Methods of High-Pressure Single-Crystal X-ray Diffraction

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- Technical challenges
- Overview of methods
- Overview of the workshop
Single crystal and powder

- Single-crystal data is 3 dimensional not 1 dimensional, intrinsically superior to powder diffraction:
  - No peak overlaps
  - No resolution problems
  - No preferred orientation problems
  - No “powder average” problems
  - Signal to noise is higher

- Single crystal diffraction allows:
  - The unambiguous determination of minute structural changes
  - The determination of small structural distortions (phase transitions)
  - Acentric crystals
  - Measurement of diffuse scattering and incommensurate structures
  - Reliable displacement parameters

- “A bad single crystal is better than a good powder” (McMahon)
Aim of the workshop is to show you ‘how’
The Diamond Anvil Cell
Diamond-anvil geometry

Transmission mode

Ronald: today
Cell parameters at high pressure

Precise diffraction angle data to measure small changes in cell parameters at high pressures:

Softening in CuCO$_3$
Spencer et al. (2011)
Determining structures at high pressure

- Workflow is similar to crystals in air

- But there are challenges:
  - Limited access
  - Low signal (but higher than powder)
  - Background scattering
  - Absorption by cell components
  - Maintaining hydrostatic conditions

- Intensity data collection
- Integration
- Absorption corrections
- Refinement
- Post-refinement analysis and publication
Limited access

Fewer reflections means:
- more sensitivity to individual data
- higher chance of systematic error
- higher influence of random error
- less resolution
Reducing background

Everything you see is background!

Conventional DAC with Be seats, steel gasket

DAC with steel seats and rhenium gasket
Determining structures at high pressure

- Because of the challenges:
  - Optimise the data collection
Reducing background

Use a point detector:
- Additional collimation
- Optimised scan speed
- Step scans
- Profile fitting
- Recovery of weak data

Ross: today, afternoon
Data collection at synchrotron sources
Indexing and integration

- Similar to crystals in air
  - But tricks and software to overcome the challenges

Intensity data collection
Integration
Absorption corrections
Refinement
Post-refinement analysis and publication

Software Fayre: today
Absorption

- Much more to correct

Intensity data collection
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Ross: tomorrow
Refinement

- Much more sensitive to outlier data
- Lower resolution data
- Approaches:
  - Robust-resistant weighting
  - Restraints
  - Careful evaluation of outliers

Intensity data collection
Integration
Absorption corrections
Refinement
Post-refinement analysis and publication

Karen + Andrzej: tomorrow
Post-refinement analysis

- Structure validation
  - Getting past the cif-checker

- Parametric data:
  - Challenges
  - Opportunities to exploit self-consistency

Intensity data collection
Integration
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Karen, Ross and others: tomorrow
Workshop overview

Today
- Cells and cell loading
- Data Collection
- Equations of state
- Data integration

Tomorrow
- Synchrotron data collection
- Absorption corrections
- Refinement
- Structure validation
- Eos fitting
- Problem solving

Intensity data collection
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