PAUL SCHERRER INSTITUT

Materials Science at Large Scale Facilities

Diffraction - Exercises

1. Crystal Orientation in a Single Crystal

Scenario:

You receive a large, millimeter-sized single crystal of a new intermetallic compound grown in a furnace. Before cutting or polishing, you need to determine its orientation to prepare samples along specific crystallographic directions for transport measurements.

Questions:

- Which diffraction technique would you use and why?
- What are the advantages of this method for this kind of sample?
- What would be the limitations if the crystal has multiple grains or twinning?

1. Crystal Orientation in a Single Crystal

Which diffraction technique would you use and why?

→ **Laue diffraction** (using polychromatic X-rays). It rapidly determines crystal orientation via back-reflection or transmission Laue patterns.

→ No need for sample rotation or detailed structure refinement — ideal for alignment.

Advantages for this sample:

→ Fast, non-destructive, requires only one exposure.

→ Works with relatively large, opaque crystals.

→ The pattern gives orientation directly by symmetry.

Limitations if twinned or polycrystalline:

→ Overlapping Laue spots from multiple domains make indexing difficult.

→ In that case, the **rotating crystal method** or **powder diffraction** may help determine phase identity and lattice parameters first.

2. Phases in a Polycrystalline Alloy

Scenario:
You are investigating a Ni–Ti–Fe alloy that underwent thermal cycling. You suspect the presence of several phases (austenite, martensite, and an oxide impurity). You have access to a laboratory diffractometer and a synchrotron beamline.

Questions:
- Which diffraction method would you choose to identify and quantify the phases?
- How would the choice change if you needed high-temperature *in situ* data during cycling?
- What additional information could you gain at a neutron facility?

2. Phases in a Polycrystalline Alloy

Which diffraction method to identify and quantify phases?

→ **Powder diffraction** (angle-dispersive) is standard for phase identification and Rietveld refinement.

→ A **synchrotron source** provides high resolution and sensitivity for minor phases.

How would the choice change for in situ high-temperature cycling?

→ **High-temperature powder diffraction** (e.g., with a heating stage) or **energy-dispersive diffraction** for fast collection at constant geometry.

→ For large-grain samples or thicker specimens, **neutron diffraction** is advantageous.

What additional information from neutrons?

→ Neutrons distinguish Ni, Ti, Fe better due to non-monotonic scattering length behavior.

→ Sensitive to light elements (O), enabling detection of oxides and hydrogen impurities.

→ Penetration allows *bulk* phase analysis.

3. Nanocrystalline Catalyst

Scenario:
A catalytic material made of nanocrystalline ceria supported on amorphous silica is under study. Bragg peaks are very broad and hard to analyze. You need to understand the short- and medium-range order.

Questions:
- Which diffraction technique allows access to local (rather than long-range) structure?
- What type of analysis would you perform on the data?
- What differences would you expect between X-ray and neutron data?

3. Nanocrystalline Catalyst

Which technique for local structure?

→ **Pair Distribution Function (PDF)** analysis from total scattering (X-ray or neutron).

→ Accesses both Bragg and diffuse scattering up to high momentum transfer Q.

What type of analysis?

→ Fourier transform of total scattering S(Q) to real-space G(r), giving atomic pair correlations.

→ Fit using small-cluster or reverse Monte Carlo models to extract local coordination.

Differences between X-rays and neutrons:

→ X-rays emphasize heavy atoms (Ce), less sensitive to O.

→ Neutrons better highlight O–O and Ce–O distances.

→ Combined analysis improves reliability of coordination numbers and bond distances.

4. In situ phase transformation

Scenario:

You are monitoring the phase transformation of an Fe–Mn–Si alloy under mechanical stress at a synchrotron beamline. The sample is thick and experiences rapid strain-induced changes.

Questions:

- Would you choose an energy-dispersive or angle-dispersive diffraction setup? Why?
- How does energy-dispersive XRD handle large strains or broad peaks?
- What trade-offs exist in terms of resolution and time resolution?

4. In situ phase transformation

Would you choose energy-dispersive or angle-dispersive diffraction? Why?

→ **Energy-dispersive XRD (EDXD)**, using a white X-ray beam and a fixed scattering angle.

→ High penetration depth suits thick specimens.

How does EDXD handle large strains or broad peaks?

→ Energy-dispersive detectors record broad energy bands corresponding to d-spacing; strain can be followed from energy shifts.

→ Some loss of resolution, but time resolution improves drastically.

Trade-offs:

→ **Pros:** Fast, high penetration, constant geometry.

→ **Cons:** Lower d-spacing resolution than angle-dispersive; more complex background corrections.

→ Choice depends on prioritizing temporal resolution over precision.

5. Hydrogen in a metal hydride

Scenario:

You are studying a hydrogen storage material (e.g., $LaNi_5H_6$). You want to determine the precise hydrogen positions and occupancies.

Questions:

- Which probe is more suitable — X-rays or neutrons? Why?
- Among neutron methods, would you prefer steady-state or time-of-flight?
- How could you combine the data with other diffraction techniques?

5. Hydrogen in a metal hydride

Which probe: X-rays or neutrons? Why?

→ **Neutrons**, because hydrogen scatters neutrons strongly and incoherently, while it’s almost invisible to X-rays.

→ Neutron scattering lengths are not correlated with atomic number.

Preferred experimental configuration:

→ **Time-of-flight (ToF) neutron diffraction**, typically at pulsed sources, provides high d-spacing resolution across a wide range.

→ Allows simultaneous refinement of heavy-atom and light-atom sublattices.

Combining with other techniques:

→ Use **X-ray diffraction** for precise lattice parameters and phase purity.

→ Neutron diffraction refines hydrogen positions and occupancies.

→ Together they yield full structural information.

6. Surface reconstruction in a thin film

Scenario:

You grow a thin epitaxial film of $SrTiO_3$ on Si(001) and suspect a surface reconstruction after annealing. You want to determine the periodicity and atomic relaxation near the surface.

Questions:

- Which diffraction method would give surface sensitivity?
- What challenges arise from substrate scattering?
- How could you complement diffraction with microscopy?

6. Surface reconstruction in a thin film

Which diffraction method gives surface sensitivity?

→ **Surface X-ray diffraction (SXRD)** in grazing incidence geometry.

→ Sensitive to topmost atomic layers (1–10 nm).

Challenges from substrate scattering:

→ Strong substrate peaks can dominate — minimize by adjusting incident angle below critical angle or using synchrotron microbeams.

→ Background subtraction and reciprocal space mapping help isolate surface features.

Complementary methods:

→ **LEED** (surface periodicity), **RHEED**, **AFM** (morphology), or **TEM** (interface structure).

→ These confirm reconstructions inferred from SXRD intensity modulations.

7. Time-resolved study of a reaction

Scenario:

You are studying crystallization during an *in situ* synthesis in a high-pressure cell, where the sample transitions from amorphous precursor to crystalline phase in milliseconds.

Questions:

- Which method allows both penetration and fast data acquisition?
- Could neutrons or X-rays be used?
- How would you capture transient intermediates?

7. Time-resolved study of a reaction

Which method allows fast data collection and penetration?

→ **Energy-dispersive XRD** at a synchrotron (fixed geometry, fast detectors).

→ Alternatively, **neutron ToF** if hydrogen or light elements are key, though typically slower.

Could neutrons or X-rays both be used?

→ Yes, depending on timescale and sample.

→ X-rays for speed (sub-second resolution).

→ Neutrons for isotopic sensitivity and bulk penetration (minutes resolution).

Capturing transient intermediates:

→ Use fast area detectors, stroboscopic acquisition, or pump–probe setups.

→ Complement with PDF analysis to capture local structure evolution during transformation.