

# SCHEDULE

	Date	Topic
1.	Wed 01.03.	Lec-1: Introduction
2.	Mon 06.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon 06.03.	<b>EXERCISE 1</b>
4.	Wed 08.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri 10.03.	Lec-4: Symmetry & Point Groups
6.	Mon 13.03.	<b>EXERCISE 2</b>
7.	Wed 15.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri 17.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon 20.03.	<b>EXERCISE 3 (Linda)</b>
10.	Fri 31.03.	Lec-7: Rietveld (Linda)
11.	Mon 03.04	<b>EXERCISE 4: Rietveld (Linda)</b>
12.	Wed 12.04.	Lec-8: ND & GI-XRD
13.	Fri 14.04.	Lec-9: XRR (Topias)
14.	Mon 17.04.	<b>EXERCISE 5: XRR (Topias)</b>
15.	Wed 19.04.	Lec-10: Synchrotron radiation & XANES & EXAFS
16.	Fri 21.04.	Lec-11: Mössbauer
17.	Fri 21.04.	<b>EXERCISE 6</b>
18.	Fri 28.04.	Seminars: AFM, EELS, XPS, FTIR
19.	Wed 03.05.	Seminars: HRTEM, ED, SEM
20.	Wed 10.05.	<b>ADDITIONAL DISCUSSION/QUESTION POSSIBILITY</b>

**EXAM: Wednesday, May 17th: 13:00 – 16, Ke5**

## **GRADING (max 100 points)**

- Exam: 0 – 44 points
- Exercises: = 0 – 36 (= 6 x 6) points
- Seminar (mandatory): 10 – 20 points

## **EXAM COMMENTS**

- **May 17<sup>th</sup>, at 13:00 – 16, Lecture Room Ke5**
- **Be prepared to work efficiently as the questions may be little laborious**
- **You will need a calculator and coloured pencils would be useful too**
- **There will be six questions; if you have time you can answer to all of them, but only the five best answers are counted**
- **Remember to explain your answers well; just the right answer (e.g. number or single word) is typically not enough to get the maximum points!**

## EXERCISE 1.1.

- A. Describe shortly by words and/or drawings the following terminologies: **oxygen vacancy, oxygen vacancy ordering, and occupancy factor**
- B. Describe shortly by words and/or drawings the following terminologies: **double perovskite and antisite defect.**
- C. Why the same transition metal is smaller as a trivalent cation than as a divalent ion? Give an example with actual numbers for a transition metal of your choice.
- D. Familiarize yourself with the units: Å and nm

You can find ionic radius values at:

<http://abulafia.mt.ic.ac.uk/shannon/ptable.php>

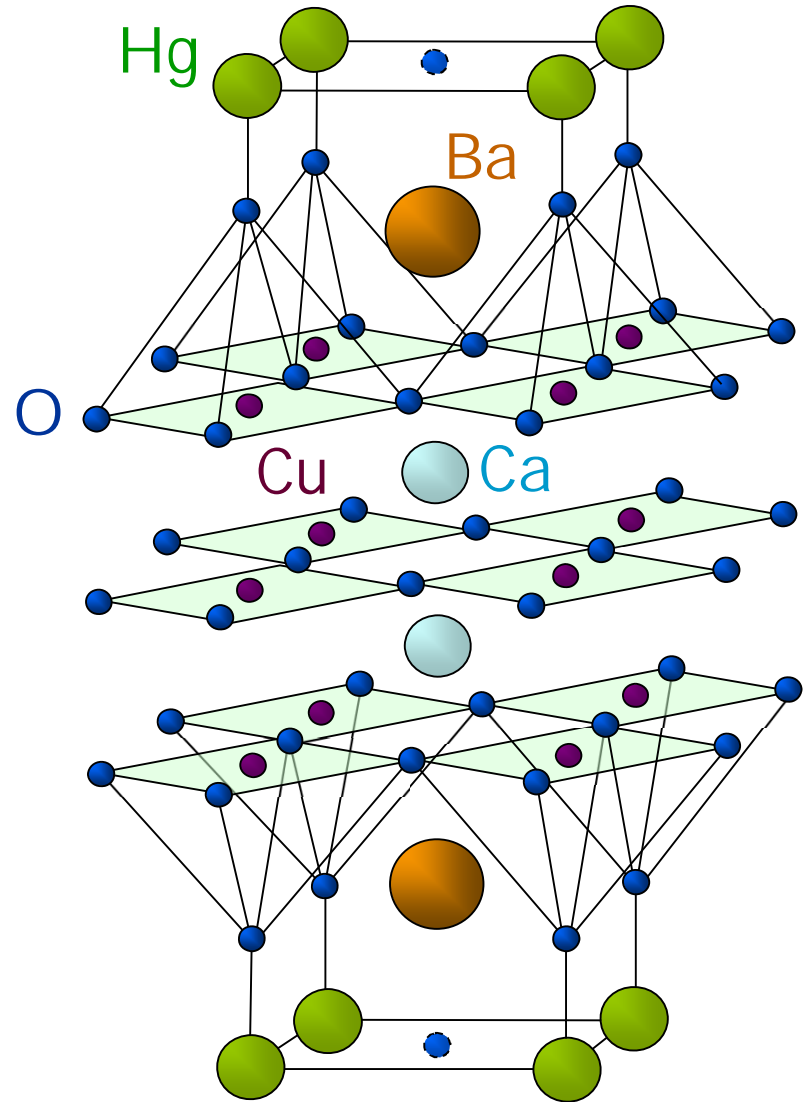
## EXERCISE 1.2.

Here is the crystal structure of the highest  $T_c$  superconductor Hg-Ba-Ca-Cu-O.

A. From this structure, derive the chemical formula of the compound. (Please explain how you ended up with the formula!):  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$

B. Do you expect fractional occupancies for any of the cation/anion sites in this structure? (Explain!): **Oxygen vacancies in Hg-O layer (otherwise Cu valence would be too high)**

C. Do the sizes of the balls properly reflect the ionic sizes of the different cations and anions in the structure?



**Hg-Ba-Ca-Cu-O**

### EXERCISE 1.3.

- A. Search for the ionic radius values for  $\text{Ca}^{2+}$ ,  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  ions, relevant to the perovskite structure (HINT: take into account the **coordination numbers**).
- B. Calculate the “tolerance factor” for the mineral perovskite  $\text{CaTiO}_3$ .

$$t = 0.966$$

- A. How well Ca and Ti match size-wise with each other considering the ideal cubic perovskite structure?
- B. To improve the match, you could as a chemist consider different modifications, for example, to control the oxygen content or to replace Ca (partly) with other alkaline earth metals. Which option you would select and why?

**For example, partial substitution of  $\text{Ca}^{2+}$  by the larger  $\text{Sr}^{2+}$**

You can find ionic radius values at:

<http://abulafia.mt.ic.ac.uk/shannon/ptable.php>

## EXERCISE 1.4.

- A. Calculate the “tolerance factor” for the perovskite  $\text{LaMnO}_3$ .  $t = 0.954$
- B. Based on this value, do you expect that Mn in this compound has a tendency to be reduced or oxidized? Explain!

**Oxidized (to decrease the ionic radius of Mn)**

- A. How do you think this predicted tendency could be realized in this compound? Explain! **Cation vacancies (as there is no space in perovskite structure for excess oxygen interstitials)**

You can find ionic radius values at:

<http://abulafia.mt.ic.ac.uk/shannon/ptable.php>

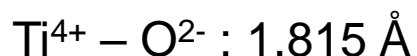
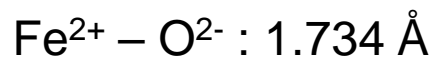
## EXERCISE 2.1.

Ilmenite structure of  $\text{FeTiO}_3$  consists of  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  ions within two types of oxygen octahedra: smaller (blue) and larger (red).

BVS calculation has been utilized to assign the locations of the metal ions; it is believed that  $\text{Fe}^{2+}$  ions are within the larger octahedra and  $\text{Ti}^{4+}$  ions within the smaller octahedra. The experimentally observed bond lengths and the BVS calculation results are shown here in the figure.

To have an idea how clear the above site-assignment conclusion is, you could calculate the BVS values for iron and titanium in the opposite case too, i.e. Fe occupying the smaller octahedra and Ti occupying the larger octahedra. Please, also repeat the original calculation to check that you get the same values as shown in the figure, with your parameters. Finally, make also a short conclusive discussion..

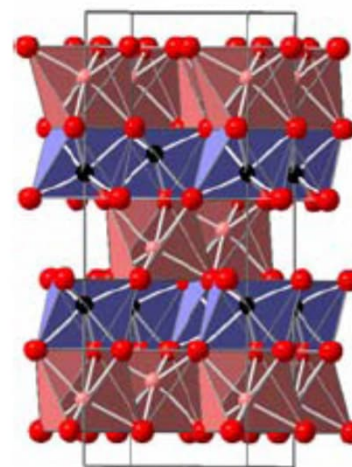
Use the following  $R^0$  values:



$$s_{ij} = \exp \left[ \frac{(R_{ij}^0 - d_{ij})}{0.37} \right]$$

$$V_i = \pm \sum_j s_{ij}$$

### $\text{FeTiO}_3$ (Ilmenite)



#### Bond Distances

$$\text{Fe-O} = 3 \times 2.07, 3 \times 2.20$$

$$\text{Ti-O} = 3 \times 1.88, 3 \times 2.09$$

#### Bond Valence Sums

$$\text{Fe} = 3 \times 0.40 + 3 \times 0.28 = 2.04$$

$$\text{Ti} = 3 \times 0.84 + 3 \times 0.48 = 3.96$$

$$\text{O} = 0.40 + 0.28 + 0.84 + 0.48 = 2.00$$

$$s_{ij} = \exp \left[ \frac{(R_{ij}^0 - d_{ij})}{0.37} \right] \quad V_i = \pm \sum_j s_{ij}$$

## EXERCISE 2.2.

- Looking at the formula to calculate the bond valence, can you see what kind of evident meaning the  $R^0$  value has?
- From this formula, what happens to the bond valence when the bond gets longer?
- Divalent copper is a typical Jahn Teller (JT) ion, meaning that when it exists in an octahedral coordination, the octahedron tends to get deformed such that two of the bonds are elongated and four are shortened. Compare the BVS values for the two hypothetical extreme cases with the same average bond length value, but in one case strongly JT-distorted and in the other case with no distortion. What kind of observation / general conclusion you can make from your calculation result?

- JT-distorted:  $4 \times 1.95 \text{ \AA} + 2 \times 2.55 \text{ \AA}$

- Non-JT:  $6 \times 2.15 \text{ \AA}$

$R^0$ :  $\text{Cu}^{2+}-\text{O}^{2-}$   $1.68 \text{ \AA}$

**JT-distorted: 2.12**

**Non-JT: 1.68**



## EXERCISE 2.3.

- A. Below given are the bond lengths determined for the Cu-O bonds in a superconducting  $\text{Cu(1)Ba}_2\text{YCu(2)}_2\text{O}_{7-\delta}$  sample. Calculate the bond valences and bond-valence-sums for Cu(1) and Cu(2) atoms.

**Cu(1) 2.30; Cu(2) 2.23**

- A. Assume that these are the true valence values for Cu(1) and Cu(2), and estimate the  $\delta$  value in the  $\text{Cu(1)Ba}_2\text{YCu(2)}_2\text{O}_{7-\delta}$  formula.

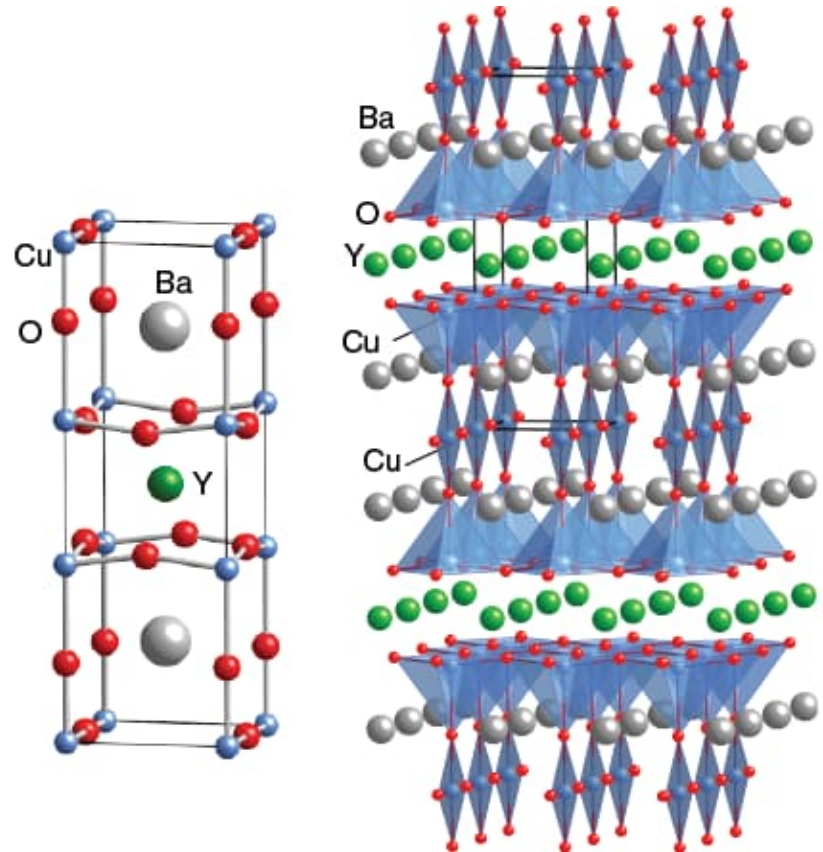
**Oxygen content: 6.88**

Cu(1)	2 x 1.86 Å
	2 x 1.91 Å
Cu(2)	2 x 1.92 Å
	2 x 1.94 Å
	1 x 2.26 Å

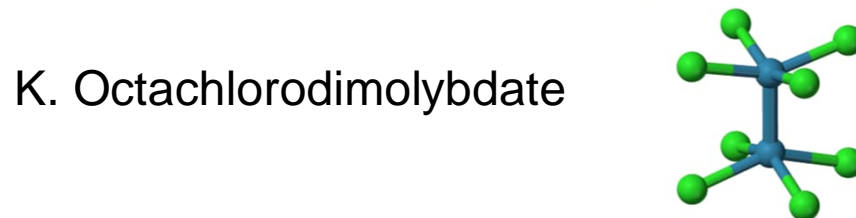
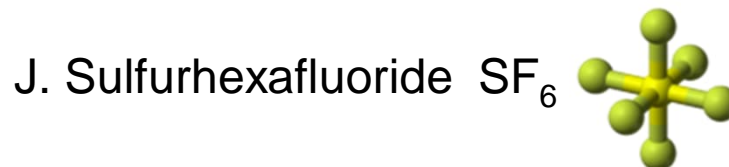
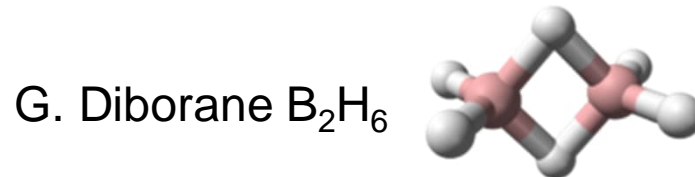
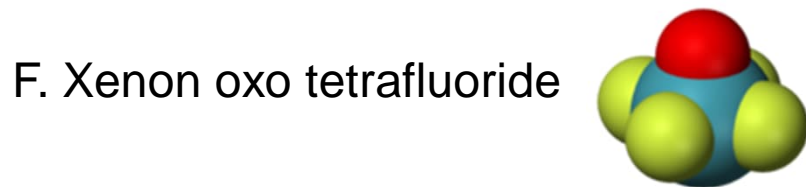
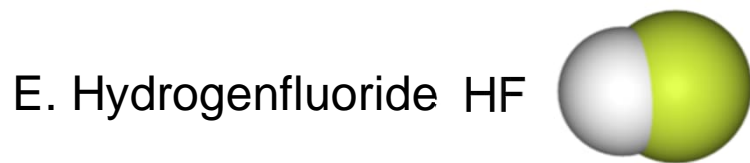
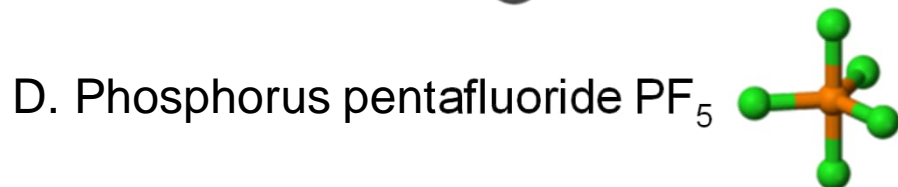
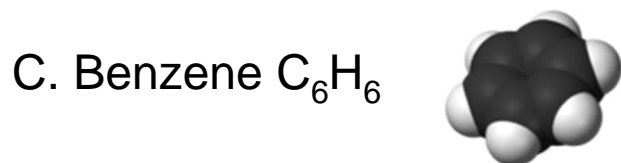
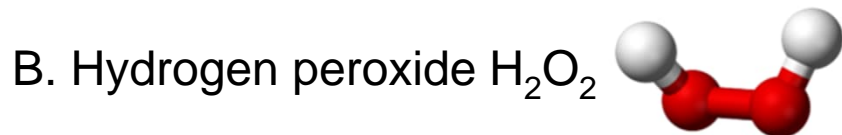
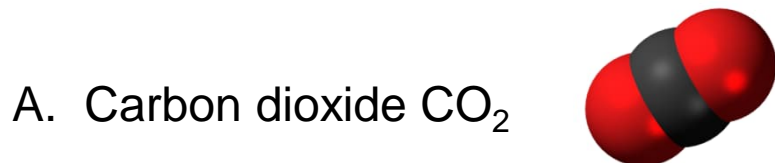
$$s_{ij} = \exp \left[ \frac{(R_{ij}^0 - d_{ij})}{0.37} \right]$$

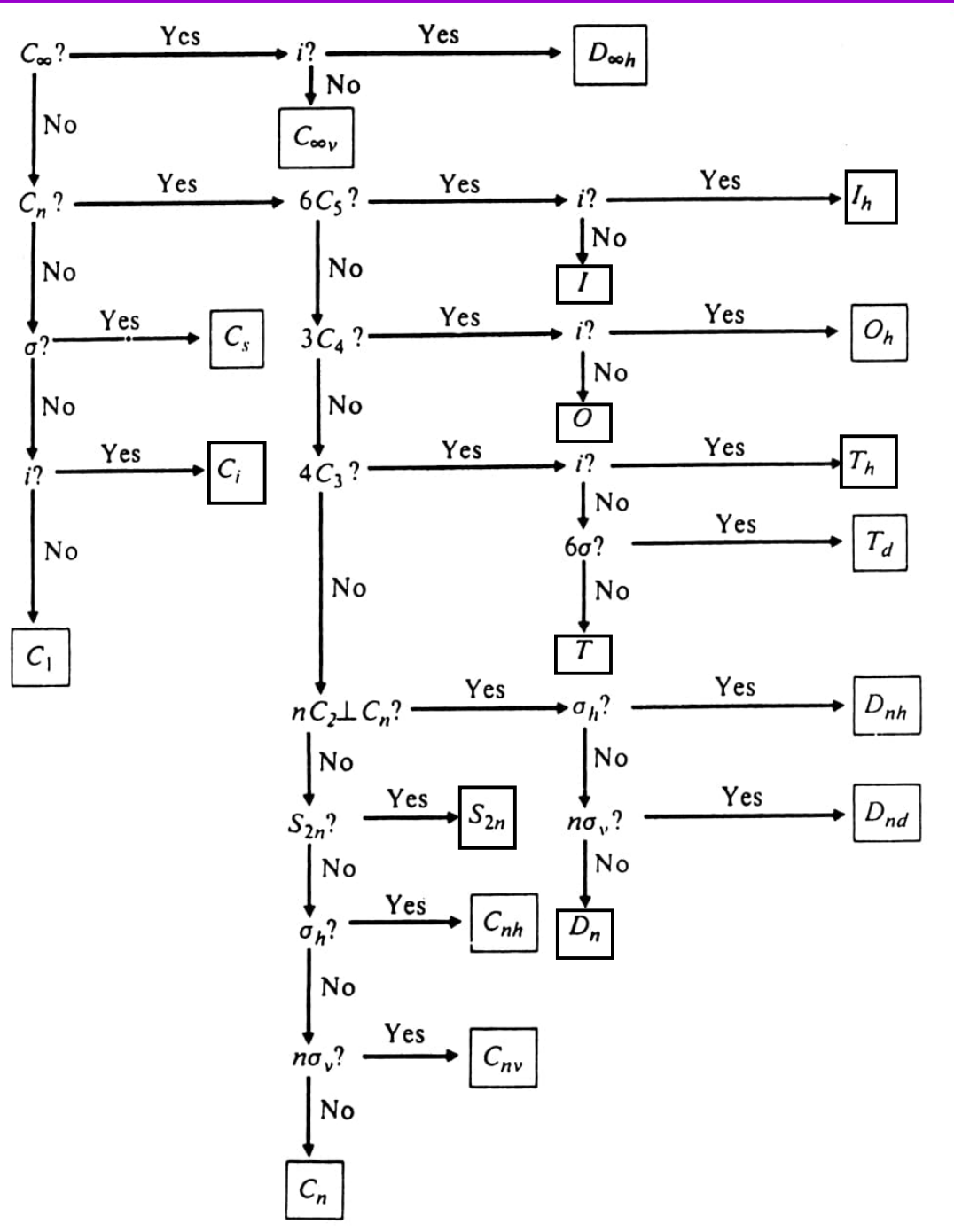
$$V_i = \pm \sum_j s_{ij}$$

$$R^0: \text{Cu}^{2+}-\text{O}^{2-}: 1.679 \text{ \AA}$$



**EXERCISE 2.4.** Determine the point group for the following molecules/ions:





# EXAMPLES

1. hiilidioksidi  $\text{CO}_2 \rightarrow D_{\infty h}$
2.  $\text{CH}_3\text{-CCl}_3$  (lomittainen)  $\rightarrow C_{3v}$
3. vetyperoksidi  $\text{H}_2\text{O}_2 \rightarrow C_2$
4. bentseeni  $\text{C}_6\text{H}_6 \rightarrow D_{6h}$
5.  $\text{SiFClBrI} \rightarrow C_1$
6. rikkiheksafluoridi  $\text{SF}_6 \rightarrow O_h$
7. vetyfluoridi  $\text{HF} \rightarrow C_{\infty v}$
8. ksenonoksitetrafluoridi  $\rightarrow C_{4v}$
9. diboraani  $\text{B}_2\text{H}_6 \rightarrow D_{2h}$
10. *trans*- $\text{C}_2\text{H}_2\text{Cl}_2 \rightarrow C_{2h}$
11. sulfyryylifluoridi  $\rightarrow C_{2v}$
12. booritrifluoridi  $\text{BF}_3 \rightarrow D_{3h}$
13. fosforipentafluoridi  $\text{PF}_5 \rightarrow D_{3h}$
14. fosforitrifluoridi  $\text{PF}_3 \rightarrow C_{3v}$
15. metaani  $\text{CH}_4 \rightarrow T_d$
16. ksenontetrafluoridi  $\text{XeF}_4 \rightarrow D_{4h}$
17.  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$  (lomittainen)  $\rightarrow D_{2d}$
18. oktaklorodimolybdaatti  $\rightarrow D_{4h}$

## EXERCISE 2.5.

$\text{Ni}(\text{CN})_4^{2-}$  ion has  $D_{4h}$  symmetry.

What can you tell about its structure based on that ?

**Symmetry elements:**

**1  $C_4$  rotation axis +**

**4  $C_2$  rotation axis perpendicular to  $C_4$**

**Conclusions: - flat molecule**

**- Ni-C-N bond angles  $180^\circ$**

**- C-Ni-C bond angles  $90^\circ$**

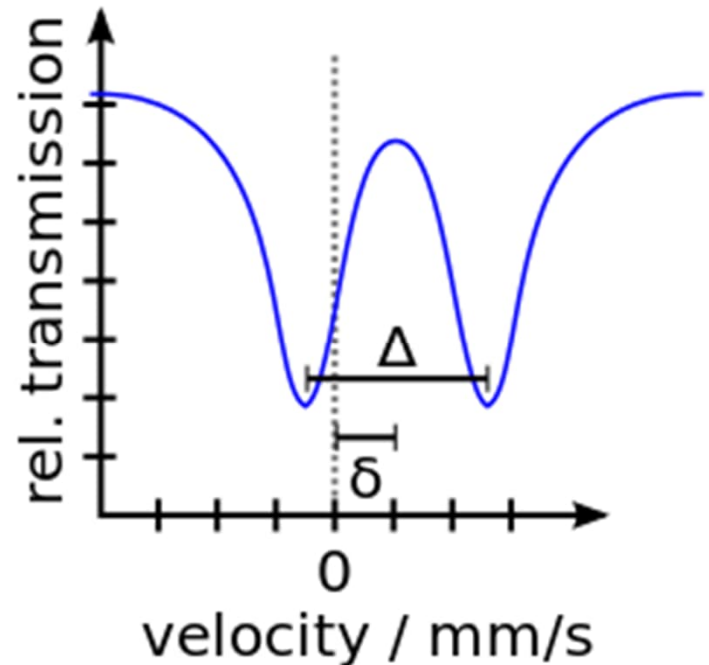
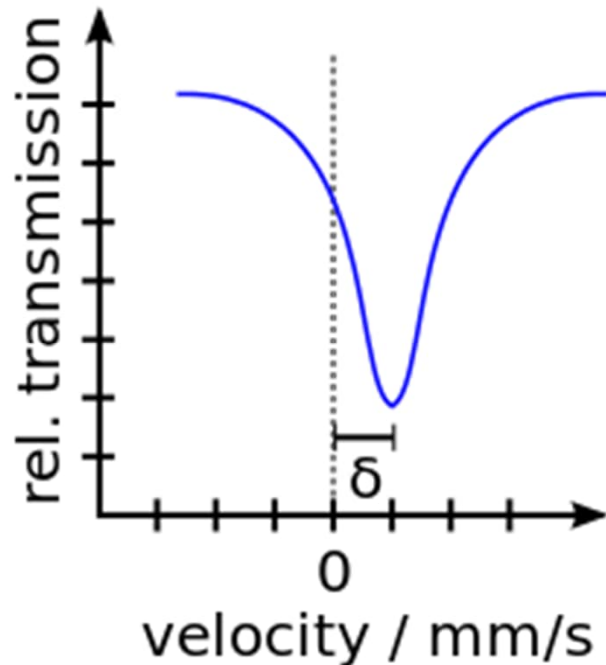
**- all four Ni-C bonds of equal length**

**- all four C-N bonds of equal length**

## EXERCISE 6.1.

Below are two  $^{57}\text{Fe}$  Mössbauer spectra. What can you tell of the two samples, individually and in comparison to each other?

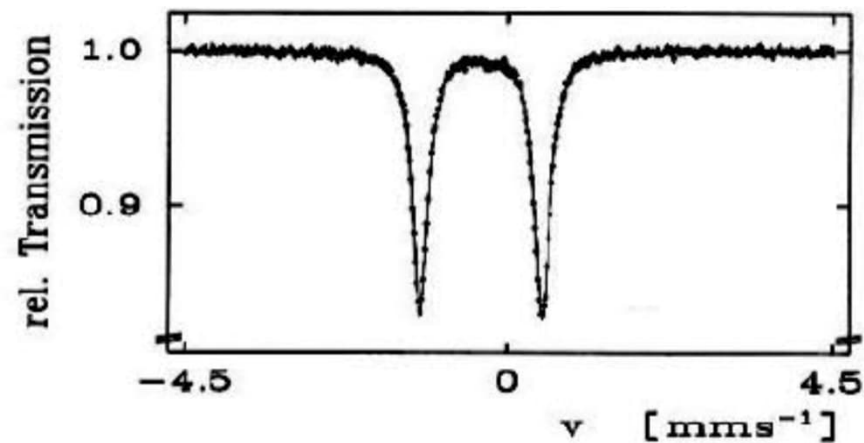
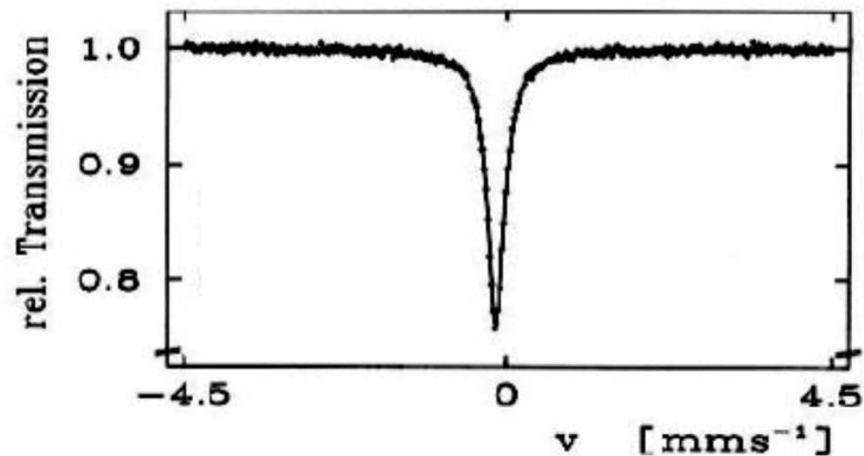
- In both samples, only one type of iron species exist
- The isomer shift values are similar, so the iron valence seems to be the same in the two samples (to judge what this valence value is, you would need to compare to the (tabulated) reference data)
- In the left-hand-side sample the iron surroundings (coordination sphere) is symmetric, while in the right-hand-side sample asymmetric
- Neither of the samples is magnetically ordered (at this temperature)



## EXERCISE 6.2.

The two Mössbauer spectra here are for the  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$  compounds.

Assign each spectrum to the correct compound; can you say anything about the oxidation states of iron in these samples? Do not forget to explain/motive your answers.



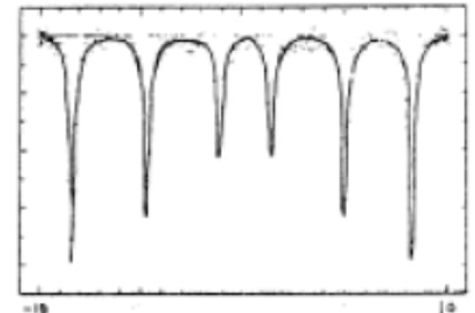
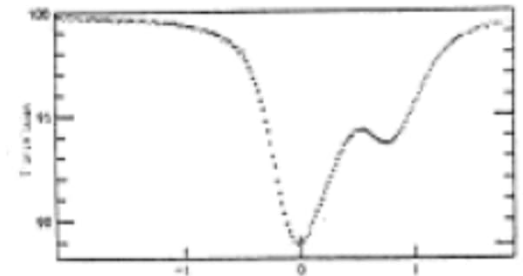
## EXERCISE 6.3.

Assign the four Mössbauer spectra to the four compounds, and explain WHY!

- $\alpha\text{-Fe}_2\text{O}_3$  (antiferromagnetic)
  - $\text{KFe(III)[Fe(II)(CN)}_6\text{]}$
  - $\text{FeSO}_4$
  - $\text{NdFeO}_3$  (perovskite)
- 
- $\alpha\text{-Fe}_2\text{O}_3$  is magnetic  $\rightarrow$  bottom spectrum
  - $\text{NdFeO}_3$  is perovskite with quite symmetric octahedron around iron  $\rightarrow$  top spectrum
  - In  $\text{KFe(III)[Fe(II)(CN)}_6\text{]}$  two different iron species with different valence states  $\rightarrow$  second from the bottom
  - In  $\text{FeSO}_4$  only one iron type, but apparently in asymmetric coordination  $\rightarrow$  second from the top



0 1 2 3 4 5





## EXERCISE 6.4.

**Please have a look at the following research article, and explain how the thin film sample was prepared for the Mössbauer measurement. Depending your interest, you may also (extra) to think what kind of information Mössbauer spectroscopy could provide in this case.**

T. Jussila, A. Philip, J. Linden and M. Karppinen, High-quality magnetically hard  $\epsilon$ - $\text{Fe}_2\text{O}_3$  thin films through ALD for room-temperature applications, *Advanced Engineering Materials* **25**, 2201262 (2023).

## EXERCISE 6.5.

**Please have a look at the two research articles referenced below, and explain why EXAFS in these cases is uniquely suitable to address the research question.**

Vega-Castillo et al,  
On the local order of amorphous  $\text{La}_2\text{Mo}_2\text{O}_{6.7}$ ,  
*Dalton Transactions* 46, 7273 (2017).

Walshe et al.,  
An EXAFS and HR-XANES study of the uranyl peroxides  $[\text{UO}_2(\eta^2\text{-O}_2)(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$  ( $n = 0, 2$ ) and uranyl (oxy)hydroxide  $[(\text{UO}_2)_4\text{O}(\text{OH})_6] \cdot 6\text{H}_2\text{O}$ ,  
*Dalton Transactions* 43, 4400 (2014).