Structure determination at high pressures: X-ray diffraction

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Outline:

- X ray diffraction at high pressures.
  - Special needs.
  - Synchrotron radiation.
  - EDXRD
  - ADXRD
  - Single crystal XRD

- Examples.
Special needs of XRD high pressure experiments

Which are the limitations imposed by high pressure to XRD?

1. Sample size.

(1) semiconductors become metals
(2) ‘metallization’ of oxygen
(3) ice X
(4) ordering transition in molecular hydrogen
(5) onset of visible absorption in hydrogen
(6) pressure at the centre of the earth

Beam diameter (μm)

0 10 20 30 40 50 60 70

0 50 100 150 200 250 300 350 400

Pressure (GPa)

MSPD, ALBA

ID27, ESRF
XRD at high pressures and synchrotron radiation

Which are the limitations imposed by high pressure to XRD?

2. Absorption from anvils and sample environment.
XRD at high pressures and synchrotron radiation

Which are the limitations imposed by high pressure to XRD?

3. Limited angular range
   Ej: XRD spectrum simulations.
   CuAlO$_2$ (R-3m, a=2.86Å, c=16.96Å).

\[
\lambda = 0.7093 \text{ Å}, \ E = 17.5 \text{ keV} \ (\text{Mo } K_\alpha)
\]
10 reflections

\[
\lambda = 0.4135 \text{ Å}, \ E = 30 \text{ keV}
\]
46 reflections

An intense, highly collimated, hard (20-50 keV) x-ray beam is needed
Outline:

- X ray diffraction at high pressures.
  - Special needs.
  - **Synchrotron radiation**.
  - EDXRD
  - ADXRD
  - Single crystal XRD

- Examples.
Synchrotron

Bending magnet

Wiggler

Undulator

Synchrotron radiation
Synchrotron Radiation

- Main advantages:
  - Brilliance
  - Wide wavelength range, from the IR to hard x-rays.
  - Linear and circular polarization.
  - Possibility of a time pulsed source.
General Structure of SR Beamline

Examples:
- Material Science and Power Diffraction BL (ALBA)
- Pression Structure Imagerie par Contraste à Haute Énergie (Psiché, Soleil)
- ID27 High Pressure BL, ID09A - White Beam Beamline, High Pressure Station (ESRF)
Two different experimental approaches

- Bragg’s law:

Fixed $\theta$, variable $\lambda(E)$: Energy dispersive XRD (EDXRD)

Fixed $\lambda$ (E), variable $\theta$: Angle dispersive XRD (ADXRD)
Outline:

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- Examples.
Energy dispersive x-ray diffraction (EDXRD)

\[
2d \sin \theta = \lambda = \frac{hc}{E}
\]

Fixed \(\theta\):
\[
d_{hkl} (\text{Å}) = \frac{6.199}{E_{hkl} (\text{keV}) \sin \theta}
\]

Main disadvantage:
The quantitative analysis of diffracted intensities is not easy.

Usually only cell parameters are obtained!
EDXRD set-up in ID30 (now ID27), ESRF

1. Entrance slit
2. HP cell (PE)
3. Cell support (translation and/or rotation)
4. Diffraction slits
5. Ge detector (next to a liquid N₂ dewar)
ZnSe$_x$Te$_{1-x}$ alloys

J. Pellicer-Porres et al.,
PRB 65, 121091 (2002)
PRB 71, 035210 (2005)
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- Examples.
Angle dispersive x-ray diffraction (ADXRD)

White beam (undulator or wiggler) → Monochromatic beam → Sample → 2D detector (image plate, CCD) → Digitalization

Monocromator
Colimador
Sample

Intensity

\[ 2d \sin \theta = \lambda \]

\[ \lambda = \lambda_0 \text{ fijo} \]

\[ d_{hkl}(\text{Å}) = \frac{\lambda_0}{2 \sin \theta_{hkl}} \]
Example: Stanford Synchrotron Radiation Laboratory (SSRL)
Berlinite (AlPO$_4$)

- Rietveld refinements at very high pressures (Mbar).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<tbody>
<tr>
<td>Al</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P</td>
<td>4c</td>
<td>0</td>
<td>0.3504(7)</td>
<td>0.2500</td>
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<tr>
<td>O</td>
<td>8g</td>
<td>0.249(1)</td>
<td>0.9794(7)</td>
<td>0.2500</td>
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<tr>
<td>O</td>
<td>8f</td>
<td>0</td>
<td>0.7519(8)</td>
<td>0.969(1)</td>
</tr>
</tbody>
</table>

Rietveld refinement to the CrVO$_4$ structure at 13.9 GPa (Residuals$^{\text{R}} R_{\text{wp}} = 13\%$, $R_p = 10\%$, $R(F^2) = 16\%$, 51 reflections). Space group $Cmcm$ (63). Lattice parameters: $a = 5.0365(7)$ Å, $b = 7.2908(9)$ Å and $c = 5.7491(9)$ Å.

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<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
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<td>Al</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P</td>
<td>1h</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.5000</td>
</tr>
<tr>
<td>O</td>
<td>2m</td>
<td>0.690(2)</td>
<td>0</td>
<td>0.330(1)</td>
</tr>
<tr>
<td>O</td>
<td>2n</td>
<td>0.774(1)</td>
<td>0.5000</td>
<td>0.814(1)</td>
</tr>
</tbody>
</table>

J. Pellicer-Porres et al.,
Outline:

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- Examples.
Single crystal diffraction

\[ \vec{k} - \vec{k}' = \vec{K} \]

The Laue condition is not so easy to fulfill!

- The single crystal analysis is complicated under HP:
  - Absorption from the sample environment.
  - Limited access to the reciprocal space.
  - Reflections from the sample environment.
  - Long experiments.
  - No global image.
  - Reconstructive phase transitions.
Advantages in single crystal XRD (1/3)
- There is no reflection overlapping (in particular for d<1.5 Å)
- There are no grain contacts
- Equations of state can be determined with high precision.

GaS equation of state
- Layered compound.
- 70x10x10 μm³ sample
- $\lambda=0.37$ Å
- Image plate
- ~40 reflections

J. Pellicer-Porres et al.,
Advantages in single crystal XRD (2/3)

- Systematic absences /spatial group.
- Access to reciprocal vectors (opposed to distances).
- Accurate determination of intensities and structural factors.
- Structural models.

Jahn-Teller distortions in CuWO₄

- Boehler-Almax DAC.
- 90 x 70 x 20 μm³ sample
- λ=0.45 Å
- NaI point detector.

<table>
<thead>
<tr>
<th>p (GPa)</th>
<th>0.0001</th>
<th>0.0001</th>
<th>7.0(1)</th>
<th>13.4(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>100</td>
<td>293</td>
<td>293</td>
<td>293</td>
</tr>
</tbody>
</table>

Data collection

| Wavelength (Å) | 0.71073 | 0.71073 | 0.45   | 0.45   |
| Detector type  | CCD     | CCD     | PD     | PD     |
| h               | 6.6     | 5.5     | 8.7    | 7.7    |
| k               | 7.7     | 6.6     | 3.3    | 3.2    |
| l               | 8.6     | 3.5     | 7.7    | 7.7    |

Observed reflections | 1776 | 1825 | 1024 | 681 |
Unique reflections   | 617  | 468  | 487  | 196 |
Reflect. $I > 2σ(I)$ | 601  | 454  | 470  | 196 |
Parameters           | 36   | 36   | 26   | 16   |
$R_{int}$            | 0.0563 | 0.0291 | 0.0518 | 0.0603 |

J. Ruiz-Fuertes et al., Chem. Mater. 23, 4220–4226 (2011)
Advantages in single crystal XRD (3/3)

- It is possible to study light elements (small atomic form factors).


- Thanks to the EDXRD configuration the contribution from the diamonds to the background (Compton scattering) is minimized.
Outline:

- X-ray diffraction at high pressures.

- Examples.
  - Equation of state.
  - Phase transitions. Hysteresis.
  - Synthesis.
Hydrogen at high pressures

-Wigner&Huntington (1935):

Transformation from a molecular solid to a monoatomic metal at 25 GPa.

- N. W. Ashcroft (1968):

Metallic hydrogen would be a high temperature superconductor.

Enormous difficulties, from both the experimental and theoretical points of view!
Hydrogen equation of state

10 GPa

14 GPa

119 GPa

Equation of state
GaS equation of state

- Layered compound.
- 70x10x10 μm³ sample
- $\lambda=0.37$ Å
- Image plate
- $\sim$40 reflections

Outline:

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Hysteresis and potential barriers

\[ \left( \frac{\partial G}{\partial P} \right)_T = V > 0 \]

M. Flórez and J. M. Recio et al., in “Introduction to High Pressure Science and Technology”

F. Decremps et al., EPL 51, 268–274 (2000)

J. Pellicer-Porres et al., APL 81, 4820-4822 (2002)
Overcoming potential barriers: berlinite

- Quartz homeotype

\[ \text{AlPO}_4 \]

- Berlines: ABO\(_4\)

- Is there a crystal-amorphous phase transition?

Memory Glass: An Amorphous Material Formed from AlPO\(_4\)

M. B. Kruger and Raymond Jeanloz  
Science 249, 647 (1990)

A glass exhibiting structural memory has been produced through the compression of a single crystal of AlPO\(_4\) berlinite to 18 gigapascals at 300 kelvin. The unique and extraordinary characteristic of this glass is that upon decompression below 5 gigapascals, it transforms back into a single crystal with the same orientation as the starting crystal. This glass has a "memory" of the previous crystallographic orientation of the crystal from which it forms.

Structural Memory in Pressure-Amorphized AlPO\(_4\)

John S. Tse and Dennis D. Klug  
Science 255, 1559 (1992)

Spirals of alternate tetrahedra in berlinite structure

Summer Under Pressure School, Madrid, 29th September 2015
Overcoming potential barriers: berlinite

- Example: Cmcm phase in AlPO\textsubscript{4}

J. Pellicer-Porres et al., Nat. Mat. 6, 698-702 (2007)

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. M. Sharma et al.</td>
<td>5.06</td>
<td>6.77</td>
<td>5.19</td>
</tr>
<tr>
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<td>5.0365</td>
<td>7.2908</td>
<td>5.7491</td>
</tr>
</tbody>
</table>
Hysteresis and potential barriers: path selection

- Phase transitions in ZnTe$_{0.2}$Se$_{0.8}$:
  - Upstroke: ZB $\rightarrow$ NaCl
  - Downstroke: NaCl $\rightarrow$ Cin $\rightarrow$ ZB

11 GPa

10.5 GPa

10.4 GPa

10.3 GPa

10.2 GPa
ZnSe$_x$Te$_{1-x}$ alloys

V. Ozolins and A. Zunger, PRL 82, 767 (1999)

J. Pellicer-Porres et al., PRB 65, 121091 (2002)
PRB 71, 035210 (2005)
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Diamond synthesis

H. Tracy Hall
1953

First diamond synthesis
1954/12/16

F.P. Bundy et al.
Nature 176, 51 (1955)

Hall, Rev. Sci. Instrum. 31, 125 (1960)
“In situ” studies

Example: Photon Factory, Ni

Industrial diamond synthesis

30000 ton press
“Belt”-type
$P_{\text{max}} = 6 \text{ GPa}$
1 liter

Kobelco: Kobe Steel Group

Additional information:

A MALTA-Consolider Initiative

An Introduction to High Pressure Science and Technology

Chapter 7

Structure Determination

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Do not forget x-ray absorption!

Thank you for your attention!