Neutron diffraction instrumentation

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Rough division

Neutron diffraction instruments

Single crystal diffractometers
  - Constant wavelength
  - Time-of-flight (TOF)

Powder diffractometers
  - Constant wavelength
  - Time-of-flight (TOF)
Single crystal diffraction

Four-circle diffractometer

- 3-D rotation of single crystal
- Access to all reflections
- Traditionally single detector
- Now: also 1D and 2D detectors
Neutrons from nuclear reactors – constant wavelength experiments

JEEP II reactor, IFE spectrum

Monochromic neutron beam

\[ 2 \cdot d_{hkl} \cdot \sin \theta_{\text{monochr}} = \lambda \]
PUS – a high resolution diffractometer

- In operation since 1997.

Soller collimator (from Risø). 15’, 30’ and “open” (60’).
PUS – a high resolution diffractometer

- In operation since 1997.

Vertically focusing Ge monochromator (from Risø).
311, 511 or 711 reflection plane can be used $\rightarrow \lambda = 0.75-2.60 \text{ Å}$
Mosaic crystal – ideally imperfect crystal

Model of real crystal:
- Mosaic of crystalline blocks
- Each dimensions $\mu$m tilted very slightly to each other
- Interference of waves within every block satisfies **kinematic diffraction theory**
- Diffraction from whole crystal = $\Sigma$ intensities each block
- **Secondary extinction**: Parallel blocks

![Mosaic model of crystal]
PUS – a high resolution diffractometer

- In operation since 1997.

Sample temperature: 8 – 1200K
Gas pressures up to 8 bar (soon 100 bar)
PUS – a high resolution diffractometer

- In operation since 1997.

Oscillating radial collimators (MURR).
PUS – a high resolution diffractometer

- In operation since 1997.
PUS – a high resolution diffractometer

- In operation since 1997.

2 detector banks with 7 vertically stacked position sensitive detectors in each. Each bank cover 20° scattering angle.
Time-of-flight diffraction (spallation)
Time-of-flight diffraction (spallation)

Sample irradiated by a pulsed neutron beam with wide range of wavelengths. Because pulsed beam ⇒ different wavelengths can be sorted by their time of arrival at the detector.
Time-of-flight diffraction (spallation)

Target → Sample → Detector

L₁ is the length of the incident flight path from the moderator to the sample

L₂ is the length of the scattered flight path from the sample to the detector

Total flight path length L is L₁ + L₂

de Broglie expression:

\[ \frac{h}{\lambda} = m_n v = m_n \left( \frac{L}{t} \right) \]

\[ t \text{ (µsec)} = 252.78 \ L \text{ (m)} \lambda \text{ (Å)} \]

\[ \lambda = \frac{ht}{m_n L} \quad + \quad \lambda = 2d \sin \theta \quad \Rightarrow \quad d = \frac{h}{2m_n L \sin \theta} t \]

h: Planck’s constant
λ: wavelength
mₙ: mass neutron
ν: velocity
t: time (L path length)
Time-of-flight diffraction (spallation)

- $\lambda = h/nmL$

**Detector**

$L_2$ is the length of the scattered flight path from the sample to the detector.

**Sample**

$L_1$ is the length of the incident flight path from the moderator to the sample.

Total flight path length $L$ is $L_1 + L_2$.

- **GEM at ISIS**
  - 7270 detectors (86 modules)
  - $L_1 = 17$ m

- **POLARIS at ISIS**

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Time-of-flight diffraction (spallation)

**HRPD at ISIS**
- \( L_1 = 96 \text{ m} \)

\[
\frac{\Delta d}{d} = \sqrt{\left(\frac{\Delta \theta}{\tan(\theta)}\right)^2 + \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta L}{L}\right)^2}
\]

\( = 4 \times 10^{-4} \)

Sun et al. (2014)
Time-of-flight diffraction (reactor)

Use of chopper(s)
Total scattering
Outline

• Bragg scattering and “the average picture”
• Total scattering and Reverse Monte Carlo (RMC) modeling
• RMC modeling of interstitial deuterides
Analysis of powder diffraction data

Bragg scattering - a perfectly periodic model
Analysis of powder diffraction data

Materials are not perfectly periodic!

- thermal motion
- defects
- non-stoichiometry
- occupational disorder
Analysis of powder diffraction data

Materials are not perfectly periodic!

- thermal motion
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Bragg scattering

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Is the average picture good enough???

It depends ......

• on the material we are interested in.
• on what we want to know about it.

• A parallell from the macrosocopic world:
  - a study of audiences
A well-ordered audience

Questions we can answer from the average picture:

• What is the typical distance between two persons?
• What do they wear?
A more disordered audience

Questions we cannot answer from the average picture:

• What is the typical distance between two persons?
• What do they wear?
The average picture of a metal hydride

Question we can answer:

• How do the hydrogen atoms relate to the metal atoms?
The average picture of a metal hydride

Question we cannot answer:
• What is the shortest distance between the hydrogen atoms?
The "solution"

Bragg scattering

Total scattering

H-H = ??
Total scattering

\[ S(Q) = \left( \frac{F(Q)}{N} \right)^2 \]

Q = 4π sin(θ)/λ

\[ G(r) = \int_{Q} S(Q) \, e^{-iQ \cdot r} \, dQ \]

\[ = \sum_{j,k=1}^{M} c_j c_k f_j f_k \cdot g_{j-k}(r) \]

Partial PDF

\[ g_{A-B}(r) = \frac{\rho_B(r)}{\rho_{overall}} \]
Total scattering

S(Q) (barn) vs Q (Å⁻¹)

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Reverse Monte Carlo (RMC)

Make a large structure model

Calculate the scattering intensity from the model, $I^{\text{Calc}}(Q)$

Calculate the agreement with the experimental data

$$\chi^2 = \sum_{i=1}^{m} \frac{(I^{\text{Calc}}(Q_i) - I^{\text{Exp}}(Q_i))^2}{\sigma(Q_i)}$$

Move one atom at random
Reverse Monte Carlo (RMC)

1. Make a large structure model
2. Calculate the scattering intensity from the model, $I_{\text{Calc}}(Q)$
3. Calculate the agreement with the experimental data
   \[ \chi^2 = \sum_{i=1}^{m} \frac{(I_{\text{Calc}}(Q_i) - I_{\text{Exp}}(Q_i))^2}{\sigma(Q_i)} \]
4. Move one atom at random
5. Calculate the scattering from the new configuration cell, and the new $\chi^2$

If $\chi^2_{\text{old}} > \chi^2_{\text{new}}$ then the new configuration cell is accepted.

If $\chi^2_{\text{old}} < \chi^2_{\text{new}}$ then the new configuration cell is accepted with the probability
\[ e^{-\frac{\chi^2_{\text{new}} - \chi^2_{\text{old}}}{2}} \]
“Hydrogen atoms in metallic hydrides must be separated by at least 2 Å”

Credible violations found in RENiInD$_{1.33}$
A model system – \( \text{VD}_{0.8} \)

- simple structure
- “mono-component”
- well-studied


Model from Rietveld refinement
Total scattering measurement

SLAD @ R2, Studsvik, Sweden

4 measurements:
• sample in vanadium can
• empty vanadium can
• empty instrument
• vanadium rod

RMC model:
6x6x6 unit cells
432 V atoms
333 D atoms
3456 “vacancies”

Program CORRECT
• instrumental background
• absorption
• multiple scattering
• normalization
RMC modeling of VD$_{0.8}$

RMC modeling of VD$_{0.8}$

RMC results

\[ \Delta g_{D-D} = g_{D-D}^{SRO} - g_{D-D}^{random} \]

VD_{0.8}

ZrCr_2D_4

Short-range order vs. long-range order

$\text{ZrCr}_2\text{D}_4$

$\text{VD}_{0.8}$

RMC modeling

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Short-range order vs. long-range order

VD\(_{0.8}\)

1.1 Å

2.2 Å

ZrCr\(_2\)D\(_4\)

1.2 Å


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Short-range order vs. long-range order

Disordered VD$_{0.8}$ (RT) with displacive moves

Short-range order vs. long-range order

Disordered $VD_{0.8}$ (RT) with displacive moves

Ordered $VD_{0.75}$ (taken from literature)

![Graph showing $g_{pp}(r)$ vs. $r$ in Å, with peaks at various $r$ values, illustrating the difference between short-range and long-range order.](image-url)
Short-range order vs. long-range order

Disordered ZrCr$_2$D$_4$ (RT) from RMC


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Short-range order vs. long-range order

Disordered ZrCr$_2$D$_4$ (RT) from RMC
Ordered ZrCr$_2$D$_4$ (150K) from RMC

Short-range order vs. long-range order

Disordered ZrCr$_2$D$_4$ (RT) from RMC
Ordered ZrCr$_2$D$_4$ (150K) from RMC
ZrCr$_2$D$_4$ with fully random D distribution


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Octahedral deuterium in VD$_{0.8}$

- Rietveld and "swap-only" RMC: ~6% of D-atoms are in octahedral sites.
- Displacive moves: D-atoms avoid the centra of octahedral sites.

Octahedral deuterium in VD$_{0.8}$

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Another case study:
bcc alloys for H storage

Based on the Ti-V system

\[ \text{bcc solid solution} \]
\[ (\text{preserved at room temperature}) \]
\[ (\beta_{\text{Ti,V}}) \]

\[ \text{Ti}_{0.7}\text{V}_{0.3} \]
- no H absorption at RT

bcc alloys for H storage

Based on the Ti-V system

(bcc solid solution)

(preserved at room temperature)

\(\text{Ti}_{0.7}\text{V}_{0.3} + 10\% \text{ M } (\text{M = Fe, Mn, Co, Cr, Ni})\)

- H saturation within minutes at RT

bcc alloy hydrides
Based on the Ti-V system

**AB$_5$ (“LaNi$_5$”) hydrides**
+ Excellent kinetics
+ Excellent thermodynamics
- Poor H capacity (~1 w%)

**MgH$_2$**
+ Good kinetics if catalysed
- High desorption temperature
+ Excellent H capacity (~7.6 w%)

**Ti-V-based bcc hydrides**
+ Excellent kinetics
+ Excellent thermodynamics
* Decent H capacity (2-3 w%)

The challenge of cost

Metal (~99.9% purity)

Price ($/kg)

Ferrovanadium alloy ($V_{0.8}Fe_{0.2}$)

www.metalprices.com

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Ferrovanadium-based bcc alloys


Structural reason for the capacity loss?


Experimental work

Synthesis: Arc melting

\[(\text{Ti}_{0.7}\text{V}_{0.3})_{0.9}\text{Fe}_{0.1}\]

\[
\approx \text{Ti}_{0.7}\text{V}_{0.3}\]

\[
\approx \text{Ti}_{0.7}(\text{Fe}_{0.2}\text{V}_{0.8})_{0.3}
\]

SR-PXD

\[Q (\text{Å}^{-1})\]

\[\ast - \text{bcc}\]
Experimental work

Synthesis: Deuteration

\((\text{Ti}_{0.7}\text{V}_{0.3})_{0.9}\text{Fe}_{0.1}\text{D}_{1.73})\)

* - fcc

SR-PXD

27 bar \(\text{D}_2\) @ 298 K

\((\text{Ti}_{0.7}\text{V}_{0.3})_{0.9}\text{Fe}_{0.1}\text{D}_{1.73})\)
Crystallography

80% of D in Zr$_3$Fe tetrahedra

90% of D in Zr$_2$Cr$_2$ tetrahedra

10% of D in ZrCr$_3$ tetrahedra

99.6% of sites OK for deuterium?

65.6% M$_4$ tetrahedra
29.2% M$_3$Fe tetrahedra
4.9% M$_2$Fe$_2$ tetrahedra
0.4% MFe$_3$ tetrahedra
0.01% Fe$_4$ tetrahedra


**ISIS, GEM total scattering**

Reciprocal space $F(Q) \xrightarrow{\text{Fourier transform}} \text{Real space } G(r)$

$$G(r) = \sum_{j,k} c_j c_k b_j b_k g_{jk}(r) = FT^{-1}(S(Q))$$

**Partial PDF**

$$g_{jk}(r) = \frac{\rho_{k}(r)}{\rho_{\text{overall}}}$$

Pairs:
- Ti-Ti
- Ti-V
- Ti-Fe
- Ti-D
- V-V
- V-Fe
- V-D
- Fe-Fe
- Fe-D
- D-D

**Graphs:**
- $F(Q)$
- $G(r)$
Pair distribution function - PDF

\[ G(r) = \sum_{j,k} c_j c_k b_j b_k g_{jk}(r) \]

Scattering lengths:
- \( b(Ti) = -3.4 \) fm
- \( b(V) = -0.3 \) fm
- \( b(Fe) = 9.5 \) fm
- \( b(D) = 6.7 \) fm

- M-M 3.06 Å
- D-D 2.18 Å
- M-D 1.88 Å
RMCProfile modelling package (ISIS)

- 10x10x10 supercell
- 10800 atoms
- 1200 vacancies
- Swap M1-M2
- Swap D-Vac
- D-D and M-D cutoffs

http://www.rmcprofile.org/
Partial PDFs

![Graph showing partial PDFs for various atom pairs.]

- Fe-D
- Fe-Va
- Ti-Va
- V-Va

Partial g(r) (arb. units) vs. r (Å)
Partial PDFs

Fe-X partial g(r) (arb. units)

Ti-Fe  
V-Fe  
Fe-Fe

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RMC models: Fe-vacancy

Initial model

Fe

Vacancy
Conclusion

• Ferrovanadium can greatly reduce the cost of V-based bcc alloys for hydrogen storage, although with the penalty of reduced capacity.

• Fe form clusters which are unfavorable for hydrogen in $(\text{Ti}_{0.7}\text{V}_{0.3})_{0.9}\text{Fe}_{0.1}\text{D}_{1.73}$. 
Conclusion

• Total scattering can provide complementary information to Rietveld refinement.

• The local structures of the disordered deuterides resemble those of the ordered phases at length scales of a few Ångstrøm.