Chemical Crystallography and Structural Chemistry

VO 270287

Lecture № 1 — 4th March 2021

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Contents

1 Administrativa

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- my homepage: `https://homepage.univie.ac.at/tim.gruene`

Course Details

04th March	Lecture № 1	11th March	Lecture № 2
18th March	Lecture № 3	25th March	Lecture № 4
1st April	Easter break	08th April	Easter break
15th April	Lecture № 5	22th April	Lecture № 6
29th April	Lecture № 7	06th May	Lecture № 8
13th May	Lecture № 9	20th May	Lecture № 10
27th May	Lecture № 11	3rd June	Lecture № 12
10th June	Lecture № 13	17th June	Lecture № 14
24th June	Lecture № 15		

- Lectures will be recorded and made available through Moodle
- Interruptions welcome during the lecture
- Lecture notes will be made available online
- `https://homepage.univie.ac.at/tim.gruene/teaching/chemcryst`

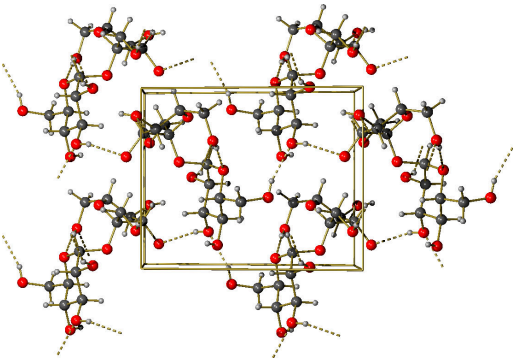
Examination

There will be an **oral** exam.

2 Course Objective

Chemical Crystallography

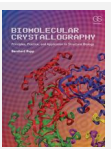
Understanding the value of a chemical structure in chemical research



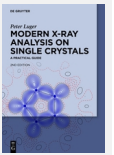
Crystal structure of sucrose, with hydrogen bonds

- what do we learn from a crystal structure?
- what are the **limits** of crystallography

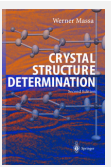
3 Resources: Literature for Crystallography



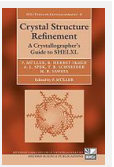
Rupp [1]



Luger [2]

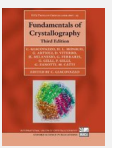


Massa [3]



Muller et al. [4]

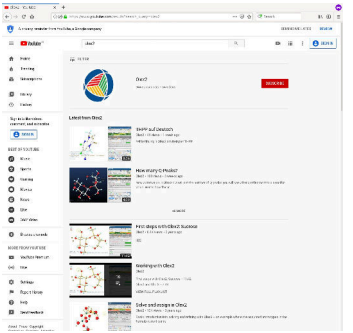
various [5]



Giacovazzo [6]

Online Resources

`http://shelx.uni-goettingen.de`



Olex2 *etc* on youtube

Journals for Chemical Crystallography

- Acta Crystallographica A–F `journals.iucr.org`: International Union of Crystallography
- Zeitschrift für Kristallographie, `https://www.degruyter.com/journal/key/ZKRI/html`
- Angewandte Chemie Int. Ed. `http://www.angewandte.org`, GDCh
- JACS, Journal of the American Chemical Society `https://pubs.acs.org/journal/jacsat`

and most other journals for chemistry

Crystallographic databases

Most journals require the deposition of structural data structures at publicly available data bases. Crystallography has long been a pioneering discipline of open access data.

Cambridge Structural Database

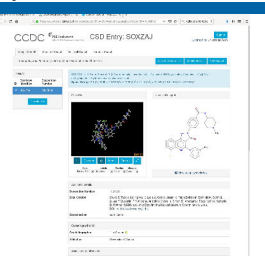
Crystallography Open Database

Inorganic Crystal Structure Database

Protein Data Bank

CRYSTMET ®

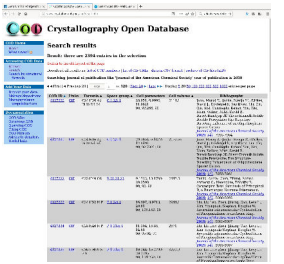
Cambridge Structural Database (CS



- `http://www.ccdc.cam.ac.uk`
- founded 1965
- curated
- Single crystal and powder diffraction
- organic and metal-organic compounds
- $> 1,000,000$ entries, $\approx 50,000$/year
- X-ray, neutron, (and electron diffraction)
- "The world repository of small molecule crystal structures"

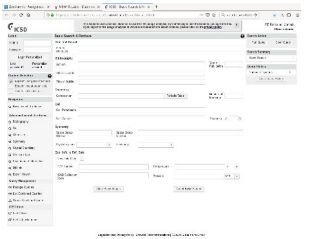
Crystallography Open Database (COD)

- http://www.crystallography.net
- Local version available free of charge
- Can be browsed (by journal, by year,...)
- Organic and inorganic structures (minerals)
- "Open-access collection of crystal structures of organic, inorganic, metal-organics compounds and minerals, excluding biopolymers."
- All data from IUCr journals, and from American Mineralogist CSD
- $> 450,000$ entries, $\approx 50,000$/year



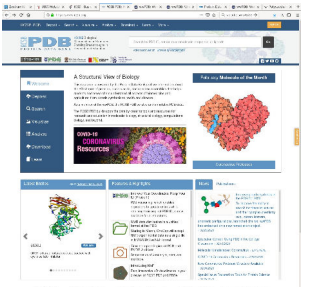
Inorganic Crystal Structure Database (ICSD)

- `https://icsd.fiz-karlsruhe.de/`
- inorganic and intermetallic structures
- only licensed access
- $> 215,000$ entries



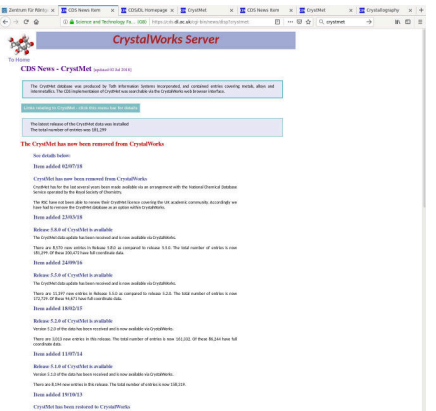
Protein Data Bank (PDB)

- `https://www.pdb.org`
  - Search from
    - `www.rcsb.org`
    - `https://www.ebi.ac.uk/pdbe`
    - `https://pdbj.org` (Japanese)
  - polypeptides (proteins) and polysaccharides (nucleic acids)
  - Crystal structures, NMR structures, EM structures
  - Since 2007: data **must** be submitted along with coordinates
  - $> 160,000$ structures



CrystMET

- `https://cds.dl.ac.uk/cds/datasets/crys/mdf/llmdf.html`
- Crystal structure data for metals and alloys
- licensed access only



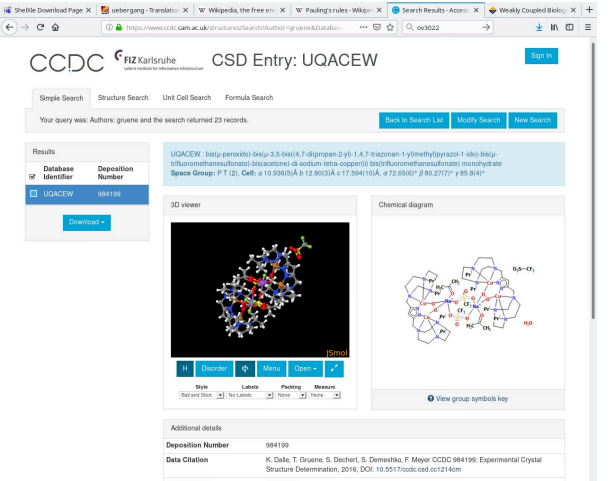
4 Structure, Data, Data Formats, and Visualisation Software

Structural Data: the CIF-file

- Main file format for published structures
- available from CSD, COD, ICSD, journal web-sites, etc
- pure text file
- Can and should contain both structure information (coordinates) and experimental data (hkl-file)

Example: CSD entry UQACEW, CIF-file: 984199.cif

Dalle et al. [7]

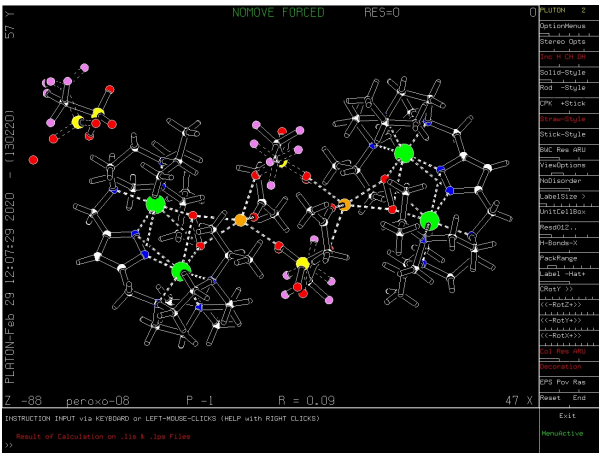


Structural Data: the RES-file

- RES/INS text file: chemical structure in computer language
- developed by George Sheldrick (SHELX programs), late 1960s
- still the most sophisticated format for chemical compounds
- "work" format: refinement and model building

Platon: Validation, format conversion

http://www.cryst.chem.uu.nl/spek/platon

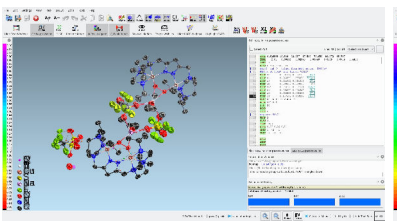


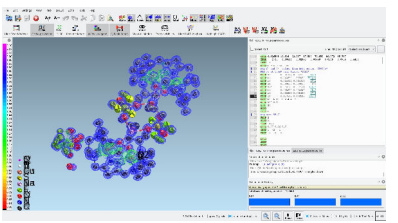
→ 984199_sx.ins and 984199_sx.hkl

ShelXle: Visualisation and Modelling

https://www.shelxle.org/shelx

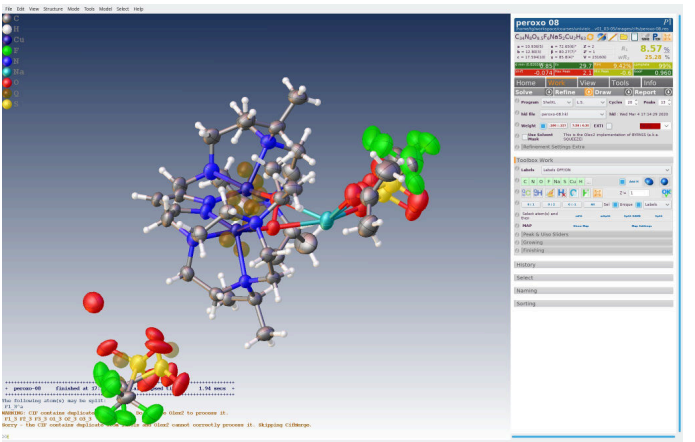
```
#> shredcif 984199.cif
peroxo-08.res extracted, checksum O.K.
peroxo-08.hkl extracted, checksum O.K.
```





Olex2: Visualisation and Modelling

https://www.olexsys.org/



5 Crystals and Crystal Growth

Crystal Types

- Crystal = Solid state compound with regular composition
- interactions responsible for crystallisation
  1. ionic bond
  2. metallic bond
  3. covalent bond
  4. van-der-Waals interaction
- often not a clear cut between these types
- crystallography can characterise bond types

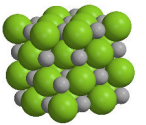
Ionic Crystals

- Composed of anions (negative charge) and cations (positive charge)
- Geometry according to Pauling's rules

Simple example: $NaCl$:

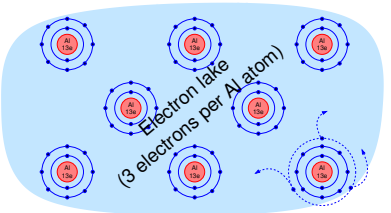
- cubic lattice
- energy difference $Na + Cl \rightarrow Na^+ + Cl^-$: $-6.4eV$

Chrome alum,
i.e. Chromium(III) potassium sulfate $KCr(SO_4)_2$



cubic lattice of $NaCl$

Metallic Crystals



various forms of iron [8]

Valence electrons dissociate from individual atoms and form an **electron lake** (conduction band)

→ electrical conductivity

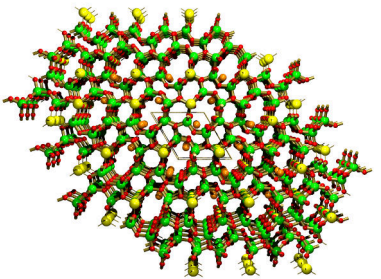
→ thermal conductivity (copper)

→ shiny surface

→ plasticity

Covalent bond

- Two atoms share an electron to reach noble gas configuration.
- Examples: zeolites, MOFs, diamond, quartz
- $\Rightarrow$ high stability
- The entire crystal is a single molecule

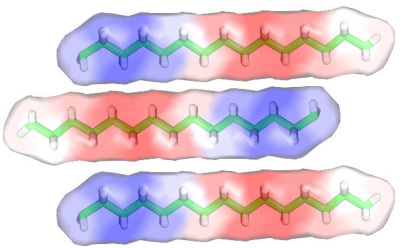


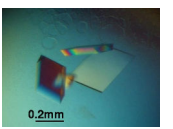
Feldspar Albite $NaAlSi_3O_8$ [9]

Albite crystals [10]

van-der-Waals interaction

- typical for organic and macromolecular compounds
- stochastic charge distribution (dipole moments) causes mutual attraction between molecules
- weak ("soft") interaction





protein crystals in mother liquor

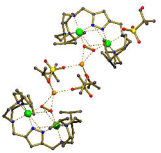
Crystals in Crystallography

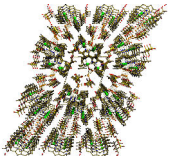
Definition *International Union of Crystallography*:

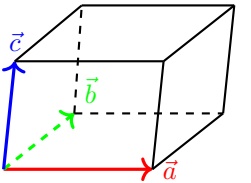
> "A material is a crystal if it has essentially a sharp diffraction pattern."

Crystal in the context of this lecture:
A crystal is composed of a chemical compounds that repeats periodically in all three directions.

Crystals in Crystallography





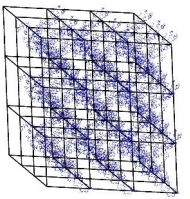


- The periodicity results in the diffraction pattern of the crystal
- The periodicity acts like a signal amplifier
- The smallest unit of the periodicity is an inclined box. It is called the **unit cell of the crystal**.

Crystal Growth

Crystals are

1. solid state materials
2. highly ordered, *i.e.* their entropy is very low compared to amorphous material



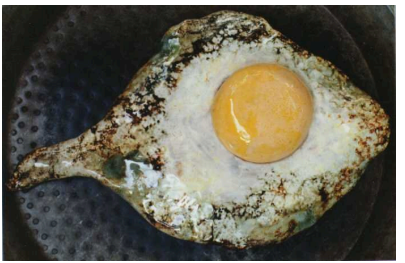
Especially for large molecules: weak interaction, *i.e.* low energy gain through crystallisation ⇒ Crystal growth can be difficult

Crystal Growth

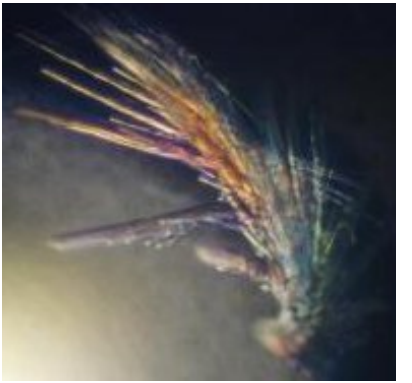
Usually: Precipitation from solution
Some means for precipitation (*cf.* LeChatelier's principle)

- Changes in temperature or pressure
  - sugar: better soluble in warm water
- precipitant
  - sugar: ethanol
  - high salt concentrations

Preliminaries for structure determination



crystallisation (instead of amorphous precipitation)

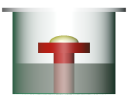


crystallisation as single crystal

Examples for Crystallisation

1. Dissolve in Tetrahydrofuran (THF) in glass vial
2. Cover with parafilm: slow evaporation of THF
3. Store at $-80°C$

1. Dissolve in organic solvent (EtOH, Isopropanol, ...)
2. Store sealed on water reservoir
3. Uptake of water (vapour) reduces solubility of compound



Twinned structures (cf. end of term) can often be improved with elevated temperature during crystal growth (30-40°C).

(see *e.g.* W. Massa, *Crystal Structure Determination*, Ch. 7)

6 X-rays and Diffraction

end of lecture, continued in lecture № 2

References

[1] B Rupp. *Biomolecular Crystallography*. 1st ed. Garland Science, 2009.

[2] P. Luger. *Modern X-ray Analysis on Single Crystals*. Walter de Gruyter, Berlin, 2014.

[3] W. Massa. *Crystal Structure Determination*. Springer Verlag Berlin, Heidelberg, 2002.

[4] P. Muller et al., eds. *Crystal Structure Refinement. A Crystallographer's Guide to SHELXL*. Oxford University Press, 2006. ISBN: 9780198570769.

[5] various, ed. *International Tables of Crystallography*. Vol. A–I. International Tables of Crystallography. Wiley, 2016. URL: https://it.iucr.org/.

[6] C. Giacovazzo, ed. *Fundamentals of Crystallography*. Oxford University Press, 1985.

[7] K. Dalle et al. 'A weakly coupled biologically relevant $Cu_2^{II}(\mu-\eta^1:\eta^1-O_2)$ *cis*-peroxo adduct that binds side-on to additional metal ions'. In: *J. Am. Chem. Soc.* 136 (2014), pp. 7428–7434. DOI: 10.1021/ja5025047.

[8] Alchemist-hp. *Iron electrolytic and 1cm3 cube*. URL: https://commons.wikimedia.org/wiki/File:Iron_electrolytic_and_1cm3_cube.jpg (visited on 03/03/2020).

[9] E. Fröjdh et al. 'Discrimination of Aluminum from Silicon by Electron Crystallography with the JUNGFRAU Detector'. In: *Crystals* 10 (2020), p. 1148. DOI: 10.3390/cryst10121148.

[10] Rock Courier. *Albite - Crete (Kriti) Island, Greece*. URL: https://commons.wikimedia.org/wiki/File:Albite_-_Crete_(Kriti)_Island,_Greece.jpg (visited on 03/03/2020).