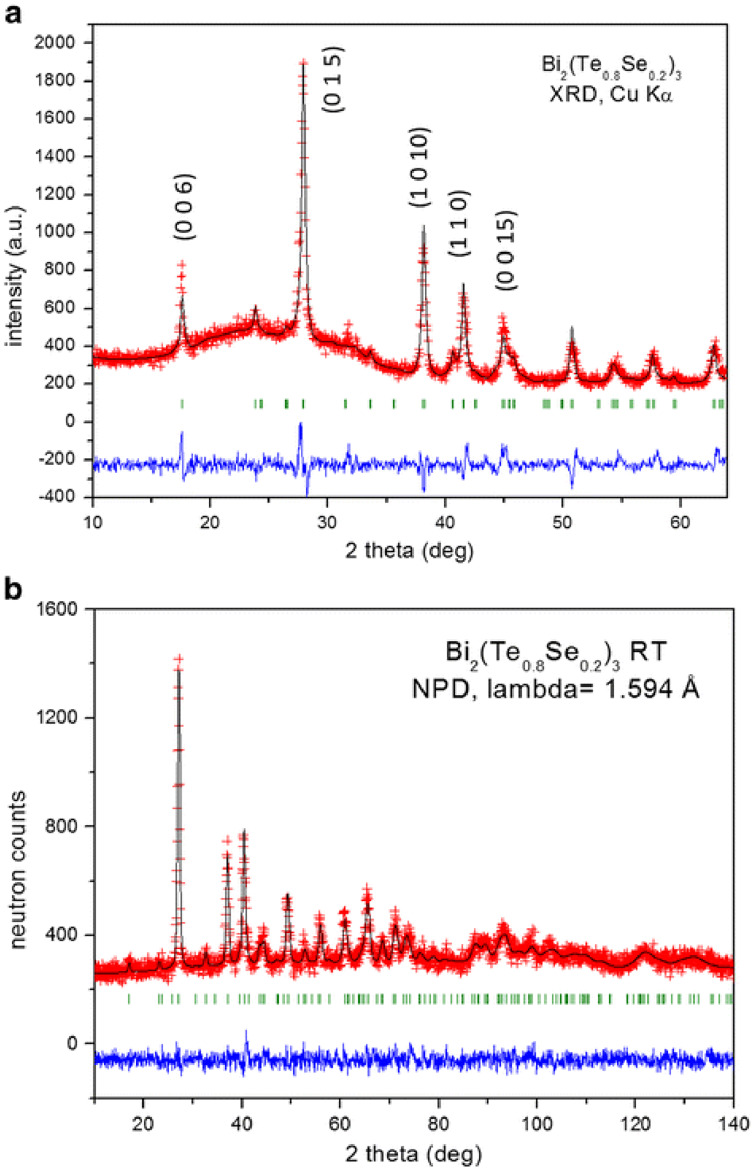
Neutrons interact with the nuclei

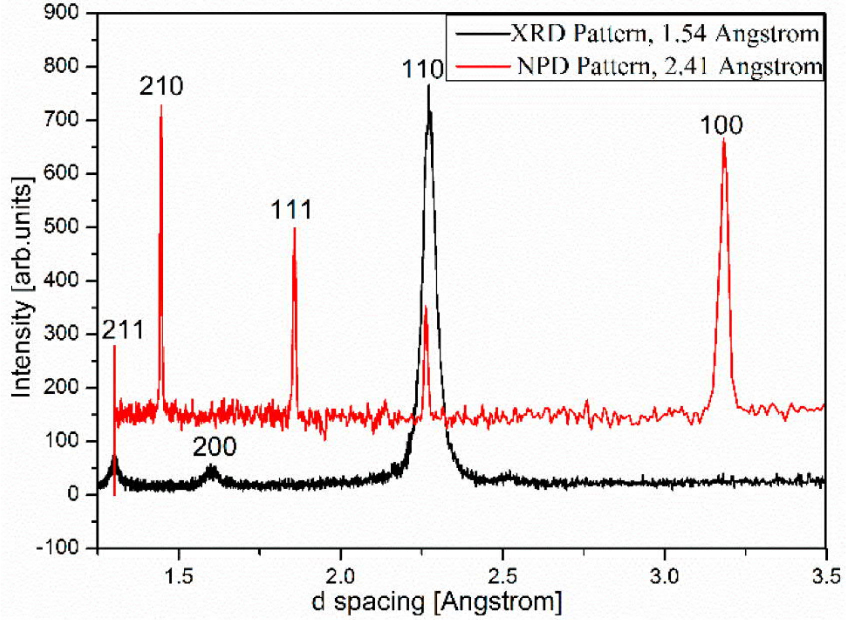
SAMPLES

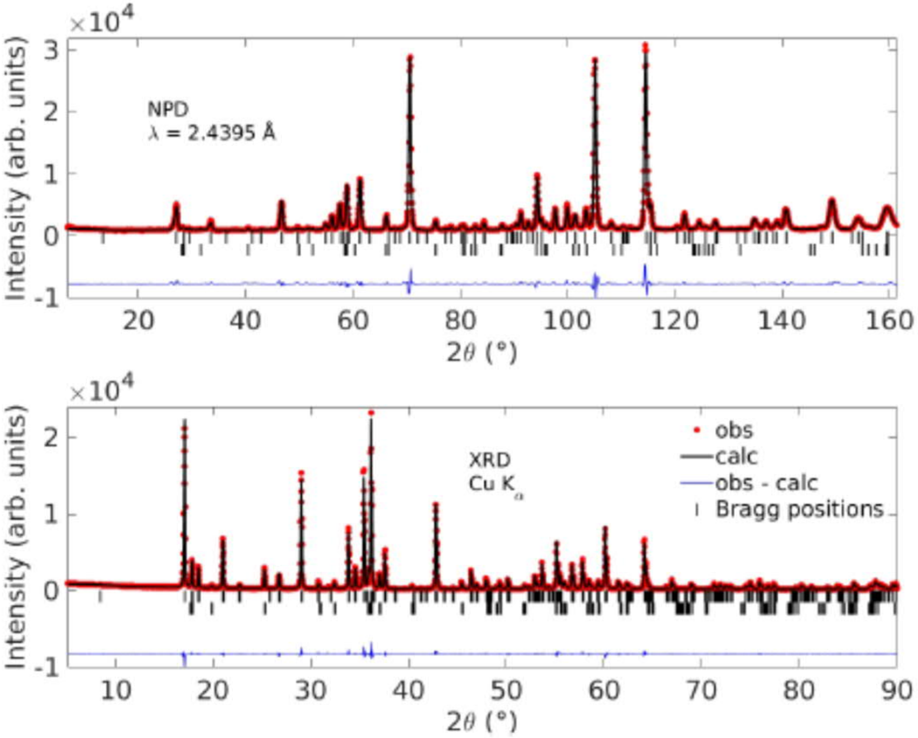
- single crystal (optimally roundish: XRD 0.1 ~ 0.3 mm, ND ~1 cm)
- **powder: XRD >10 mg , ND preferably >1 g**
- thin film: XRD, ED
- amorphous material: XRD, ND
- liquid: XRD (θ-θ geometria)
- gas (ED); electron diffraction is a very local method

Vanadinium
SAMPLE HOLDERS
for ND

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





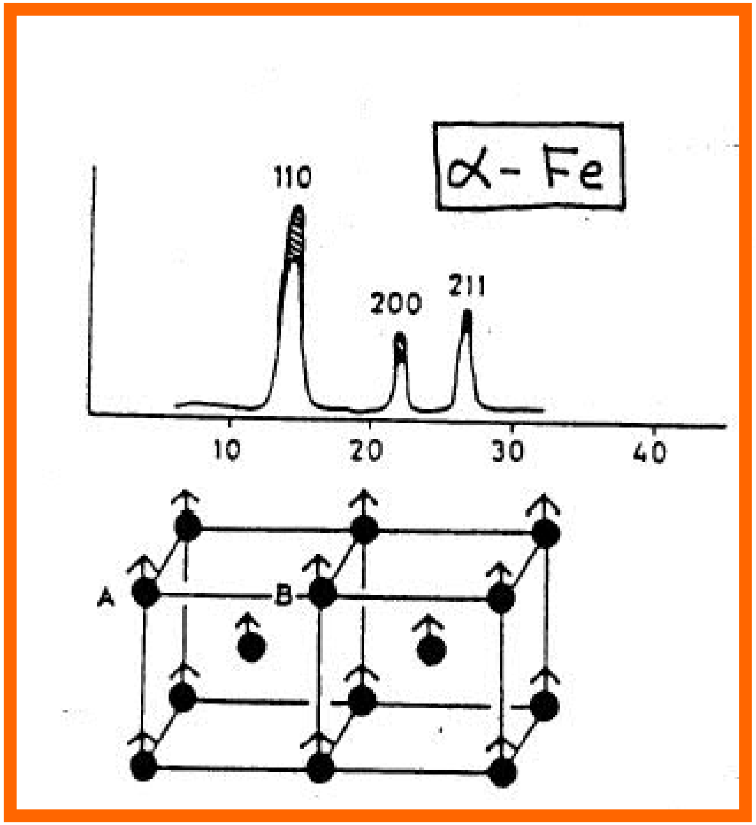


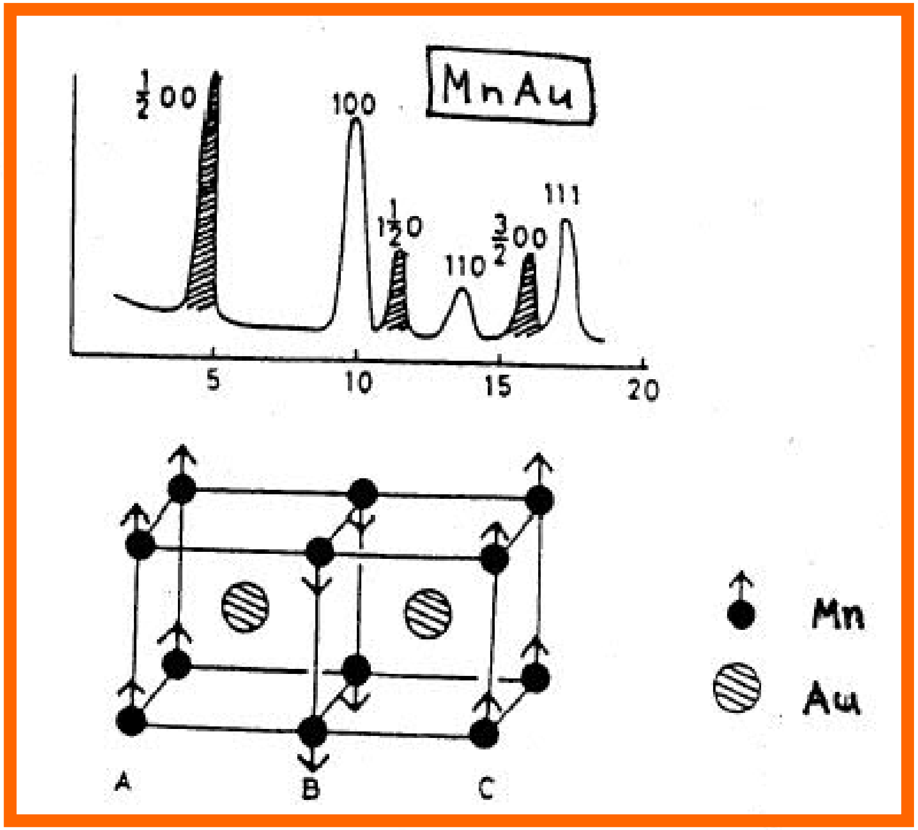
Why ND and XRD patterns for the same sample look different ?

- Different λ → To make them similar, plot in terms of d
- Wavelength range narrower for XRD (sharper peaks)
- 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

Neutrons possess magnetic moment

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





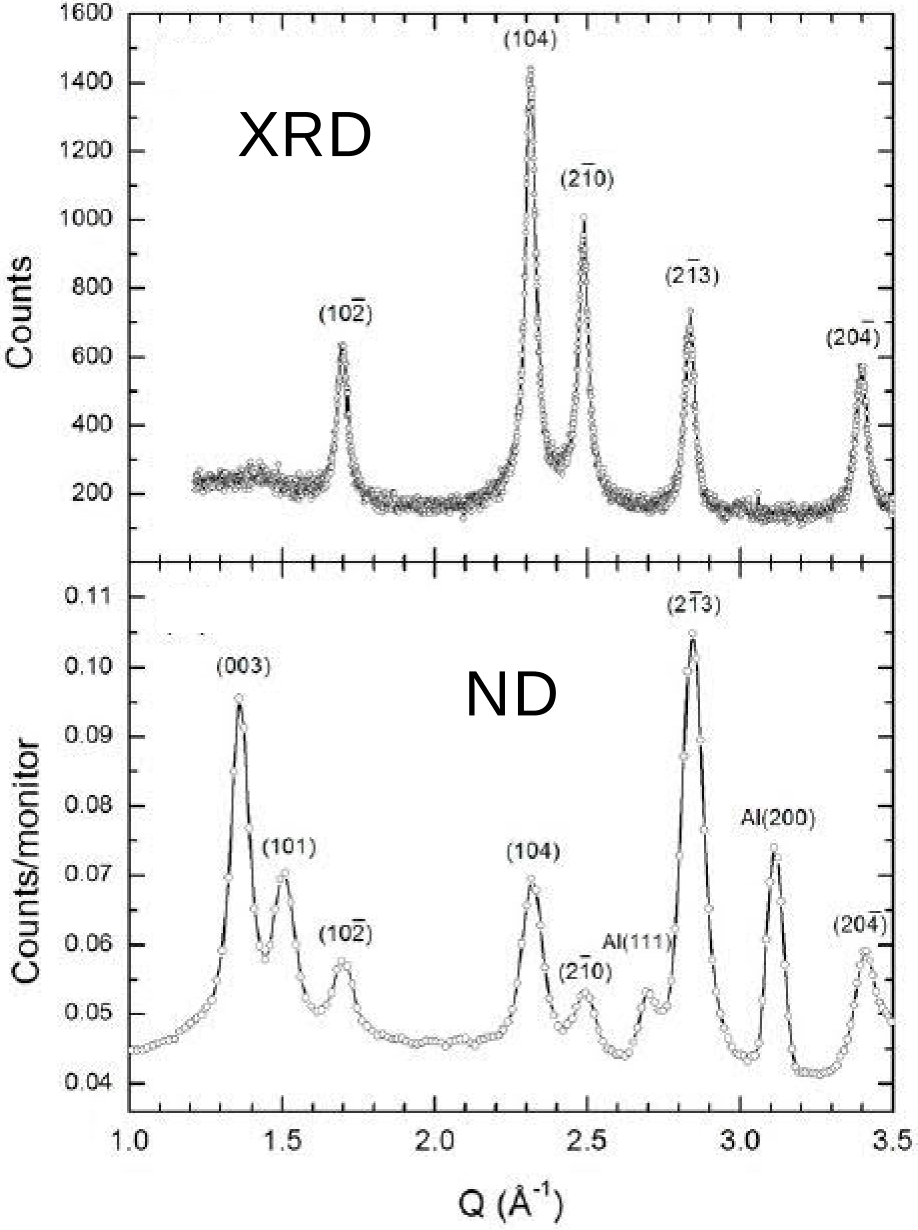
Ferromagnetic:

- changes in peak intensities

Antiferromagnetic:

- additional peaks

Antiferromagnetic hematite Fe_2O_3



Antiferromagnetic MnO ($T_N \approx 120$ K)

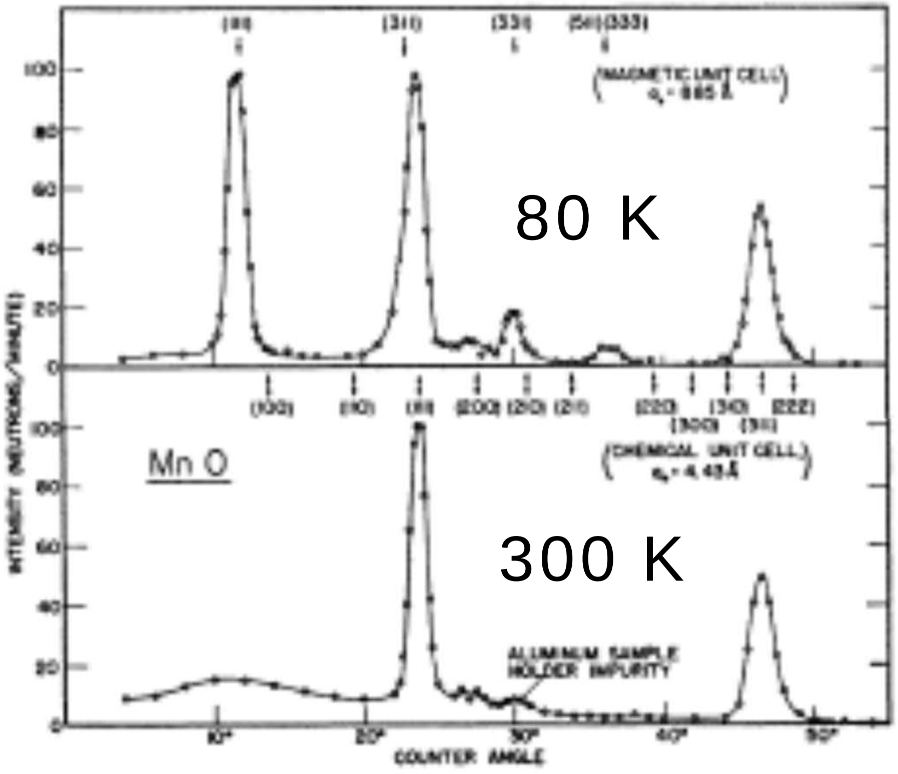
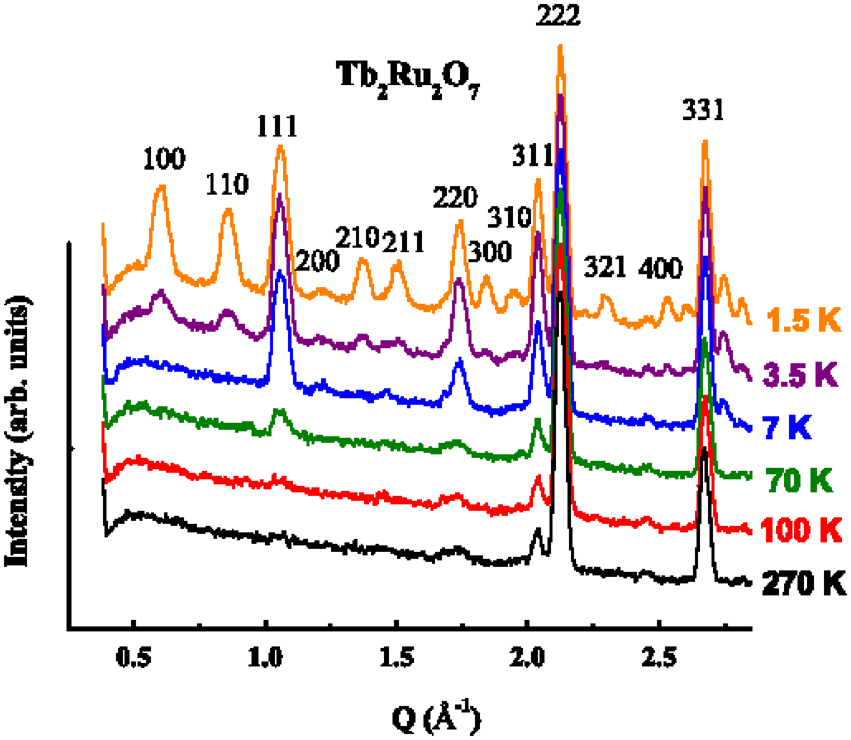
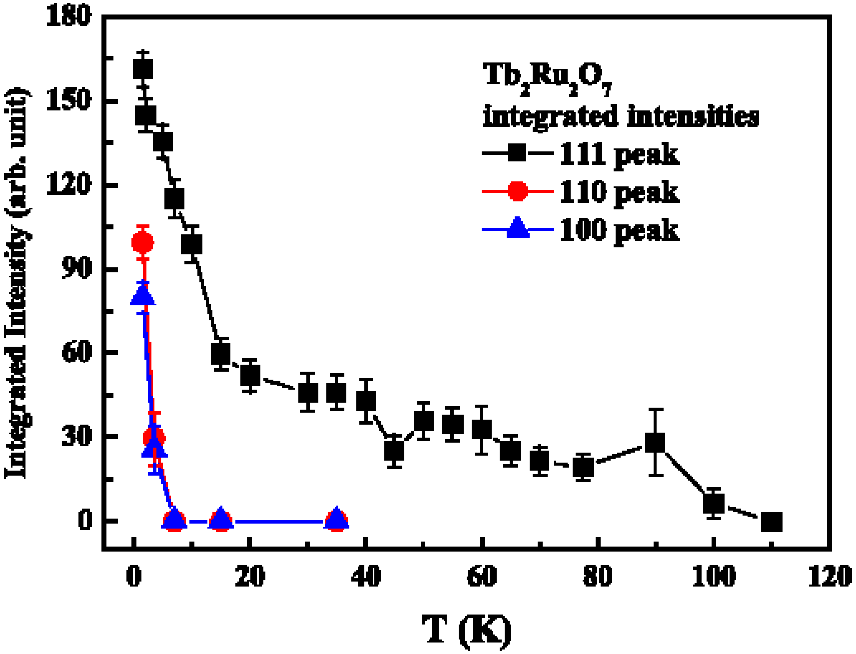
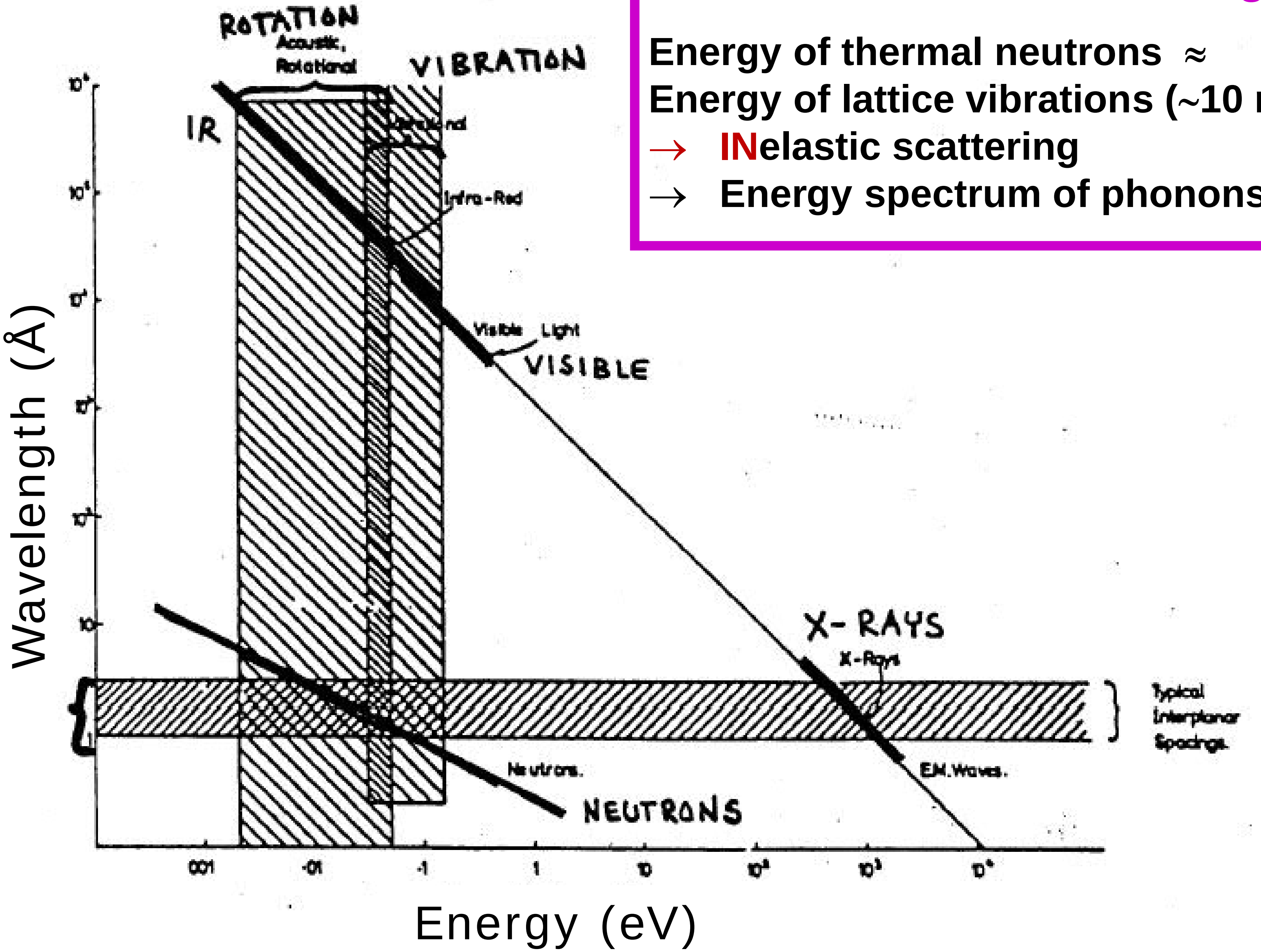


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.


Tb$_2$Ru$_2$O$_7$
222
331
111
100
110
311
220
310
300
200
210
211
321
400
1.5 K
3.5 K
7 K
70 K
100 K
270 K
Intensity (arb. units)
Q (Å^{-1})
0.5
1.0
1.5
2.0
2.5


Tb$_2$Ru$_2$O$_7$
integrated intensities
111 peak
110 peak
100 peak
Integrated Intensity (arb. unit)
T (K)
0
30
60
90
120
150
180
0
20
40
60
80
100
120



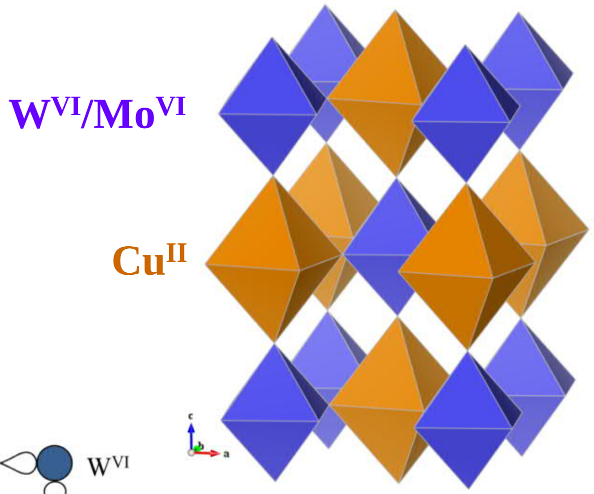
Inelastic neutron scattering

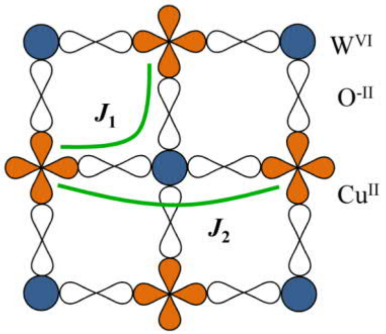
Energy of thermal neutrons ≈
Energy of lattice vibrations (~10 meV)
→ INelastic scattering
→ Energy spectrum of phonons

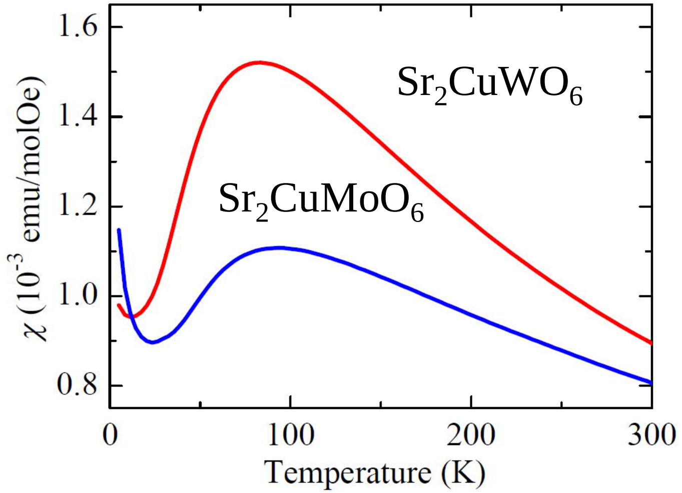
RESEARCH EXAMPLE from our lab

Double Perovskites $Sr_2Cu(W,Mo)O_6$

- ***B*-site ordered DP**
- **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 EXPECTED:**
  - 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 ?)**







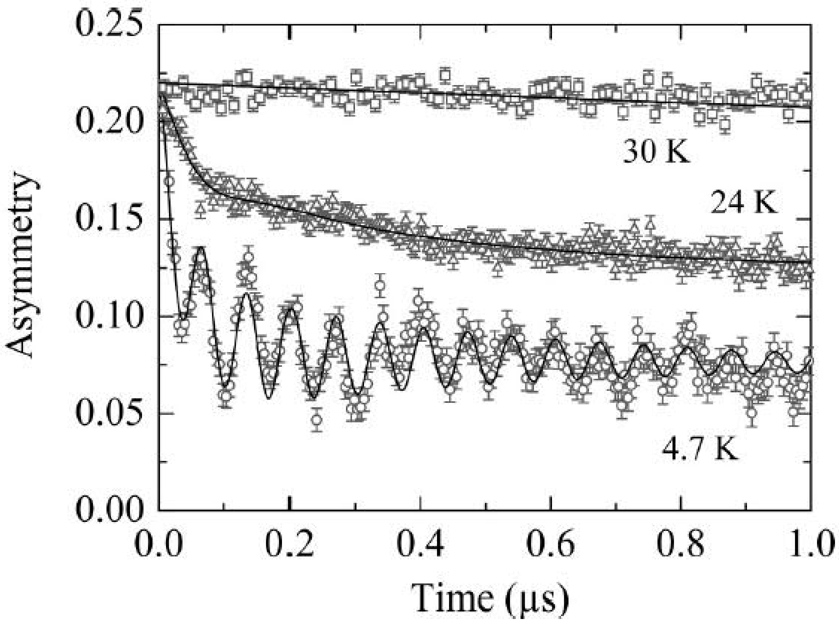
S. Vasala, J.-G. Cheng, H. Yamauchi, **J.B. Goodenough** & M. Karppinen, $Sr_2Cu(W_{1-x}Mo_x)O_6$: a quasi-two-dimensional magnetic system, *Chemistry of Materials* **24**, 2764 (2012).

We started with: Sr_2CuWO_6

(normal-pressure synthesized)

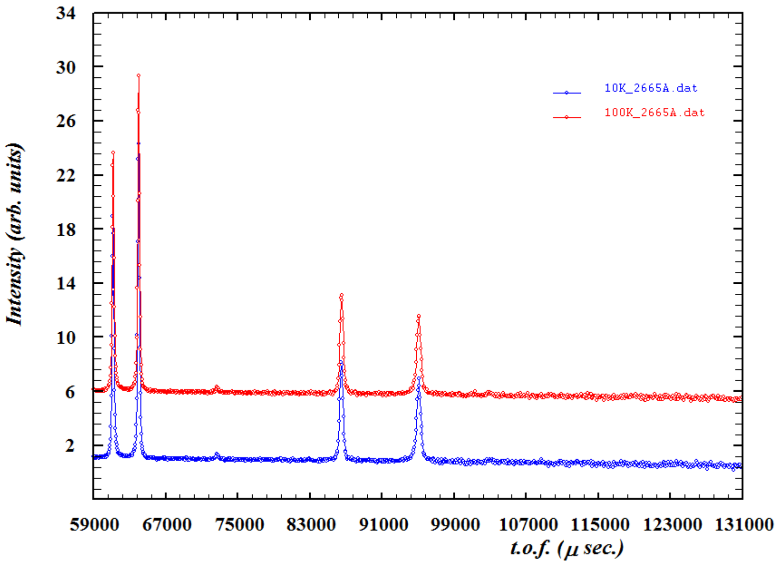
MUON SPIN EXPERIMENTS

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



NEUTRON DIFFRACTION

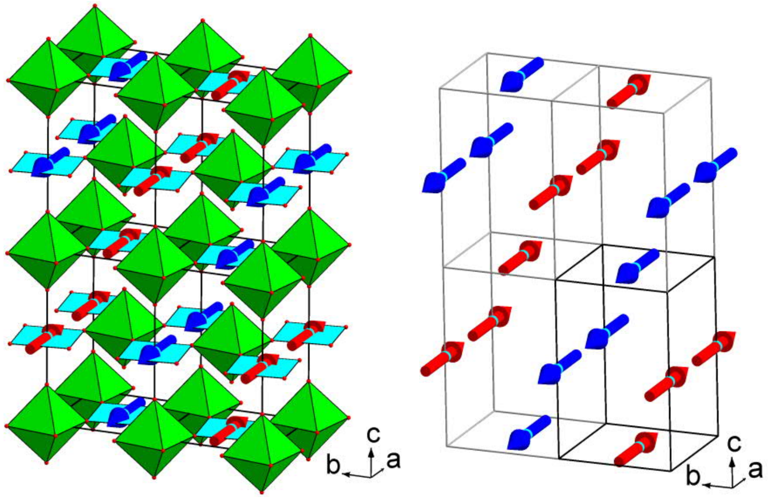
- POWGEN beamline, SPS, Oak Ridge National Laboratory, USA
- No additional magnetic reflections (10 K versus 100 K) seen, WHY ?
- Sample amount large (~5 g) but the expected magnetic moment small ($< 0.5\ \mu_B$)



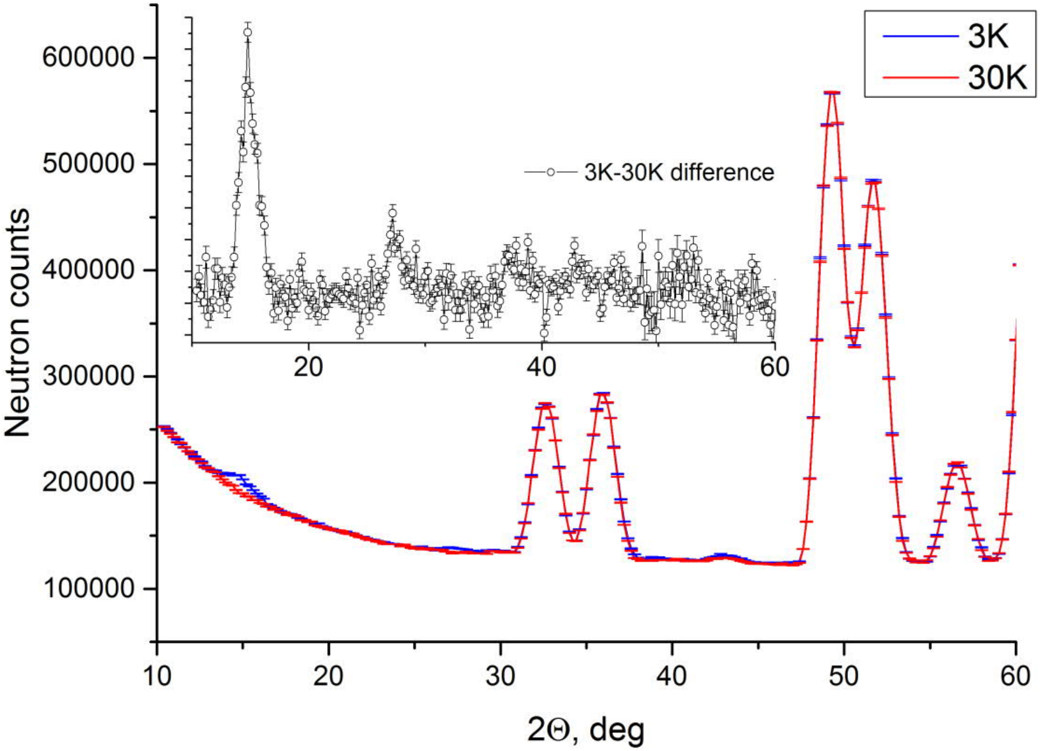
Vasala, Saadaoui, Morenzoni, Chmaissem, Chan, Chen, Hsu, Yamauchi & MKarppinen, Characterization of magnetic properties of Sr_2CuWO_6 and Sr_2CuMoO_6, *Physical Review B* **89**, 134419 (2014).

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)



Sr_2CuWO_6



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

RESEARCH CONTINUES …

- Magnetic structures of **high-pressure synt.** Sr_2CuBO_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)
- Later: **discovery of rare spin-liquid-like state** in $Sr_2Cu(Te_{0.5}W_{0.5})O_6$

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