Single crystals diffraction using Laue neutron techniques

1. Neutrons vs X-rays
2. ILL the European neutron source
3. Crystal testing using neutrons
4. Small Crystal Crystallography using neutrons
5. Concluding remarks
1. Neutrons vs X-rays

→ Scattering by nuclei (not proportional to \( Z \)), isotope dependent
- spin \( \frac{1}{2} \) → Magnetism
- energy few meV → Non-destructive interaction + inelastic

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>Ti</th>
<th>D</th>
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<td>6</td>
<td>7</td>
<td>8</td>
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<td>14</td>
<td>15</td>
<td>22</td>
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</table>

X-rays → Scattered from electrons (proportional to \( Z \))
1. Neutrons vs X-rays

### Neutron-matter interaction: nuclear interaction (+magnetic)

→ absorption: depend on nucleus structure

<table>
<thead>
<tr>
<th>Z</th>
<th>H</th>
<th>Li</th>
<th>B</th>
<th>C</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>La</th>
<th>Gd</th>
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<tr>
<td></td>
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<td>3</td>
<td>5</td>
<td>6</td>
<td>13</td>
<td>22</td>
<td>26</td>
<td>57</td>
<td>64</td>
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<table>
<thead>
<tr>
<th>$\sigma_{\text{abs}}$</th>
<th>H</th>
<th>Li</th>
<th>B</th>
<th>C</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>La</th>
<th>Gd</th>
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<tbody>
<tr>
<td>Nat</td>
<td>0.33</td>
<td>70.5</td>
<td>767</td>
<td>0.004</td>
<td>0.23</td>
<td>6.09</td>
<td>2.56</td>
<td>8.97</td>
<td>497000</td>
</tr>
<tr>
<td>isot. (barns)</td>
<td>1/0.33</td>
<td>6/940</td>
<td>10/3835</td>
<td>46/</td>
<td>54/</td>
<td>138/57</td>
<td>152/735</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/0.00</td>
<td>7/0.05</td>
<td>11/0.005</td>
<td>47/</td>
<td>56/</td>
<td>139/8.9</td>
<td>154/85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48/</td>
<td>57/</td>
<td>155/61100</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>49/</td>
<td>58/</td>
<td>156/1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50/</td>
<td></td>
<td>157/259000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For X-rays absorption $\sim 10^6$ – $10^7$ barns

1 barn = $10^{24}$ cm$^2$
1. Neutrons vs X-rays

**X-rays**

- \( \frac{d\sigma}{d\Omega} = |b|^2 = \text{const.} \)

**Neutron high pressure cells (courtesy of L. Melesi)**

**weak interaction**

- Very complex sample environments
- Large samples (few cm\(^3\) down to 0.1mm\(^3\))

+ Incoherent scattering (isotopic and spin)
2. Institut Max von Laue – Paul Langevin

Grenoble, France
2. Institut Max von Laue – Paul Langevin

ILL High Flux Reactor:

- Thermal neutrons (D$_2$O at 300K) 1.2Å
- Hot neutrons (Graphite 2400K) 0.8Å
- Cold neutrons (Liq D$_2$ at 25K) 3Å
High Flux Reactor

54MW thermal $\leftrightarrow 10^{15} \text{n}_{300K}/\text{cm}^2/\text{s}$

Beamtime 200 days/year

- Condensed matter physics
- Chemistry
- Biology
- Nuclear physics
- Materials science

40 instruments

- Diffraction
- Large Scale structures
- Time of Flight
- Triple Axis
- Nuclear and Particle Physics
Neutron diffraction under combined extreme conditions

- Low temperature: down to 65mK
- High temperature: up to 1300K

More details available on http://oslo.ill.fr/YellowBookCDrom/index.htm
Neutron diffraction under combined extreme conditions

- High pressure: up to 100kbar
- High magnetic field: up to 10T

More details available on http://oslo.ill.fr/YellowBookCDrom/index.htm
Actual trends in condensed matter research:

- New materials with more and more highly sophisticated composition
  → chemical contrast (H, light elts…)
  → delicate synthesis

- Magnetism

- Complex external conditions (high pressures, very low temperatures …)

- Out of equilibrium phenomena: time-resolved in-situ investigations
Crystallography using neutrons

Few neutrons ...

Monochromatic techniques
1000Å ↔ 1mm³

→ neutron optics
→ 2-D detectors
→ Laue diffraction
3. Crystal testing using neutrons

Magnetic neutron laue diffraction study of the domain distribution in $\alpha$-Fe$_2$O$_3$ at room temperature

J. C. Marmeggi $^1$, D. Hohlwein $^2$, E. F. Bertaut
Physica Status Solidi A 39, 57-64 (1977)

• Observation of magnetic domains.
• Intensity changes of antiferromagnetic reflections caused by an external magnetic flux density of 0.6 T but no mono-domain.
• Intensity changes versus the rotation of the applied field around the threefold axis
### S42 INSTRUMENT DETAILS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam tube</td>
<td>end of H24 (thermal neutron guide)</td>
</tr>
<tr>
<td>Maximum flux at specimen</td>
<td>$10^{8}$ cm$^{-2}$s$^{-1}$</td>
</tr>
<tr>
<td>Incident wavelengths</td>
<td>$0.8 , \text{Å} \leq \lambda \leq 3.5 , \text{Å}$ (max. around 1.5 Å)</td>
</tr>
<tr>
<td>Size of specimen</td>
<td>$\equiv 1 , \text{mm}^3$</td>
</tr>
<tr>
<td>Diameter of the beam</td>
<td>usually 3 mm</td>
</tr>
<tr>
<td>Angular range</td>
<td>$2^\circ \leq 2\theta \leq 68^\circ$ or $112^\circ \leq 2\theta \leq 178^\circ$</td>
</tr>
<tr>
<td>Distance crystal-film range</td>
<td>8 to 300 mm</td>
</tr>
<tr>
<td>Beam divergence</td>
<td>$\equiv 8^\circ$</td>
</tr>
<tr>
<td>Min. angular distance to separate 2 spots</td>
<td>$\equiv 15^\circ$</td>
</tr>
<tr>
<td>Accuracy of intensities</td>
<td>$\equiv 8%$</td>
</tr>
<tr>
<td>Minor intensity detection</td>
<td>$\equiv 6 \times 10^{-4}$ of the strongest reflections (taking into account the noise of the cryostat)</td>
</tr>
<tr>
<td>Detector</td>
<td>flat photographic cameras $130 \times 180; 18 \times 24$ mm$^2$ or BF$_3$ counter, $\Omega = 2 , \text{cm}$</td>
</tr>
<tr>
<td>Converter screens</td>
<td>1) $\beta$-$\text{LiF-ZnS}$ charged Ag ($\alpha \rightarrow \theta$) resolution $\equiv 0.3 , \text{mm}$ on Kodak &quot;Regulix&quot; films</td>
</tr>
<tr>
<td></td>
<td>2) Gd ($\text{n}$-$\beta$) $\rightarrow \theta$ internal conversion, energy $\equiv \text{keV}$ Resolution $\equiv 0.05 , \text{mm}$ on Kodak &quot;Periapical Ultra-Rapid&quot; films</td>
</tr>
<tr>
<td>Sample environment on loan</td>
<td>magnetic field up to 18 kOe from D2 variable temp. cryostat ($0.2 - 300 , \text{K}$)</td>
</tr>
<tr>
<td></td>
<td>gas blower furnace ($300 - 950 , \text{K}$) from CNRS</td>
</tr>
<tr>
<td></td>
<td>thick graphite filter from CNRS</td>
</tr>
<tr>
<td></td>
<td>cooperation can be arranged, contact the responsible</td>
</tr>
</tbody>
</table>
3. Crystal testing using neutrons

What we need:

- With high spatial resolution
- Large area detector
- High counting rate and Rapid readout system

Possible detector devices

- **Photographic film**
  - With a Gd foil
  - High spatial resolution (less than 1mm) but low efficiency
  - Standard Polaroid camera ZnS(Ag)-$^6$LiF

- **Gas proportional counters**
  - Low spatial resolution but high efficiency

- **Anger camera: Neutron scintillator plates and photomultiplier tubes based detectors**
  - Medium resolution

- **Image plate detectors**
  - Good spatial resolution but medium efficiency

- **Scintillator-CCD detectors**
  - Good spatial resolution and high efficiency
OrientExpress
Experimental setup

On H24 thermal neutron guide

- Evacuated tube
- Crystal on goniometer
- Neutron beam
- CCD detectors in backscattering
Two-tilt stages goniometer

TV camera for crystal alignment
On H24 thermal neutron guide
\[ \lambda_{\text{min}} = 0.7 \text{ Å} \quad \lambda_{\text{max}} = 5 \text{ Å} \]
divergence 3.5 \( \lambda \) mrad Å

CCD detectors in backscattering

Neutron beam

TV camera for crystal alignment

Crystal on goniometer
Double-stage detection

- **Neutron scintillator**

  \[ ^6\text{Li} + n^0 \rightarrow ^3\text{He} + ^3\text{H} + 4.8\text{MeV} \]
  - High absorption for thermal neutrons
  - Emission color: blue 450nm
  - Low gamma sensitivity

- **Two intensified cameras**
  (light transparent substrate)

  - Intensifier photocathode coupled to CCD
    (coherent tapered fibre-optic) → Maximum transmission and high sensitivity
  - Input active area: 252 x 198 mm\(^2\)
  - Pixel Resolution: 1680 x 1320
  - Input Pixel Size: 150 microns square
**Image Pro interface on PC**

- Interfacing with the PC: IEEE1394
- Stiched Images
- Map file for distortion correction
- Binning (higher sensitivity at lower resolution)
- Automatic flat field correction is included in the driver
Ruby test crystal

• 10 minutes with photographic film
• 10 seconds with neutron CCD camera
3. Crystal testing using neutrons
3. Crystal testing using neutrons

**Interface of nickel-base welded superalloys**

OrientExpress

→ Beam size of 1mm and a step of 2 mm

Setting used on **SALSA**

- Single crystal
- Polycrystal

G. Bruno et al.
3. Crystal testing using neutrons

NbFe2 crystal:
Quality check and orientation

(B. Fak et al)
How to access to OrientExpress?

ILL Visitor's club access
EASY access

Friday
3/10/2008

Grenoble Area
Weather Forecast

Welcome,
Max

Access granted to all

- Experimental reports:
  - Find an experimental report

To complete an Experimental Report, connect to The Visitors Club: you will have access to the list of all your proposals (as proposer or co-proposer) for which experimental reports are still missing.

Your privileged access

- Scientific visitor
  - Electronic EASY Submission
  - Modify your personal data
  - Health Physics Training
EASY Proposal

Should be submitted for the cycle starting from 30/10/2008 to 19/12/2008

Characteristics of proposal

The Easy Access System (EASY) allows a rapid structural characterisation of samples and data analysis, *all year long*. The system offers one neutron day per cycle, on four instruments (D1A, D2B, VIVALDI and ORIENTEXPRESS) to perform very short experiments at room temperature. We recommend that you read the [detailed guidelines](#) before submitting a proposal.

**Title:**
(140 chars max)

**Suggest a keyword:** EASY: easy proposals

**Main research area:** Please Select

**Abstract**

**Abstract** (1200 chars max, 11 lines) Length of abstract at the moment:

[Instruments’ list]
# EASY access

## The Visitors Club

### EASY Proposal

Should be submitted for the cycle starting from 30/10/2008 to 19/12/2008

### Instruments and measuring time

**Select an instrument**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description</th>
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<tbody>
<tr>
<td>Please Select</td>
<td>high-resolution 2-axis diffractometer</td>
</tr>
<tr>
<td>Please Select</td>
<td>high-resolution 2-axis diffractometer</td>
</tr>
<tr>
<td>D1A</td>
<td>laue diffractometer</td>
</tr>
<tr>
<td>D2B</td>
<td>thermal neutron laue diffractometer</td>
</tr>
</tbody>
</table>

**Wavelength range:**

**Resolution in Wavelength:**
Sample description

Required information are indicated by bold text, others are useful for scientific evaluation.

**Substance/Formula**, give isotopic composition if not natural. (250 chars max)

Mass (mg):   Size (mm3):   Surface area (mm2): 

State: Please Select

Space group: 

Unit cell dimension at T (k) a(Å): b(Å): c(Å):

α: β: γ:

Sample container: Please Select

When will it be available (150 chars max):

**Sample environment**: ambient

Safety aspects: check the risk(s) associated with your sample
You are responsible for any accident that your sample could produce at ILL during the experiment

☐ No risk

☐ alpha-emitter ☐ biological ☐ carcinogenic ☐ combustion promoting

☐ corrosive ☐ explosive ☐ inflammable ☐ pyrophoric

☐ radioactive ☐ toxic

< Instruments' list  EASY proposal creation
1972  D6-hedgehog at ILL

100 single detectors that could be positioned individually within a small solid angle

discontinued in 1975 because of mechanical inaccuracies and limited computing power

ILL took risks - technology was not ready
4. Single crystal diffraction at the ILL

D9: Hot neutron 4-circle diffractometer

- Wavelength 0.35 – 0.85Å
- Cu(220) monochromator
- Beam size 6 x 6 mm²
- 32x32 PSD

\[ \text{px: } 2\times2\text{mm}^2 = 0.25^\circ \times 0.25^\circ \]

- 4-circle ranges
  - -20<2θ<120°
  - -34<ω<48°
  - 80<χ<200°
  - -179<ϕ<179°

Lifting counter range

- 12.5<ν<25°
- > 10^7 n cm⁻² s⁻¹
4. Single crystal diffraction at the ILL

D19: Thermal neutron 4-circle diffractometer with large 2D detector

→ Crystallography of large uit-cells
1000 - 500,000 Å³


D19: Thermal neutron 4-circle diffractometer with large 2D detector

Goal: to multiply the angular coverage of the previous banana by a factor 15

- $120^\circ \times 29^\circ$ (r ~ 76 cm)
- Detection efficiency: ~ 60% at 1Å
- Spatial resolution: ~ 3mm FWHM
4. Single crystal diffraction at the ILL

Fundamentals of Laue diffraction:

- white beam diffraction technique
- fixed detector
- single crystal

Problem of multiple scattering

but not for ~ 83% of spots
(with $\lambda_{\text{min}} < \lambda < 2\lambda_{\text{min}}$

Laue suite [http://www.ccp4.ac.uk/main.html](http://www.ccp4.ac.uk/main.html)
Laue diffraction at the ILL:

white beam → end position on neutron guide

LADI: for large unit-cells
(proteins, complex molecules)
(cold neutrons)

VIVALDI:
Very
Intense
Vertical
Axis
Laue
Diffractometer
(thermal neutrons 0.8 – 5.2 Å)

OrientExpress: crystal testing instrument
(historical neutron Laue diffractometer J.C. Marmeggi)
4. Single crystal diffraction at the ILL

VIVALDI: Very Intense Vertical Axis Laue DIffractometer

- white beam for maximum flux
- thermal neutron for maximum reflectivity ($0.8 < \lambda < 5.2\text{Å}$)
- large image plates ($\text{Gd}_2\text{O}_3$ in $\text{BaFBr}:\text{Eu}^{2+}$) for 8 sterad
- high resolution ($200\times200\mu\text{m}^2$) and large dynamics range ($10^8$)
- vertical geometry to allow complex sample environments

→ factor 10 to 100 gain over monochromatic data collection as fast as powder diffraction!

Laue diffraction pattern of incommensurate $\text{La}_2\text{Co}_{1.7}$ within a day of the first neutrons (G. McIntyre et al)
Data reduction of conventional structures (mostly) by programs of the CCP4 X-ray Laue suite

www.dl.ac.uk/SRS/PX/jwc_laue/laue_top.html

Quick inspection of integration ellipsoid boundaries

Vitamin B12
~10 000 reflections in each 8-hour exposure, mean I/σ(I)= 10, 6 mm³ crystal
G. McIntyre, S. Mason, Wagner, Luger
First experiments on VIVALDI

Very fast data collection over all of reciprocal space
for very small samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Volume (mm³)</th>
<th>Unitcell (Å³)</th>
<th>Expose (hr)</th>
<th>No. Peaks</th>
<th>I/σ(I)</th>
<th>Total (hr)</th>
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<tbody>
<tr>
<td>Vitamin B12</td>
<td>6</td>
<td>8853</td>
<td>2</td>
<td>7596</td>
<td>10.1</td>
<td>60</td>
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<tr>
<td>Cs₃VCl₆.4H₂O</td>
<td>2</td>
<td>446</td>
<td>0.7</td>
<td>647</td>
<td>6.6</td>
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<td>Na₂Pb(OH)₂</td>
<td>2</td>
<td>147</td>
<td>0.8</td>
<td>263</td>
<td>7.9</td>
<td>5</td>
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<tr>
<td>LiAlSi₂O₆</td>
<td>1.4</td>
<td>389</td>
<td>0.33</td>
<td>442</td>
<td>11.9</td>
<td>2</td>
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<tr>
<td>Co(NH₃)₆.CuCl₅</td>
<td>1</td>
<td>2691</td>
<td>0.7</td>
<td>1865</td>
<td>6.0</td>
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<tr>
<td>Co₄C₂₂H₃₆</td>
<td>0.6</td>
<td>8254</td>
<td>2.5</td>
<td>4340</td>
<td>4.8</td>
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<tr>
<td>dabcoHBF₄</td>
<td>0.21</td>
<td>473</td>
<td>1</td>
<td>384</td>
<td>5.0</td>
<td>10</td>
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<tr>
<td>C₂₆H₃₂FeN₉O₂S₄</td>
<td>0.2</td>
<td>3293</td>
<td>2</td>
<td>2786</td>
<td>5.0</td>
<td>16</td>
</tr>
<tr>
<td>C₄H₄N₂O₂</td>
<td>0.00075*</td>
<td>451</td>
<td>4</td>
<td>272</td>
<td>1.1</td>
<td>48</td>
</tr>
</tbody>
</table>

*10 kbar TiZr pressure cell !!

Data analysis based on the CCP4 suite, but adapted to take into account very anisotropic crystal shape, twinning, phase coexistence...
Structure of high-spin $d^4$ complexes
$(M^1)_2Cr(H_2O)_6(SO_4)_2$

Electronic transition
$S=0, 1, 2$

Cr$^{2+} d^4$
$S=2$

*Dobe et al, JACS 2004, 126, 16639-16652*
Structures versus temperature for modeling the electronic properties

\[(M^{I})_{2}Cr(H_{2}O)_{6}(SO_{4})_{2}\]
P2\(_{1}/a, \ Z=2\)
a=9.5 Å, b=13 Å, c=6 Å
\(\beta = 107^\circ\)
Hydrogen bonding: 3,4, 5 or 6?
R. Bau et al

$H_1 - Y = 2.16(1) \text{ Å}$
$2.20(1) \text{ Å}$
$2.24(1) \text{ Å}$
$2.17(1) \text{ Å}$


Spin transition in transition-Metal complexes: d-electrons

Fe$^{II}$ d$^6$

$\Delta_{\text{oct}}$ strong

$\text{eg}$

$t_{2g}$

$\Delta_{\text{oct}}$ weak

$\text{eg}$

$t_{2g}$

Strong ligand field
$L=\text{CN}^-$

Low Spin

Weak ligand field
$L=\text{H}_2\text{O}$

High Spin

$L = \text{complex organic ligand}$

$\rightarrow$ Intermediate ligand field

$\Delta_{\text{oct}} \sim k_B T$

Low Spin $\Leftrightarrow$ High Spin

Spin transition triggered by temperature, pressure, light...
Photo-induced spin crossover of \([\text{Fe(ptz)}_6](\text{BF}_4)_2\)

- At equilibrium transition \((T, P)\)

- Out of equilibrium transition
  - photo-induced by long light pulses
    - (LIESST and reverse-LIESST)

Neutron Laue diffraction
→ continuous photoinduced transformation

Marie-Hélène Lemée-Cailleau
Institut Max von Laue – Paul Langevin
CRISTECH Oléron, October 2008

A. Goujon et al, PRB 2006
[Fe(L)(CN)₂]

(Ph. Guionneau et al)

RX: Spin crossover + Fe coordination change
+ disordered water molecule (H calculated)

Neutrons:
complete information about all the H atoms
Smaller, Faster ...

**CYCLOPS**  (Cylindrical Ccd Laue Octogonal Scintillator)

- $h=400\text{mm}$  \( \varnothing 400\text{mm} \)

- 16 CCD cameras (16 bits)
- Scintillator $^6\text{LiF}:\text{ZnS}:\text{Ag}$ (0.4mm thick.) thermal neutron efficiency~25%
- Very low $\gamma$ sensitivity
- Exposure 1ms to few hours

- Multistage Image intensifier
- \(~2.7\text{s readout}\)
- Pixel 500$\mu$m
- Final image= 7500x2260pixels
Single crystals diffraction using Laue neutron techniques

Concluding remarks

- **Neutrons vs X-rays** → contrast (light elts), magnetism combined external conditions (T,P,B,\(h\nu\)...)

- Crystal testing using neutrons → OrientExpress and EASY

- Neutron diffraction for very Small Crystals → down to 0.1mm\(^3\) using VIVALDI

- Future: CYCLOPS...
Acknowledgments

**ILL** collaboration with

Bachir Ouladdiaf  
Garry J. McIntyre  
John Archer  
Sax Mason  

(\text{http://www.photonic-science.co.uk/})

Chemistry Dept, Durham University UK  
Clive Wilkinson
neutrons compare to X-rays

Neutron:
- nuclear interaction
- spin $\frac{1}{2}$

→ Incoherent scattering
- isotopic
- spin

\[
\sigma_{coh} = 1.5 \text{ barns} \\
\sigma_{incoh} = 80.0 \text{ barns} \\
\sigma_{coh} = 5.6 \text{ barns} \\
\sigma_{incoh} = 2.1 \text{ barns}
\]