Powder Neutron Diffraction
- an introduction

Neutron scattering course – February 16, 2010

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Scope

- The advantages of neutrons vs. X-rays
- Examples of neutron diffraction studies
- Neutron diffraction at IFE
The glory of neutrons

• There is no systematic correlation between atomic number and the scattering length.
  • Can get information about light and heavy elements simultaneously.

• The neutron interacts weakly with matter.

• The neutron has a magnetic moment.
Metal hydrides

- Materials that contain chemical bonding between metal- and hydrogen atoms.

$M(s) + \frac{x}{2} H_2(g) \leftrightarrow MH_x(s) + \text{energy}$

- Mg$_2$NiH$_4$
- LaNi$_5$H$_6$
- Liquid H$_2$
- H$_2$ gas (200 bar)

4 kg H$_2$
300 kg
Alanates

\[ 3 \ \text{NaAlH}_4 \xrightarrow{\text{TiCl}_3} \ \text{Na}_3\text{AlH}_6 + 2 \text{Al} + 3 \text{H}_2 \]

3.7 wt%  \hspace{1cm} \sim 120^\circ\text{C}

\[ \text{Na}_3\text{AlH}_6 \xrightarrow{\text{TiCl}_3} 3 \text{NaH} + \text{Al} + 3/2 \text{H}_2 \]

1.9 wt%  \hspace{1cm} \sim 180^\circ\text{C}

\[ \text{NaH} \xrightarrow{} \ \text{Na} + 1/2 \text{H}_2 \]

1.9 wt%  \hspace{1cm} 425^\circ\text{C}

5.6 wt%

Crystal structure of alanates

- NaAlH₄
- Na₃AlH₆
- LiAlH₄
- β-LiAlH₄
- Li₃AlH₆
- KAlH₄
- Mg(AlH₄)₂
- Sr₂AlH₇
- BaAlH₅
- Ba₂AlH₇
- Na₂LiAlH₆
- K₂NaAlH₆
- LiMg(AlH₄)₂
- LiMgAlH₆
- Ca(AlD₄)₂
- CaAlD₅

PUS - high resolution diffractometer

The JEEP-II reactor

Li₃AlD₆ seen by X-rays

X-ray cross section

Neutron cross section

Li₃AlD₆ seen by neutrons
Crystal structure of alanates

Diversity

- Symmetries ranging from cubic to monoclinic
- A variety of local configuration.

LiAlD$_4$
CN(Li-D) = 5
$P2_1/c$ [1]

NaAlD$_4$
CN(Na-D) = 8
$I4_1/a$ [2]

KAlD$_4$
CN(K-D) = 10
$Pnma$ [3]

Crystal structure of alanates

Diversity

- Symmetries ranging from cubic to monoclinic
- A variety of local configuration

Similarities

- Average Al-D: 1.60-1.64 Å (AlD$_4^-$)
  1.74-1.80 Å (AlD$_6^{3-}$)

Na$_2$LiAlD$_6$
Al-D = 1.760(1) Å, a = 7.385 Å [1]

K$_2$NaAlH$_6$
Al-H = 1.759(1) Å, a = 8.118 Å [2]

Crystal structure of alanates

Diversity
- Symmetries ranging from cubic to monoclinic
- A variety of local configuration

Similarities
- Average Al-D: 1.60-1.64 Å (AlD$_4^-$)
  1.74-1.80 Å (AlD$_6^{3-}$)
- Anion sublattice often related to simple sphere packing structures.

Li$_3$AlD$_6$
pseudo-bcc packing of AlD$_6^{3-}$
Li$^+$ in $1/2$ of tetrahedral sites

$R3$  $a = 8.071$ Å  $c = 9.513$ Å
The glory of neutrons

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  - Can get information about light and heavy elements simultaneously.
  - Can distinguish neighboring elements in the periodic table.
- The neutron interacts weakly with matter.
  - The neutron has a magnetic moment.
Alloys

$\beta$-Mn: Cubic, complex structure, $a = 6.31$ Å, $Z = 20$

$\text{Mn}(1)_{12}\text{Mn}(2)_8$

What happens if 40% of the Mn is substituted with Co?
Alloys

$\beta$-Mn: Cubic, complex structure, $a = 6.31$ Å, $Z = 20$

$[\text{Mn}_{0.6}\text{Co}_{0.4}]_{12} [\text{Mn}_{0.6}\text{Co}_{0.4}]_{8}$

What happens if 40% of the Mn is substituted with Co?
β-Mn: Cubic, complex structure, \( a = 6.31 \, \text{Å} \), \( Z = 20 \)

\[ \text{Mn}(1)_{12}\text{Co}(2)_{8} \]

What happens if 40% of the Mn is substituted with Co?
Which model is right for $\text{Mn}_{0.6}\text{Co}_{0.4}$?

Random Co distribution
Ordered Co distribution

X-rays:
$Z(\text{Mn})=25$
$Z(\text{Co})=27$
Which model is right for Mn$_{0.6}$Co$_{0.4}$?

X-rays:
- $Z$(Mn)$=25$
- $Z$(Co)$=27$

Neutrons:
- $b$(Mn)$=-0.373$
- $b$(Co)$=+0.249$
Which model is right for $\text{Mn}_{0.6}\text{Co}_{0.4}$?

Co selectively occupy the 8-fold position!
The glory of neutrons

• There is no systematic correlation between atomic number and the scattering length.
  • Can get information about light and heavy elements simultaneously.
  • Can distinguish neighboring elements in the periodic table.

• The neutron interacts weakly with matter.
  • **Complicated sample environment is possible.**

• The neutron has a magnetic moment.
Sample environment

- Neutrons can penetrate several millimeters of materials like aluminium and steel.

Sample container (Inconel super-alloy) rated to 3000 bar and 600°C.
Sample environment

- Neutrons can penetrate several millimeters of materials like aluminium and steel.

Furnace
Sample environment

- Neutrons can penetrate several millimeters of materials like aluminium and steel.

Cryostat
The glory of neutrons

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  • Can get information about light and heavy elements simultaneously.
  • Can distinguish neighboring elements in the periodic table.
• The neutron interacts weakly with matter.
  • Complicated sample environment is possible.
  • Large samples can be studied.
• The neutron has a magnetic moment.
Study of large samples

- How did the machining of the hole influence the material?
Study of large samples
Study of large samples

3D residual stress-field can be mapped in a non-destructive way!

Loading a sample at the NRSF2 instrument at Oak Ridge National Lab (US)
The glory of neutrons

• There is no systematic correlation between atomic number and the scattering length.
  • Can get information about light and heavy elements simultaneously.
  • Can distinguish neighboring elements in the periodic table.
• The neutron interacts weakly with matter.
  • Complicated sample environment is possible.
  • Large samples can be studied.
  • Easy interpretations of scattering intensities are easily.
• The neutron has a magnetic moment.
Scattering intensity

\[ I = \left| F_K \right|^2 = \left| \sum_i b_i \cdot e^{2\pi i (r_i \cdot \vec{K})} \right|^2 = \left| \sum_i b_i \cdot e^{2\pi i (h x_i + k y_i + l z_i)} \right|^2 \]

- Can (usually) neglect effects of multiple scattering, extinction and absorption.
The glory of neutrons

• There is no systematic correlation between atomic number and the scattering length.
  • Can get information about light and heavy elements simultaneously.
  • Can distinguish neighboring elements in the periodic table.
• The neutron interacts weakly with matter.
  • Complicated sample environment is possible.
  • Large samples can be studied.
  • Easy interpretations of scattering intensities are easily.
• The neutron has a magnetic moment.
  • Can study magnetic ordering.
Magnetic neutron scattering

- The neutron has a magnetic moment.
- This will interact with the magnetic moment of atoms with unpaired electrons.

\[ \vec{F}_{\text{magnetic},hkl} = \sum_i \vec{m}_i f_i \cdot e^{2\pi i (hx_i + ky_i + lz_i)} \]

\[ \vec{m} = \vec{K} (\vec{K} \cdot \vec{M}) - \vec{M}, \quad |\vec{m}| = \sin \alpha \]

\[ |\vec{m}| = 0, \quad \vec{K} \parallel \vec{M} \]

\[ |\vec{m}| = 1, \quad \vec{K} \perp \vec{M} \]

\[ I_{hkl} \propto |F_{hkl}|^2 = |F_{\text{nucl},hkl}|^2 + |F_{\text{magnetic},hkl}|^2 \]
Magnetic neutron scattering

Nuclear scattering

Intensity (arb. units)

2θ (deg.)

100 110

111
Magnetic neutron scattering

Ferromagnetic

Nuclear scattering
Magn. scattering
Total scattering
Magnetic neutron scattering

Antiferromagnetic

Nuclear scattering
Magn. scattering
Total scattering

Intensity (arb. units)

$2\theta$ (deg.)
PUS – a high resolution diffractometer

- In operation since 1997.
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Soller collimator (from Risø). 15’, 30’ and “open” (60’).
PUS – a high resolution diffractometer

• In operation since 1997.

Vertically focusing Cu monochromator (from Risø).
311, 511 or 711 reflection plane can be used $\Rightarrow \lambda = 0.75$-2.60 Å
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.

2 detector banks with 7 vertically stacked position sensitive detectors in each. Each bank cover 20° scattering angle.
R2D2
- a second-hand powder diffractometer
R2D2
- a second-hand powder diffractometer

- moved from Risø (TAS3) to Studsvik in 2000.
- moved from Studsvik to Kjeller in 2005.
- resolution as PUS.
- ... but only 1/6 of the intensity.
- operational in a few months
ODIN

- a brand new powder diffractometer
ODIN
- a brand new powder diffractometer

- Optimized Diffractometer for Neutrons
- All aspects of the design is optimized by Monte Carlo simulations.
- 3.5 times higher intensity at slightly better resolution than PUS.
- Or 15 times higher intensity at lower resolution.
Conclusion

- Powder Neutron Diffraction give unique structural information about:
  - Compounds that contain both light and heavy elements.
  - Compounds that contain elements of similar weight.
  - Samples under high pressure and extreme temperatures.
  - Large samples like machine parts.
  - Magnetic materials.