Webinar 04 – Crystallography (Feedback Session)

Polished summary of the session

Housekeeping

Eight project teams have been formed and started; seven have submitted a work plan. Feedback will be sent by email following this session.

The Bilbao Crystallographic Server, a key tool for this module, has been unavailable for several days. The maintainers have been contacted. While it is down, some tasks from the past week cannot be completed. Screenshots shown in this webinar illustrate the intended workflow; there is no penalty if you could not perform the affected tasks.

About This Module

Crystallography often splits opinions: some find it dry, others value its visual, hands■on character compared with the more abstract work on Kohn–Sham and Hohenberg–Kohn theorems. Our emphasis is practical crystallography for preparing DFT inputs.

1. CIF Files and Their Role

CIF (Crystallographic Information File) captures space group, unit cell parameters, and atomic positions—typically via unique sites plus symmetry operations. CIF connects experimental reports and computational inputs.

Using a shared format avoids a proliferation of pairwise converters among DFT codes. If each code can convert from CIF (e.g., with cif2cell), only one converter per code is needed.

Example: Converting CIF to Quantum ESPRESSO

Starting from a CIF (e.g., neptunite), cif2cell can generate Quantum ESPRESSO input. Unit■cell shape and size can be specified via CELL_PARAMETERS vectors rather than a, b, c, α, β, γ. Quantum ESPRESSO typically lists all symmetry■equivalent atomic positions explicitly.

Typical conversion notes:

• Element labels: Non■numeric suffixes (e.g., “Si■A”) can cause errors—remove such labels.

• Site occupancies: Missing occupancies default to 1.0—appropriate for DFT inputs; partial occupancies require supercells.

• Formula units per cell: Z may exceed 1 (e.g., 40 atoms in the formula but 80 in the QE unit cell).

• Negative coordinates: CIF may include negative fractional coordinates; converters adjust to target code conventions.

2. Space Group, Unit Cell, and Wyckoff Positions

The space group encodes symmetry; the unit cell defines the box (a, b, c and α, β, γ); Wyckoff positions list unique sites that, under symmetry operations, generate the full atomic set. Databases (e.g., COD) and the Bilbao server (when available) provide these data.

Case Study: Litharge (PbO)

From the mineral name, determine composition (PbO) and space group (P4/nmm, No. 129). Multiple database entries may reflect polymorphs, improved measurements, or alternate settings—choose a reliable entry.

Wyckoff identification: Pb atoms occupy 2c sites at (¼, ¼, z) and (¾, ¾, 1–z) with z ≈ 0.23. Here, z is a free internal parameter: varying z in [0, 1) preserves the symmetry, though each compound realizes a single value.

Origin Choices

P4/nmm has origin choices related by a translation. Origin choice 2 places an inversion center at the origin, which can simplify calculations (e.g., using real rather than complex quantities) and is generally preferred when available.

3. Building a CIF from Scratch

Motivations include hypothetical structures, defects, and supercells. Write a P1 CIF listing each unique atom once (respecting periodic boundary conditions), then use a symmetry■finding tool such as FINDSYM to recover the space group and reduce to Wyckoff positions.

Common pitfalls: do not list periodic images explicitly (e.g., all cube corners or both faces). Corner atoms contribute 1/8, face■center atoms 1/2; specify a single representative per unique site.

4. Tools and Visualization

Use COD viewers or VESTA to inspect unit cells and extract coordinates. If the Bilbao server is down, rely on screenshots and offline tools; no penalties apply for blocked tasks.

Logistics and Next Steps

Submit a one■paragraph summary and propose an exam question. Next, we begin two weeks on geometry optimization, which is essential for the project work. Europe switches to daylight saving time next weekend; local time within Europe is unchanged, but the UTC time shifts by one hour for other time zones.

Closing

Follow the “Let’s Play” steps for the week’s practical tasks. Questions are welcome on the forum or chat. See you next week.