Structural aspects of B K edge XANES of minerals

O. Šipr,[1] A. Šimůnek,[1] J. Vackář,[1] F. Rocca[2], G. Dalba[3]

[1] Institute of Physics, Academy of Sciences of the Czech Republic, Prague

[2] Istituto di Fotonica e Nanotecnologie del CNR, Sezione "ITC-CeFSA", Povo (Trento), Italy

[3] INFM and Dipartimento di Fisica, Università di Trento, Povo (Trento), Italy

Outline

- Introducing XANES technique

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- Spectra of minerals with pure BO_3 or BO_4 coordinations

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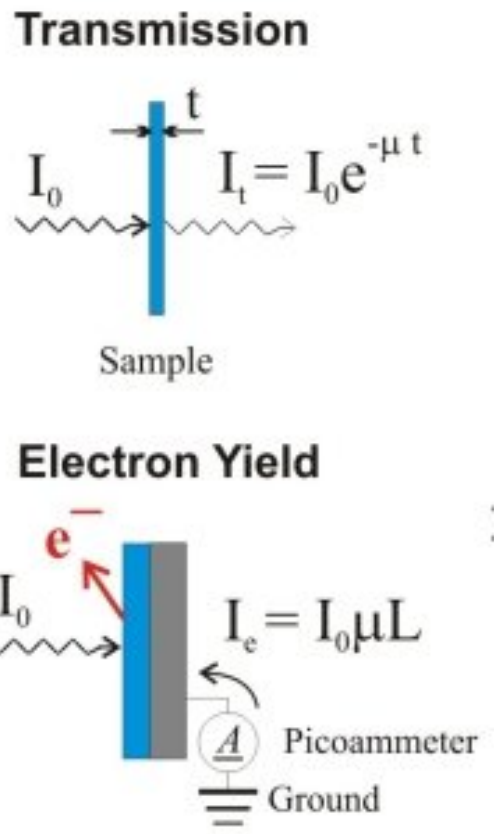
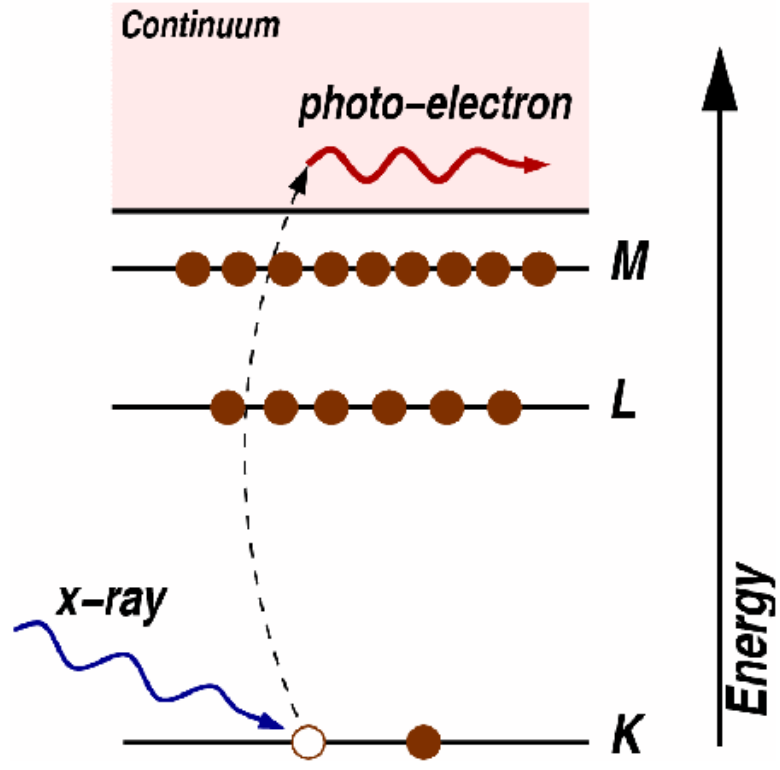
- Search for markers of BO_3 and BO_4 coordinations in XANES spectra
- Explore influence of technical parameters (scattering potential, core hole, size of cluster)
- Inspect prospective use of B K edge XANES in quantitative studies of structure of glasses

X-ray absorption spectroscopy in a nutshell

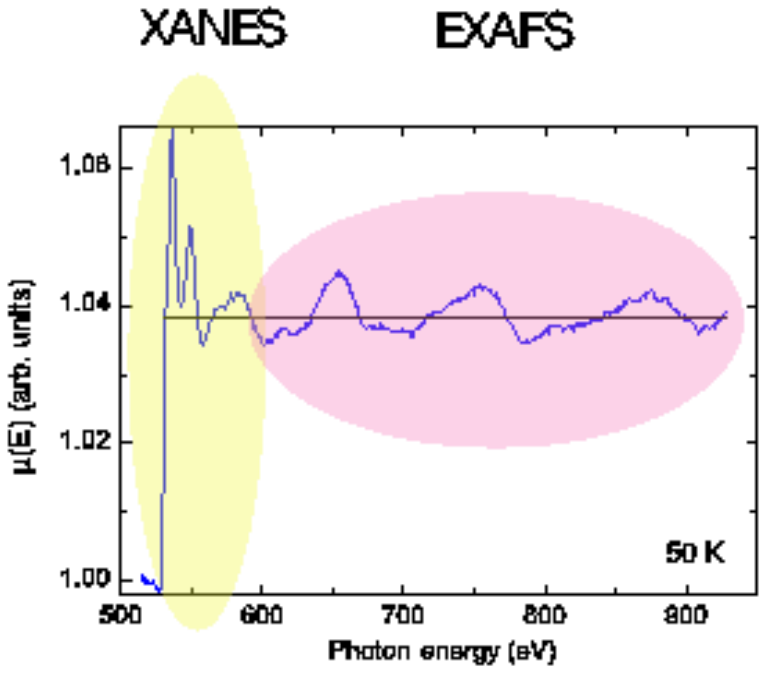
X-ray absorption spectroscopy





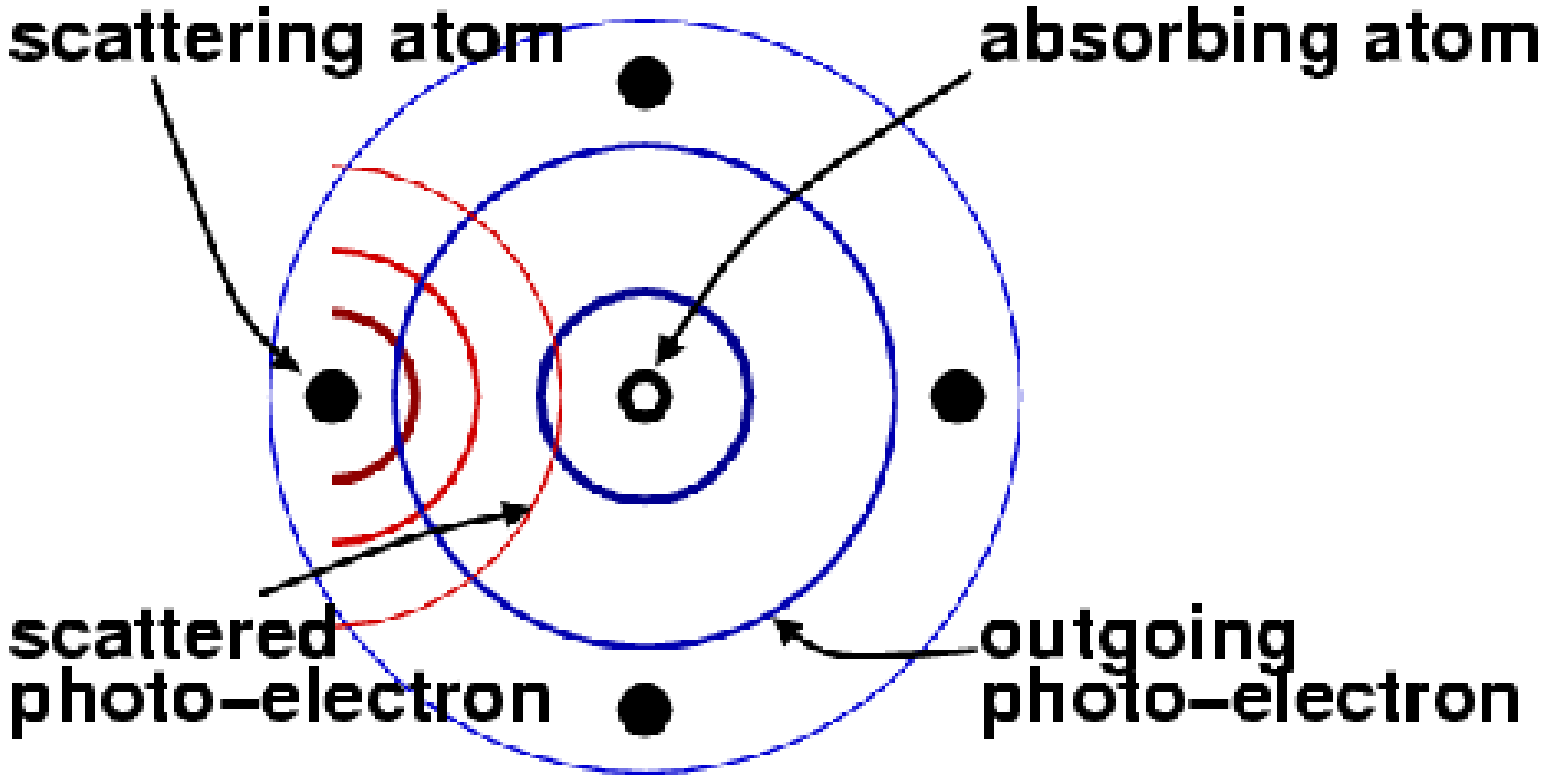
- x-rays are absorbed in the sample via a photoelectron effect
- more detection techniques are possible

Taxonomy



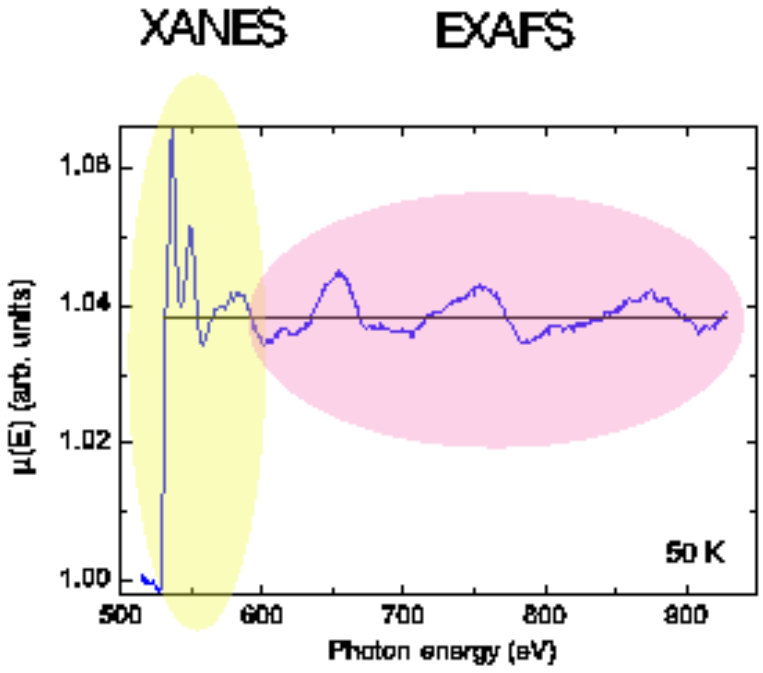
- Low photoelectron energies (≤ 50 eV) $\rightarrow$ XANES
  (**X**-ray **A**bsorption **N**ear **E**dge **S**tructure)
- High photoelectron energies (100–1000 eV) $\rightarrow$ EXAFS
  (**E**xtended **X**-ray **A**bsorption **F**ine **S**tructure)

Local probe



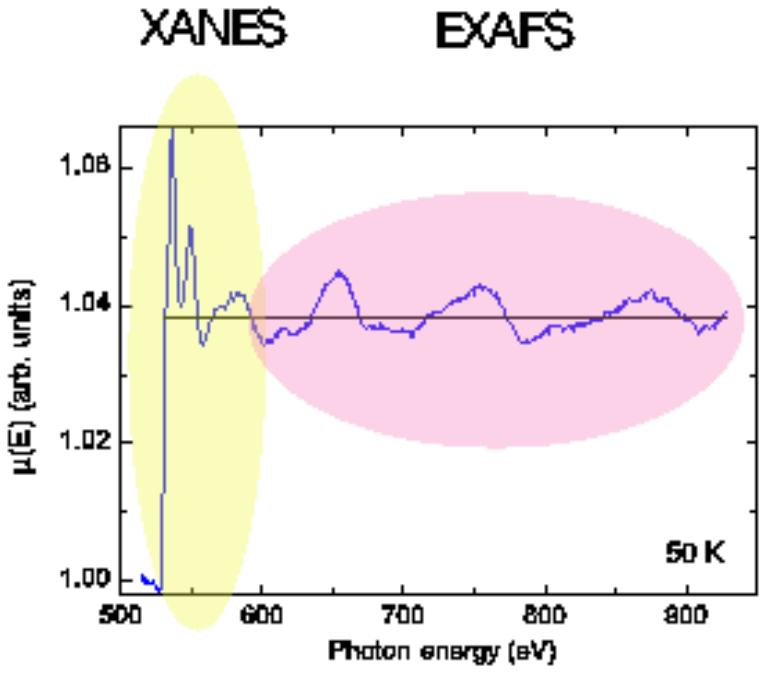
- Offers a view from one particular site (chemically selective)
- Outgoing photoelectron is scattered by the neighbors
- Constructive/destructive interference depending on interatomic distance

EXAFS



- Several approximations possible in the EXAFS region
- Structural information can be “straightforwardly” extracted
- EXAFS oscillations are sometimes too faint to measure

XANES



- Physics more complicated
- Some structural information is there but difficult to extract
- “Fingerprinting” may be dangerous (no unique correspondence between structural elements and spectral features)

Theoretical framework

- Spectra calculated in a real space (finite clusters of 100-250 atoms)

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- Spectra calculated in a real space (finite clusters of 100-250 atoms)
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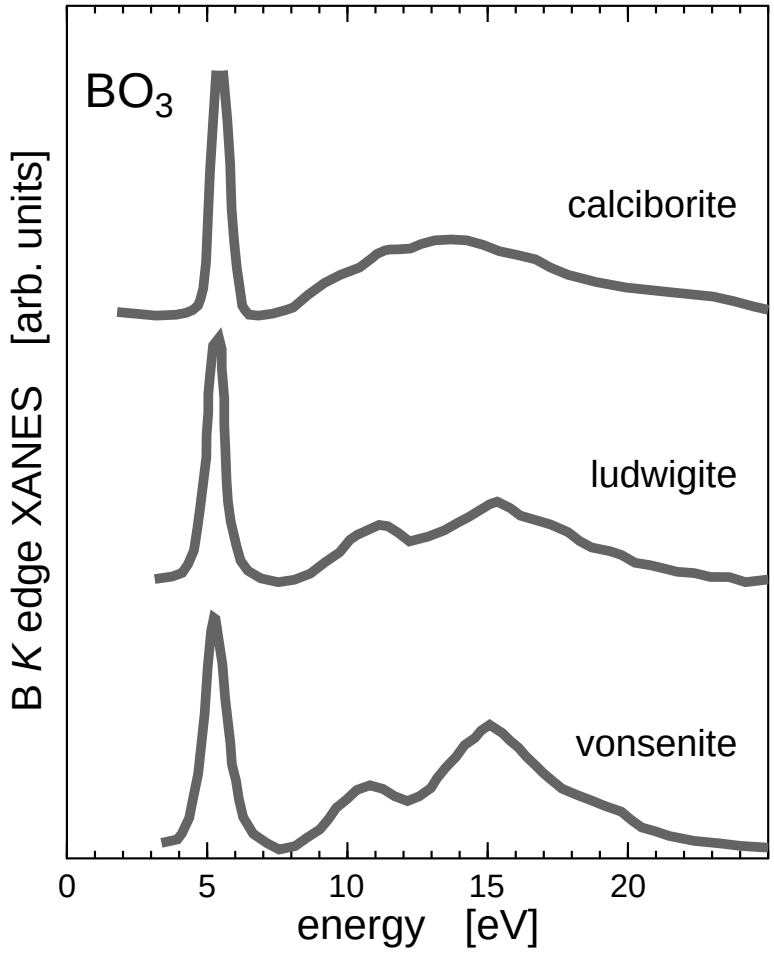
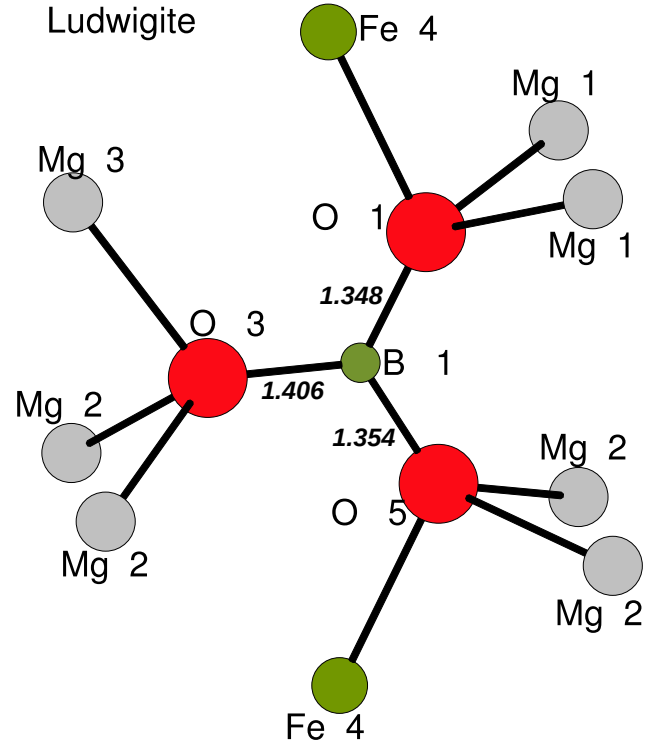
- Scattering potentials mostly non-self-consistent (Mattheiss prescription) [checked that self-consistent potentials yield similar results]
- Core hole treated statically (final state rule, “relaxed and screened” model)

Minerals with only one boron site

Minerals with only BO_3 units





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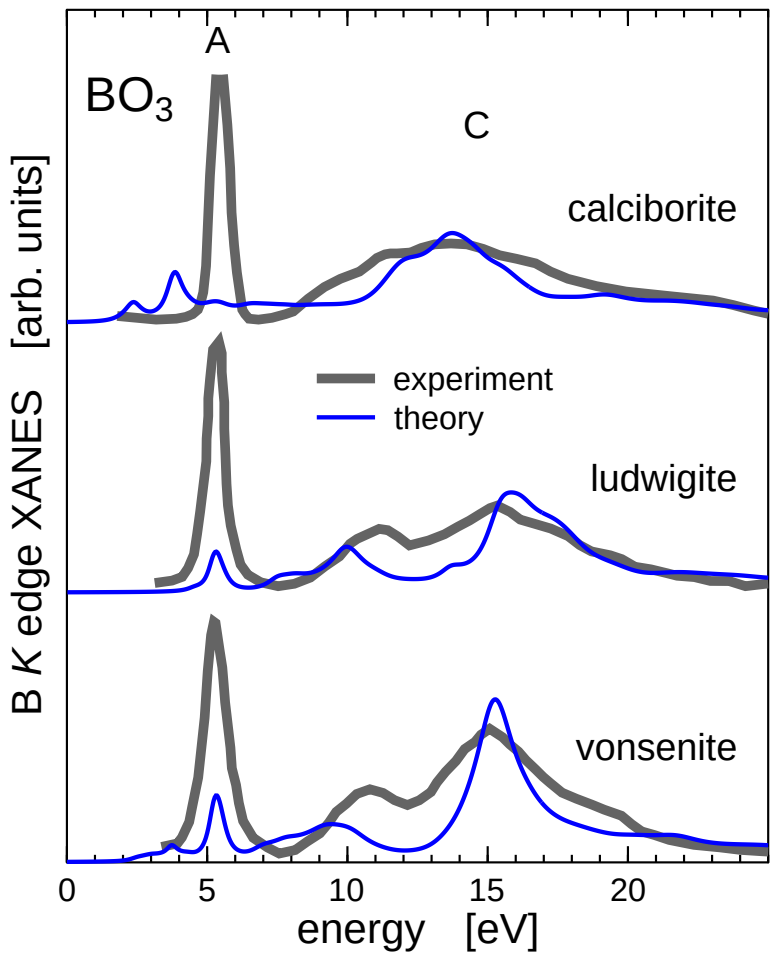
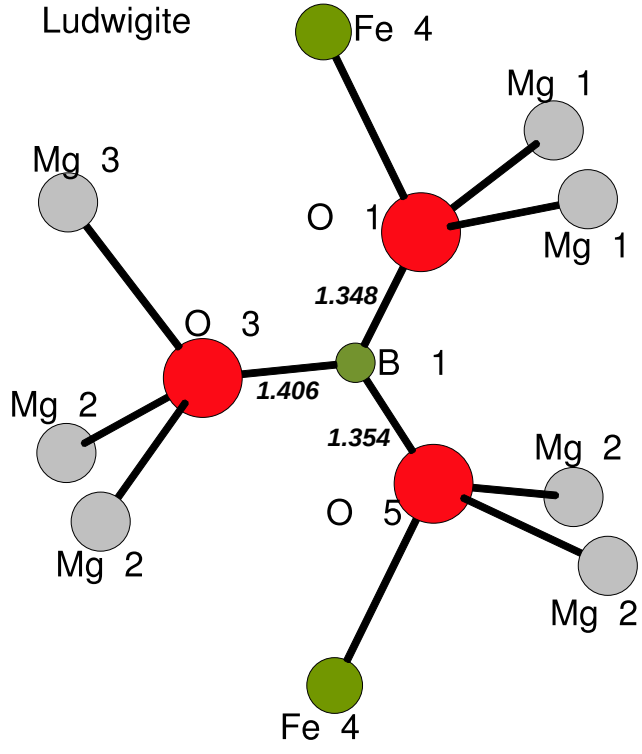
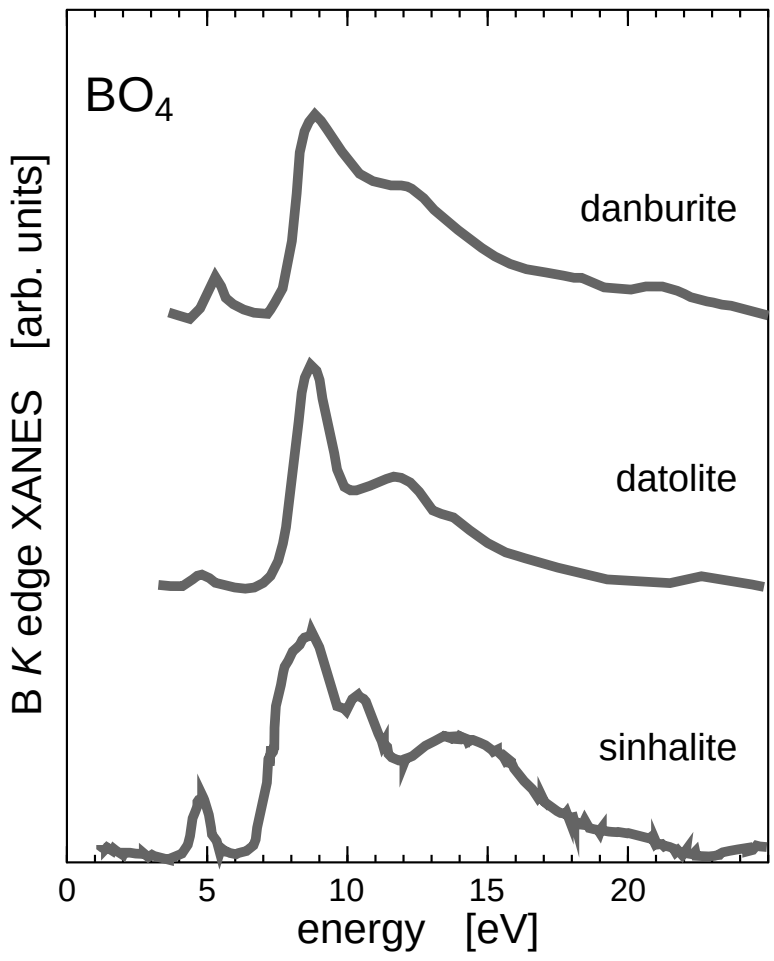
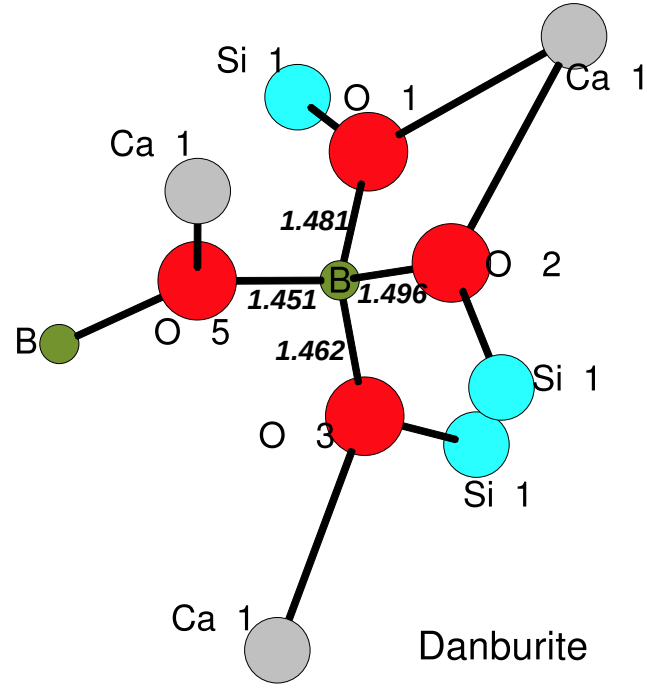




- Pre-peak followed by a main peak, about 10 eV apart

Minerals with only BO_4 units





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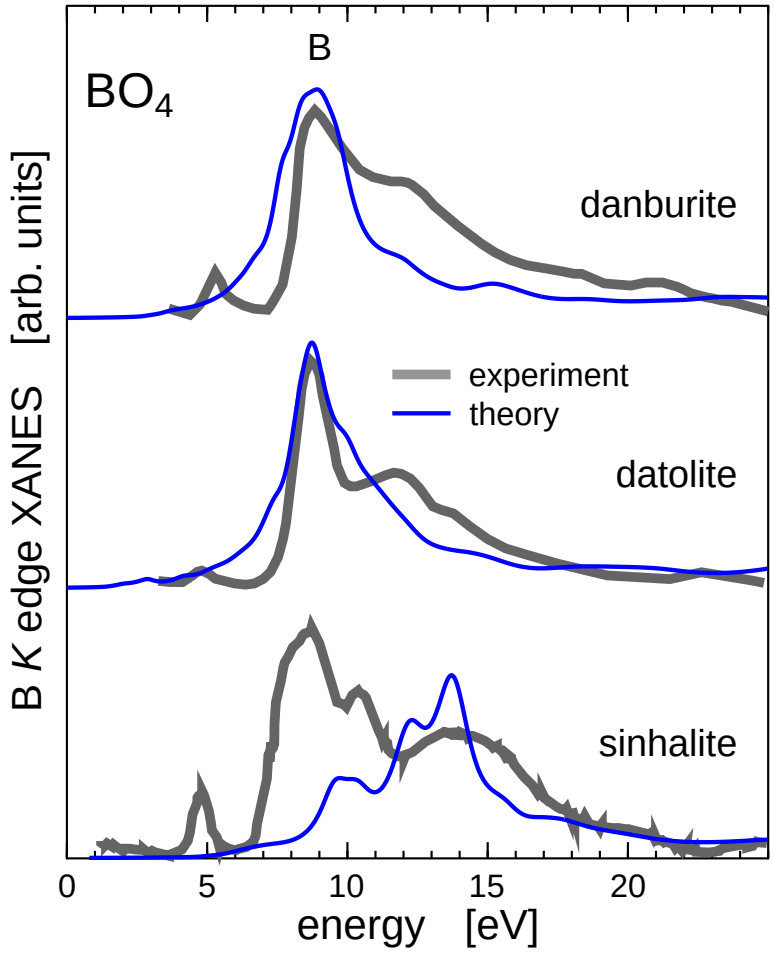
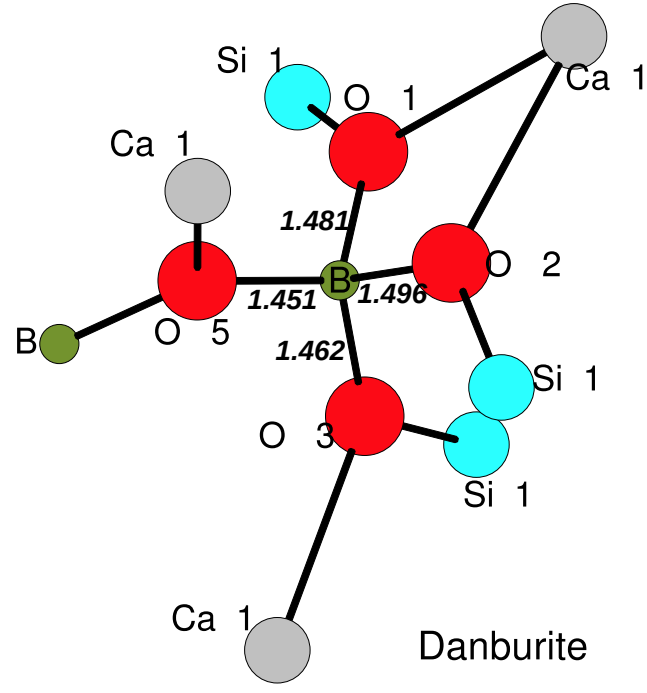
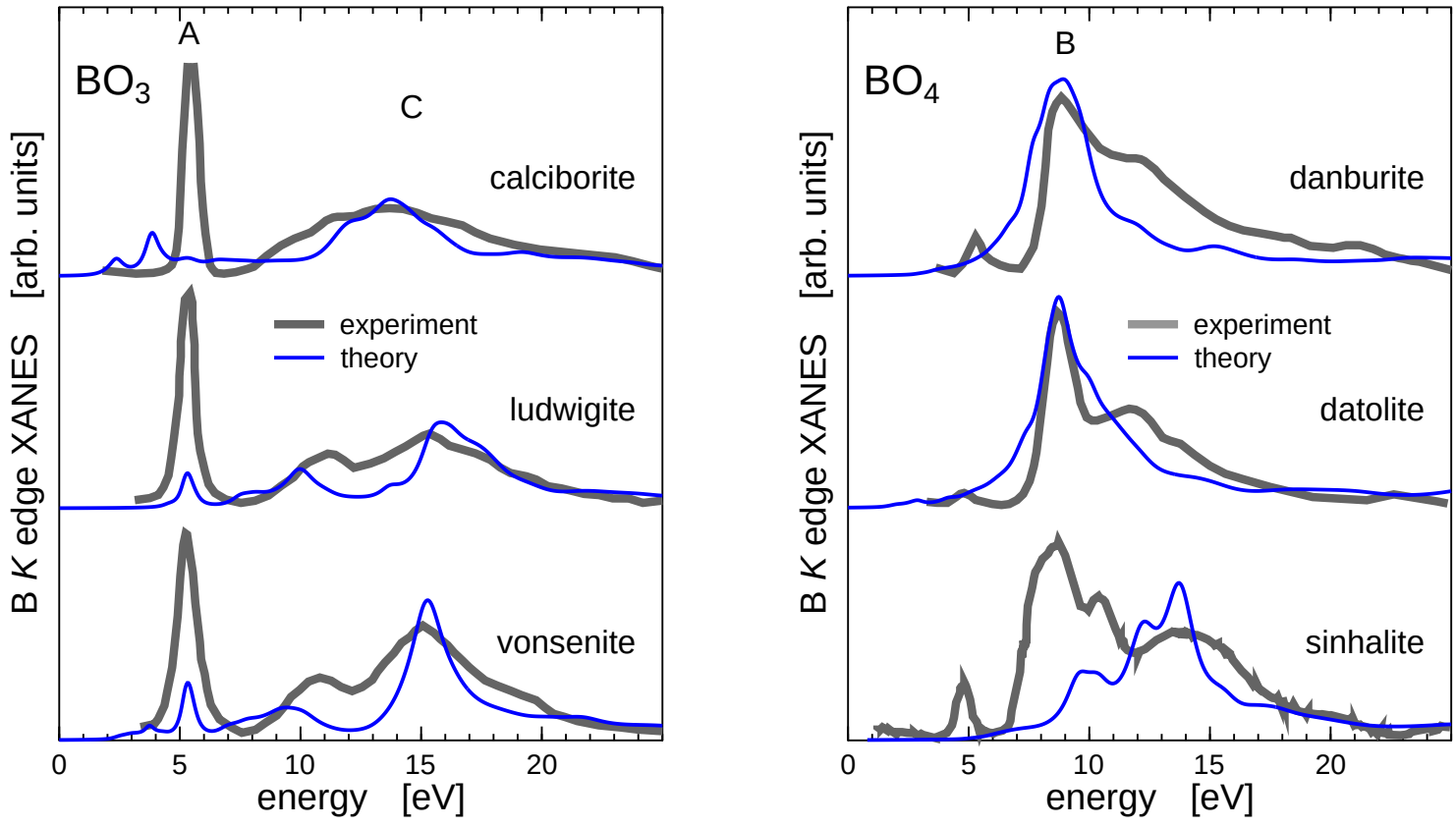




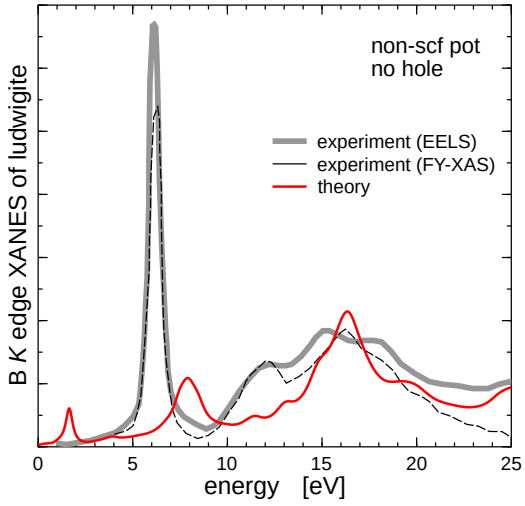
- Experiment: Main peak with a shoulder
- Theory: Single peak

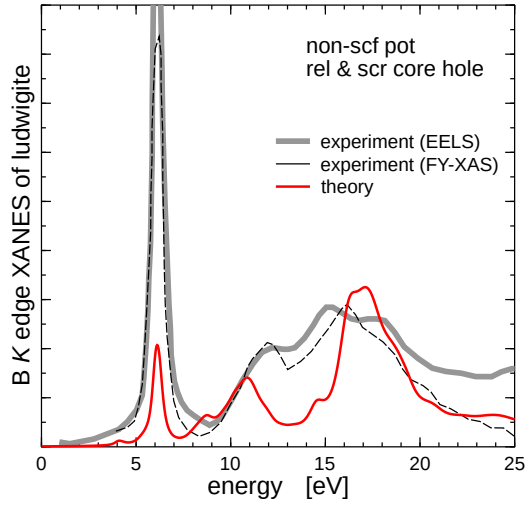
Basic typology

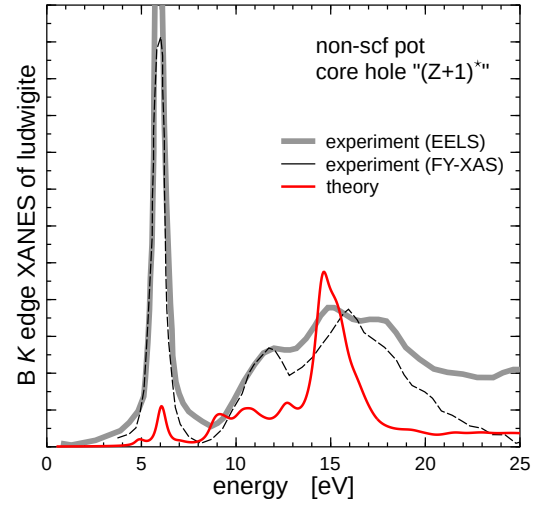


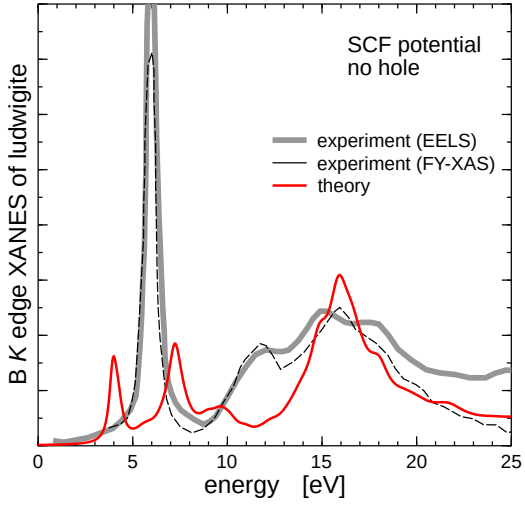
- Characteristic shapes of XANES spectra depend on the presence of either BO_3 or BO_4 unit

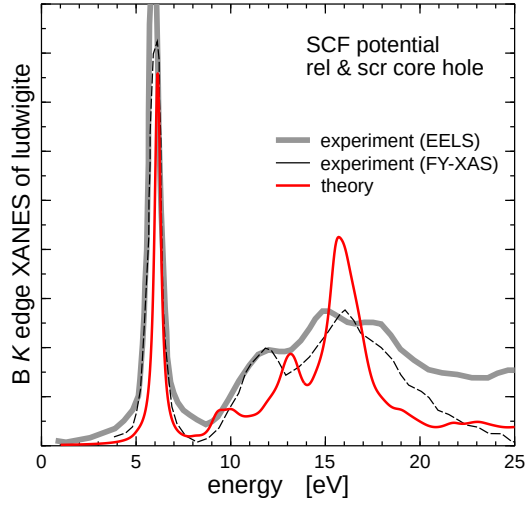
Using various scattering potentials

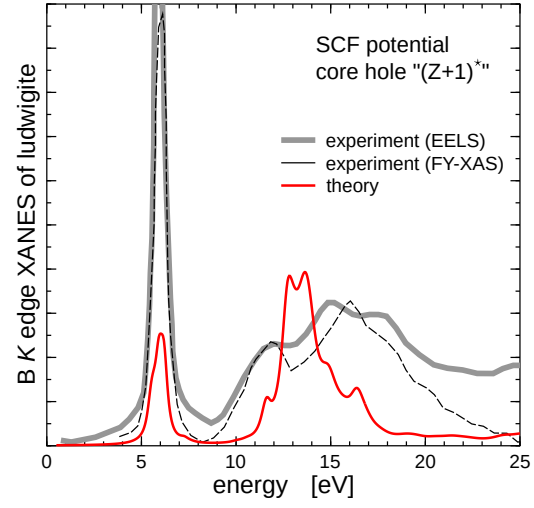




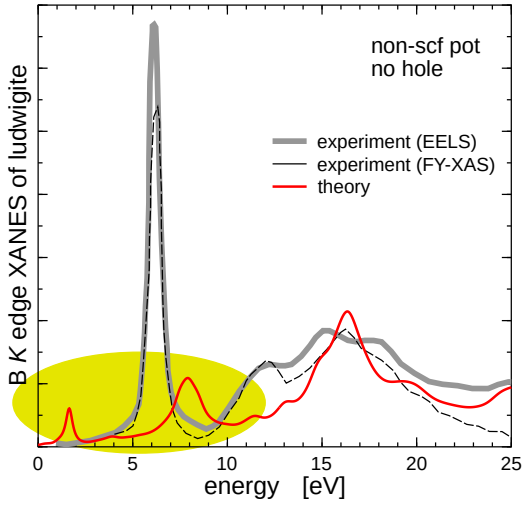


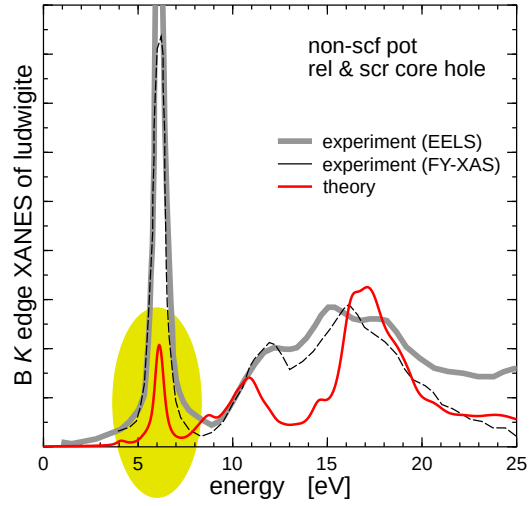


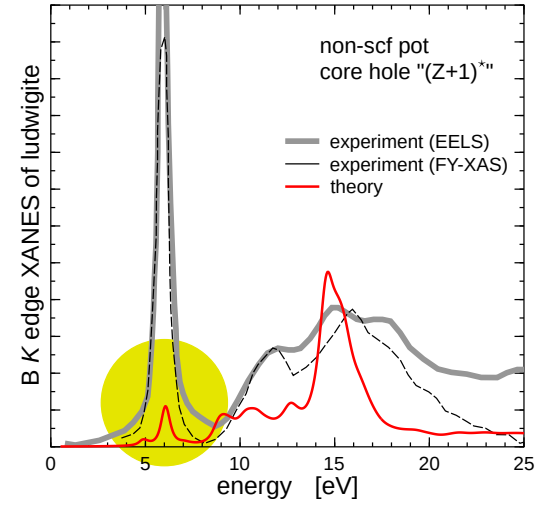


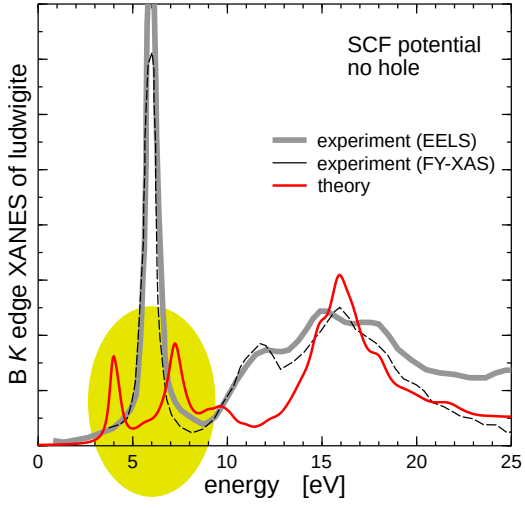


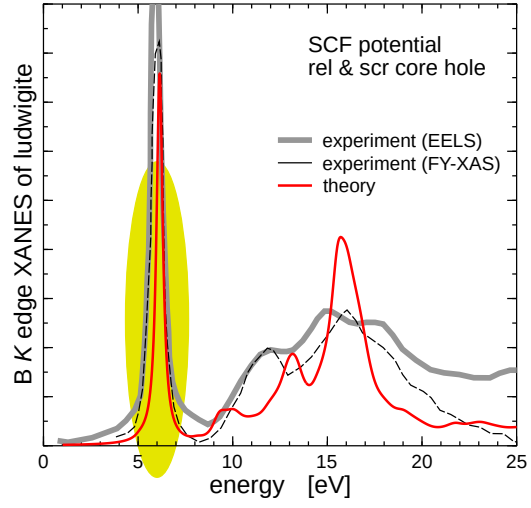
Core hole effect at the pre-edge

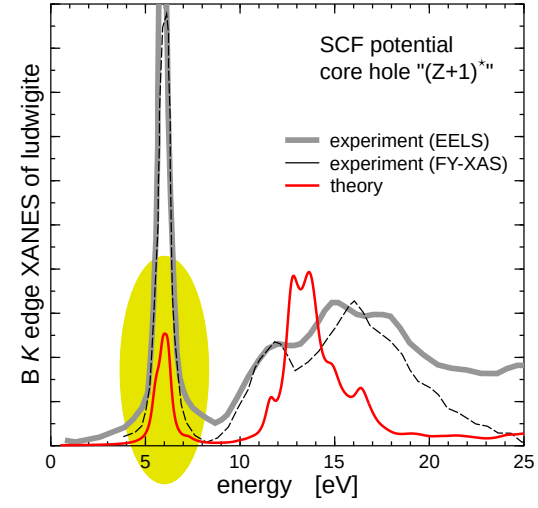




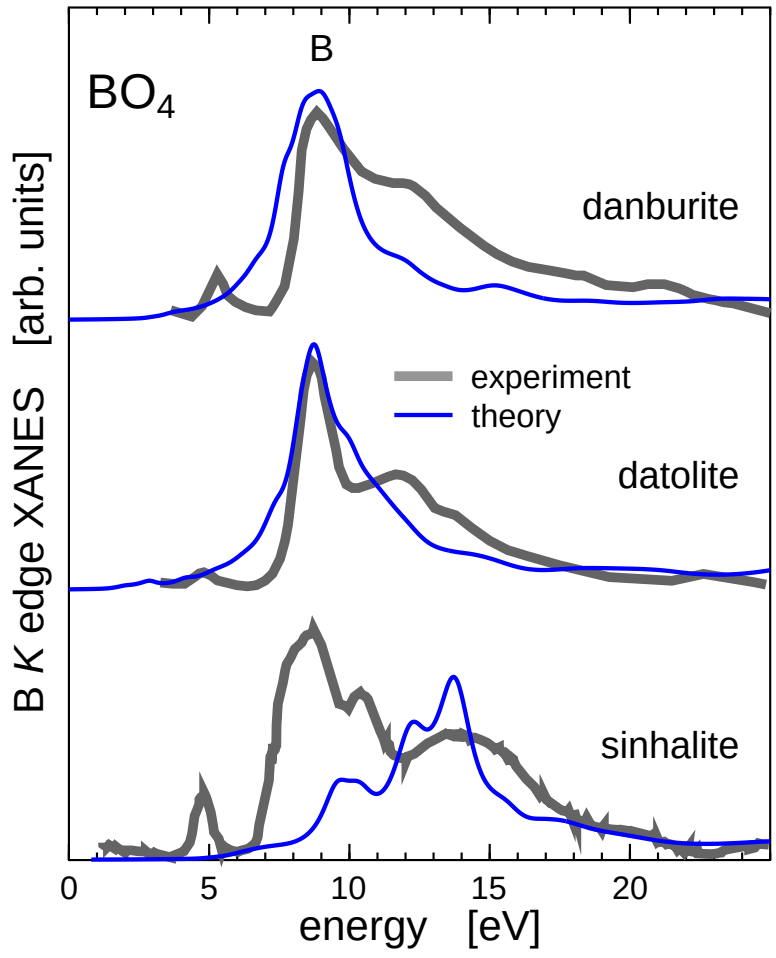








Sinhalite does not quite follow the herd



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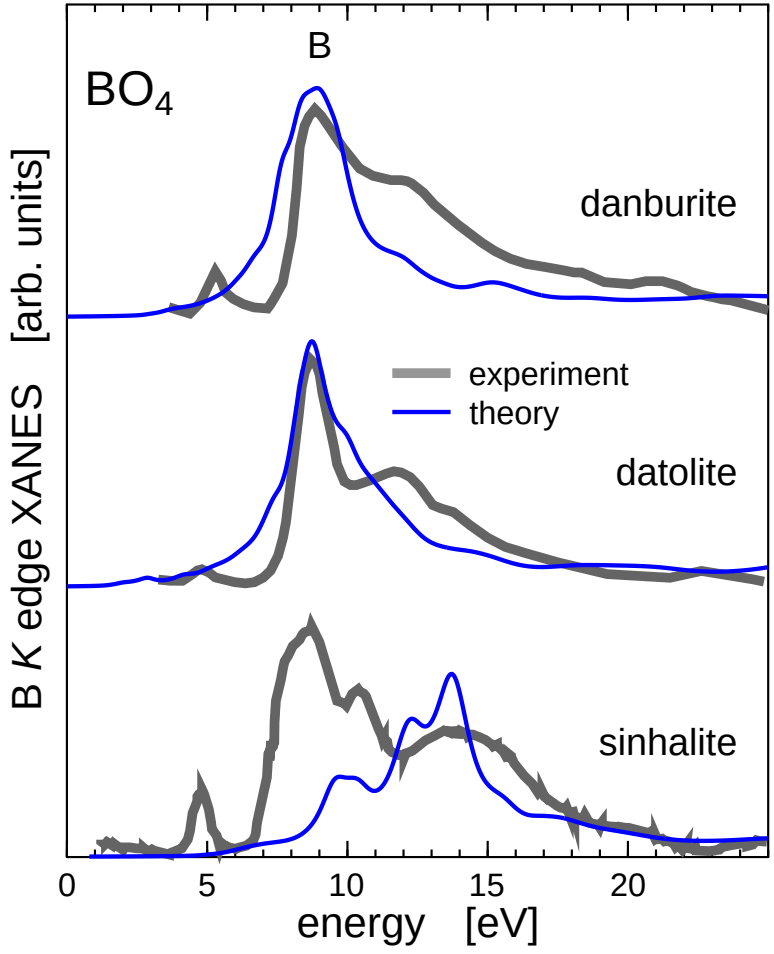
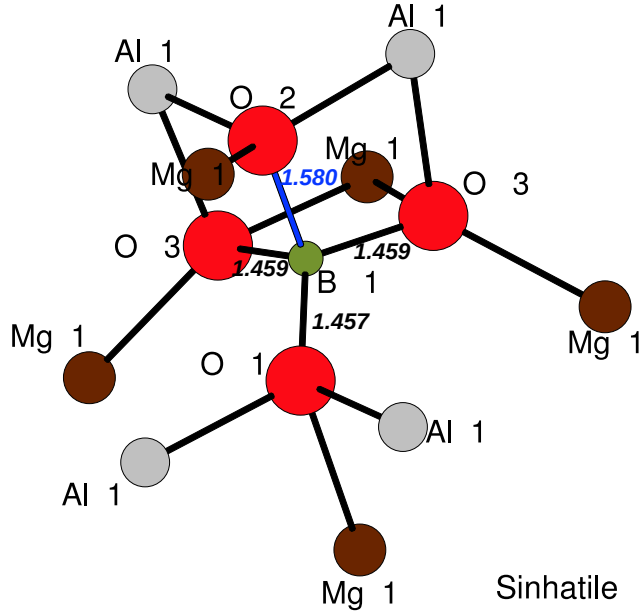
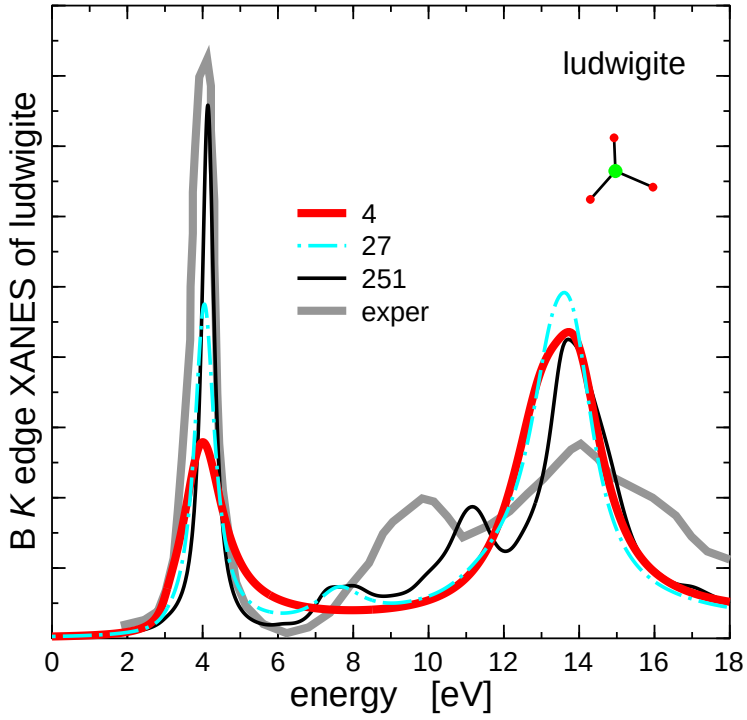
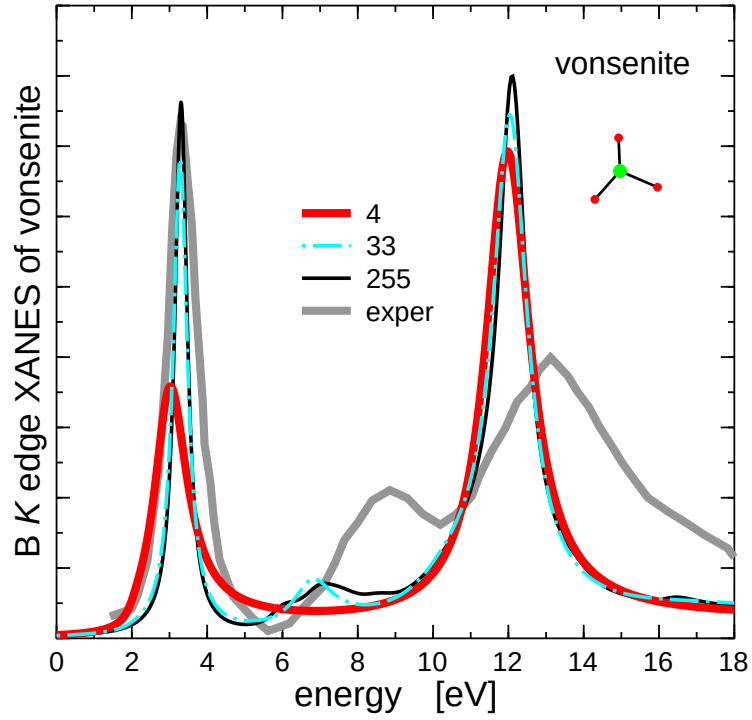




- Three B-O bonds of 1.46 Å, one bond of 1.58 Å
  $\Rightarrow$ it is rather a 3+1 coordination

Cluster size effect — BO_3 units





- Spectra for clusters of 4 atoms and of 250 atoms are very similar

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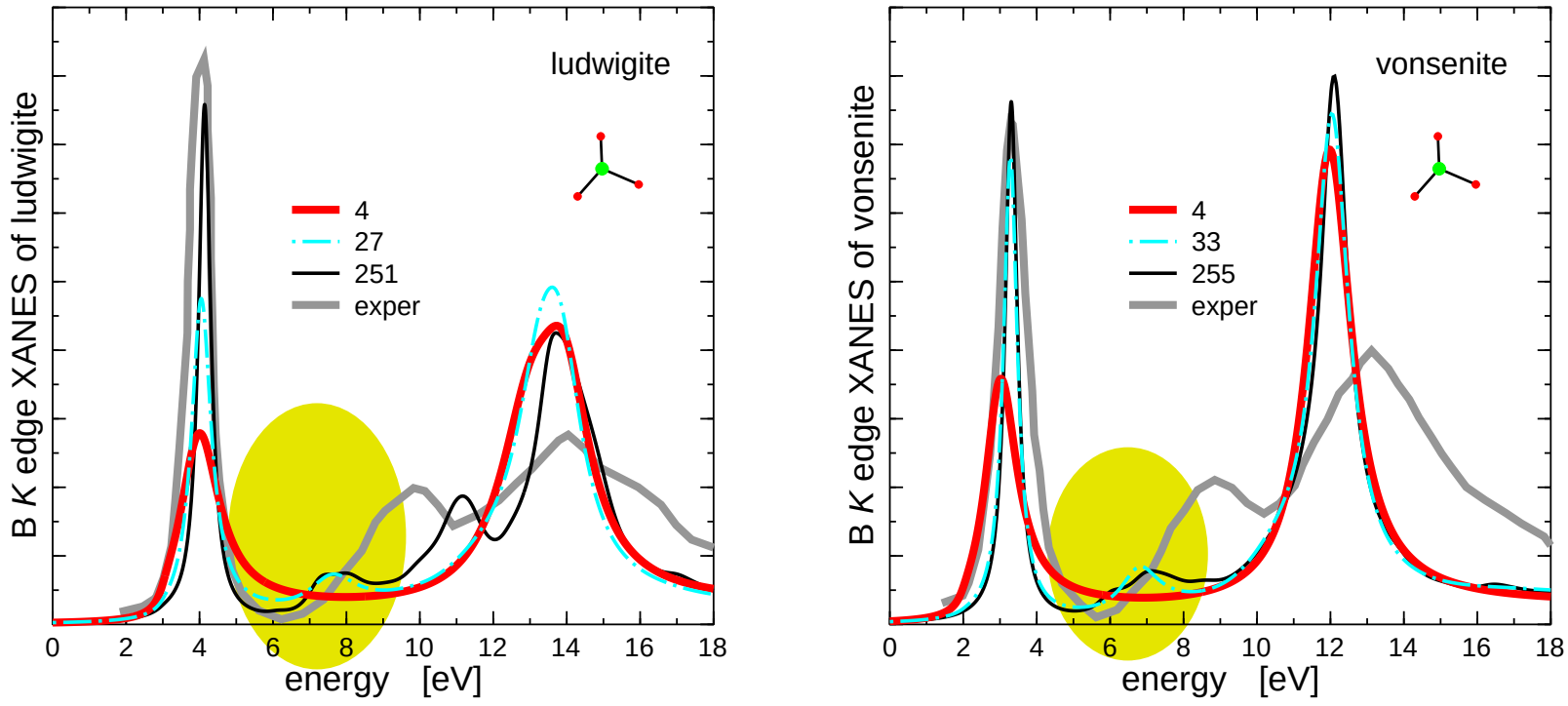
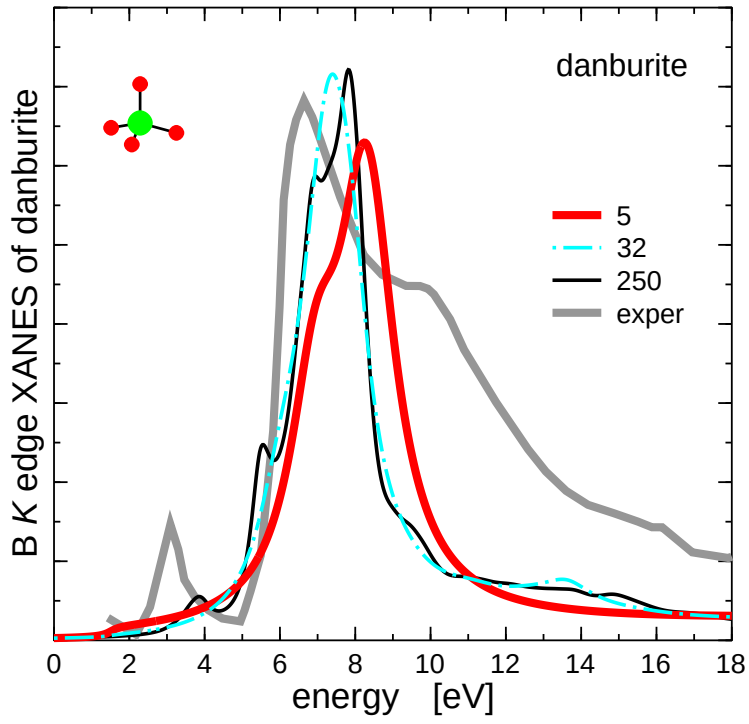
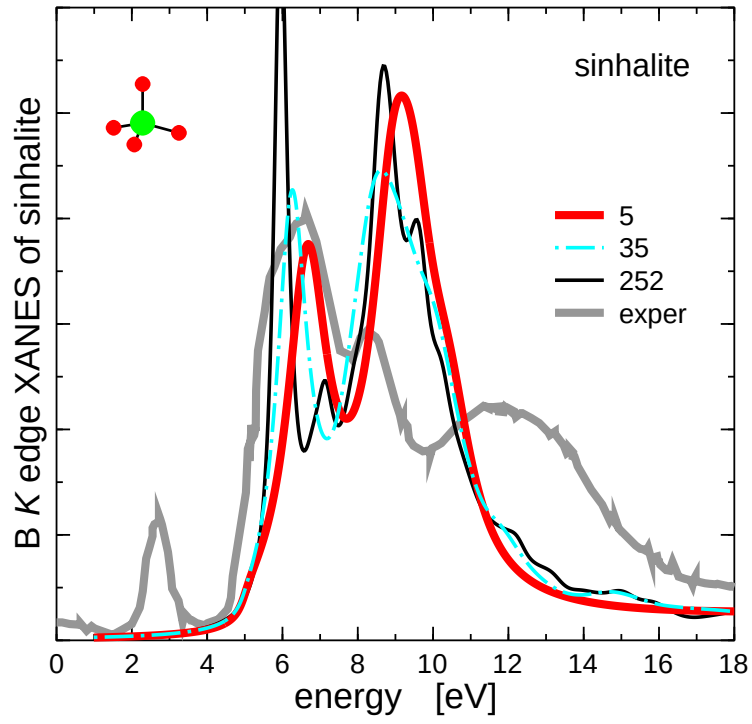


- Spectra for clusters of 4 atoms and of 250 atoms are very similar
- Fine structure between the pre-peak and the main peak is due to medium- and long-range order

Cluster size effect — BO_4 units





- Spectra for clusters of 5 atoms and of 250 atoms again very similar

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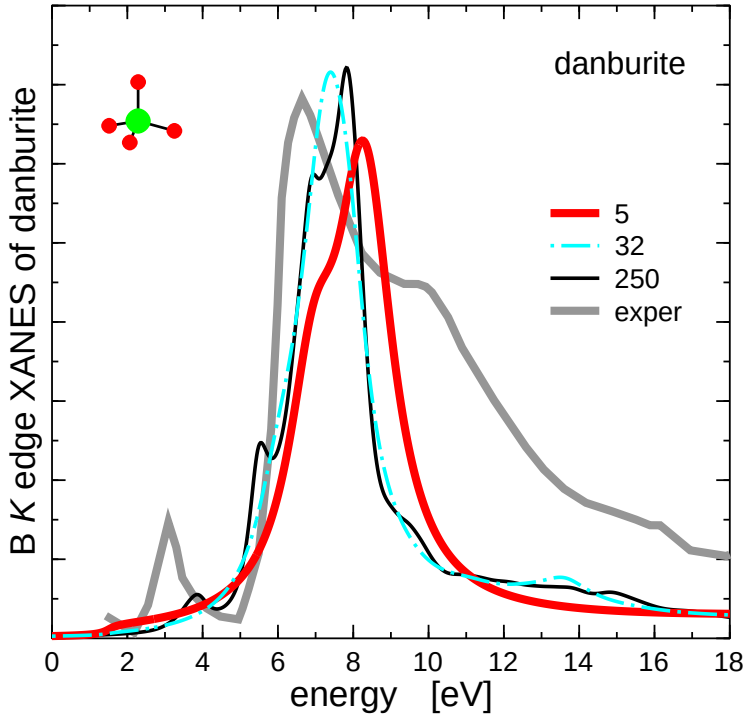
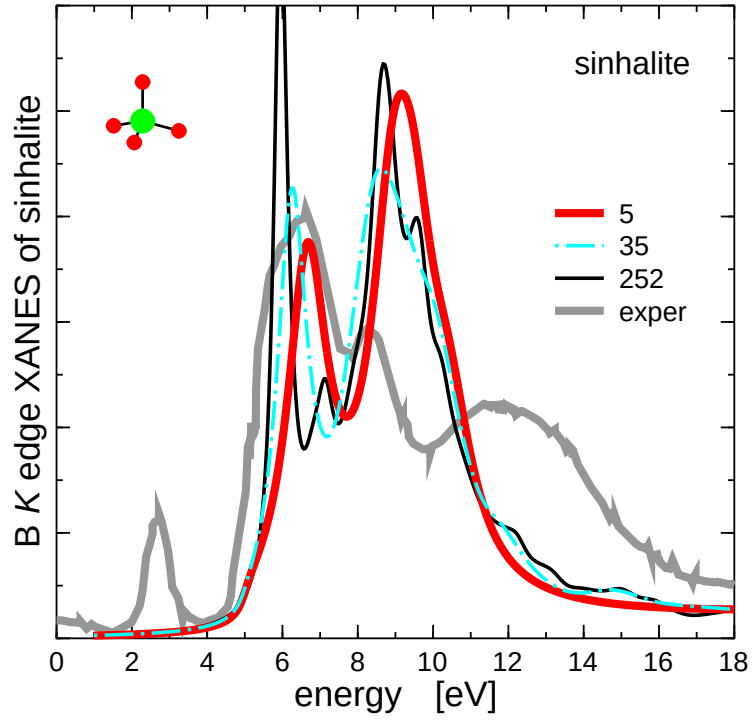
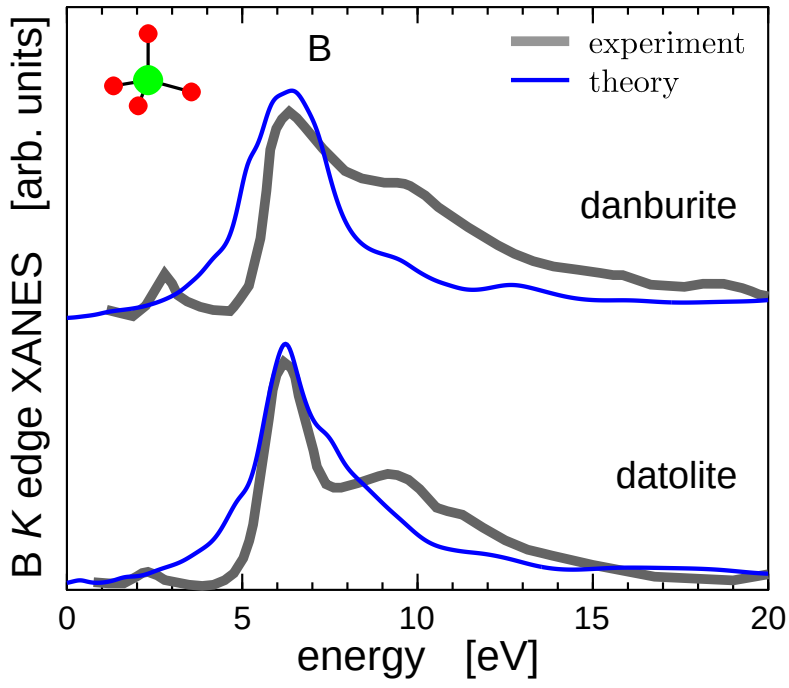




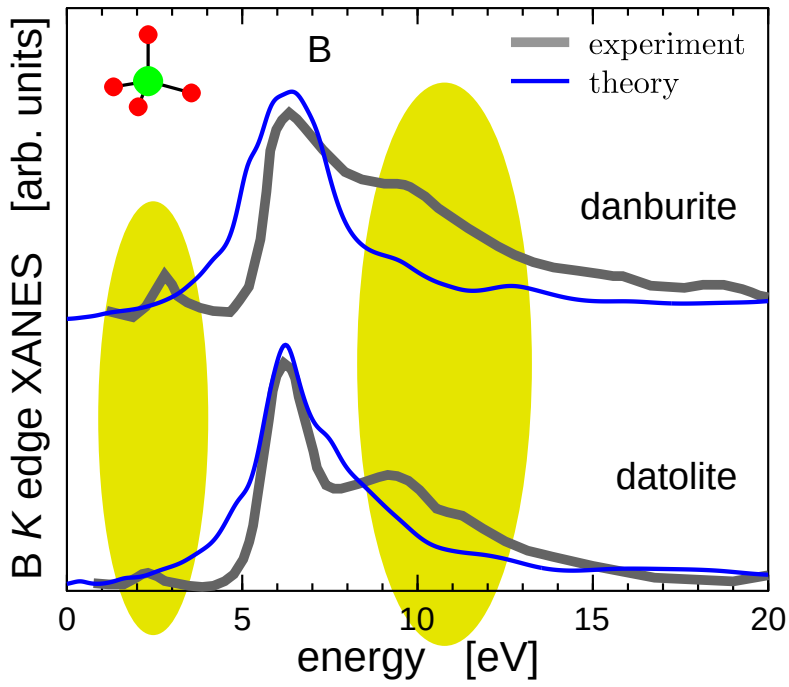
- Spectra for clusters of 5 atoms and of 250 atoms again very similar
- Pre-peak and shoulder do not appear for any size of cluster

Pre-peak and shoulder for BO_4 units



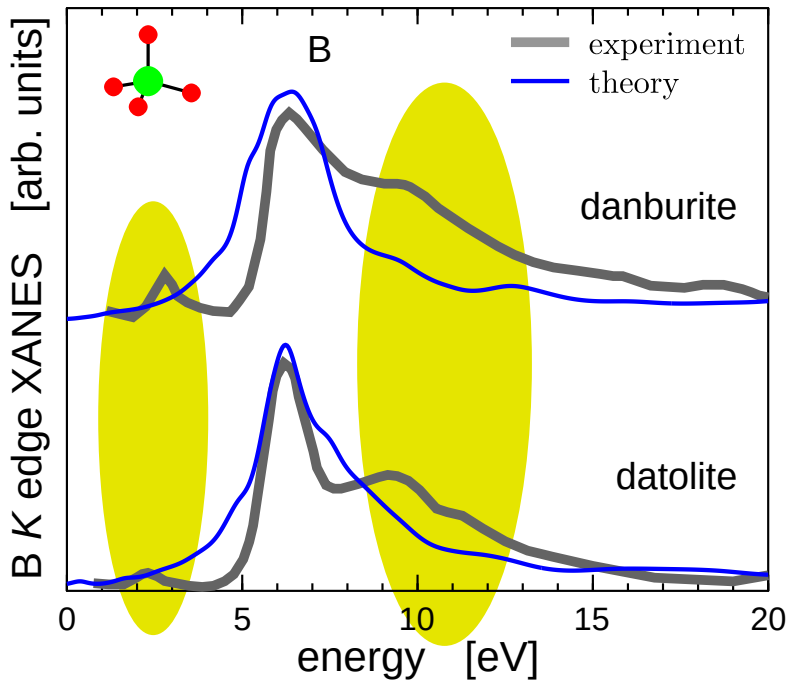
- "Systematic" deviations between theory and experiment

Pre-peak and shoulder for BO_4 units



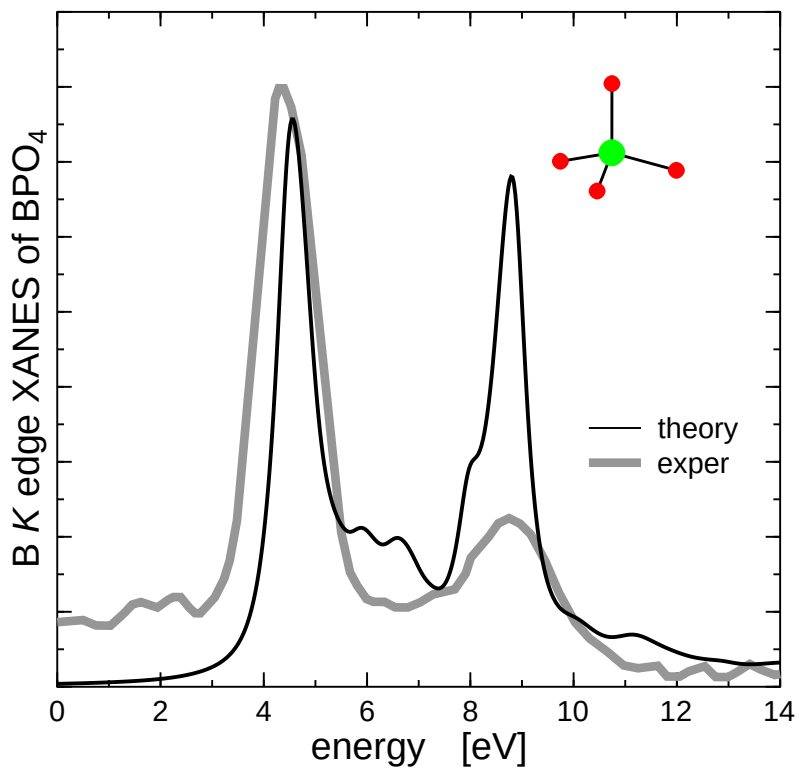
- "Systematic" deviations between theory and experiment
- Pre-edge region XANES is prone to radiation damage — just consequence of BO_3 defects?

Pre-peak and shoulder for BO_4 units



- "Systematic" deviations between theory and experiment
- Pre-edge region XANES is prone to radiation damage — just consequence of BO_3 defects?
- Shoulder region: Displayed by none of the theoretical spectra at the BO_4 sites. Disorder, impurities, main peak of BO_3 units, . . . ?

BPO_4 is peculiar



- XANES of BPO_4 does not fit into the typology

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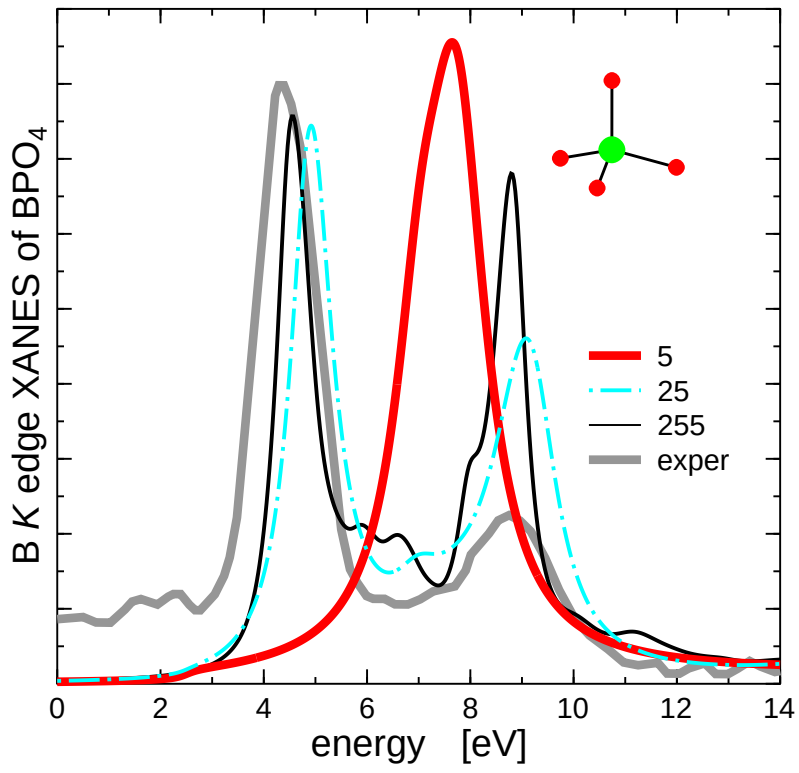
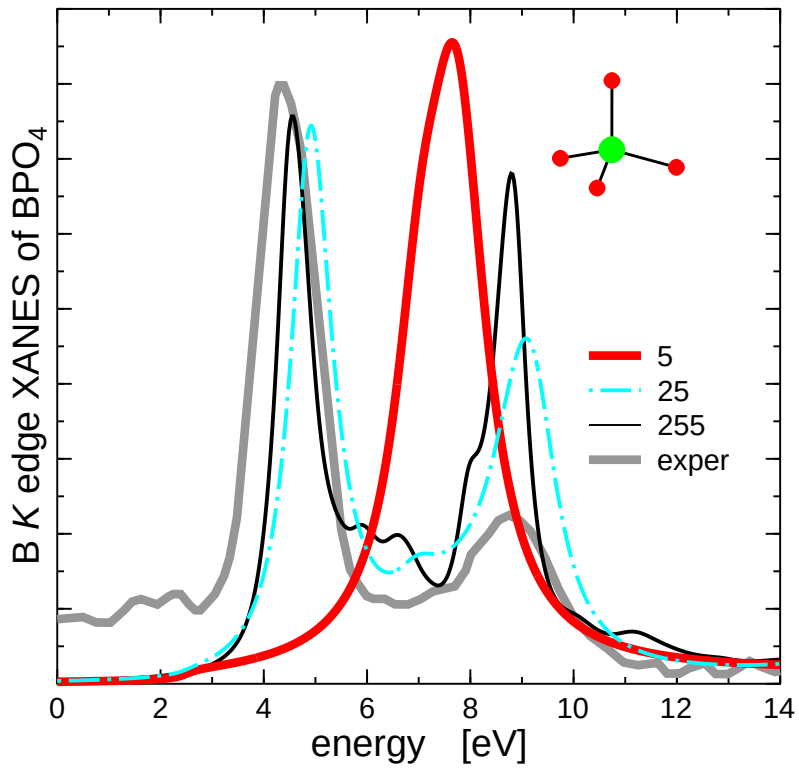


- XANES of BPO_4 does not fit into the typology
- Spectra for small and large clusters differ considerably

BPO_4 is peculiar (and not useful)



- XANES of BPO_4 does not fit into the typology
- Spectra for small and large clusters differ considerably
- XANES governed by medium- and long-range order
- Too symmetric to smooth out the contributions from distant atoms

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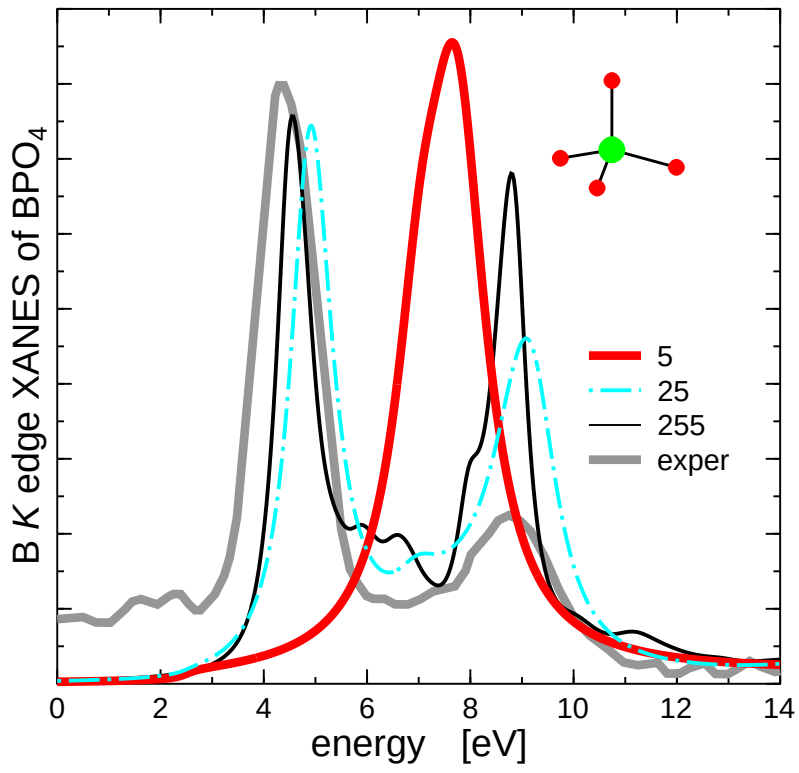


- XANES of BPO_4 does not fit into the typology
- Spectra for small and large clusters differ considerably
- XANES governed by medium- and long-range order
- Too symmetric to smooth out the contributions from distant atoms
- Not useful for fingerprinting XANES of glasses

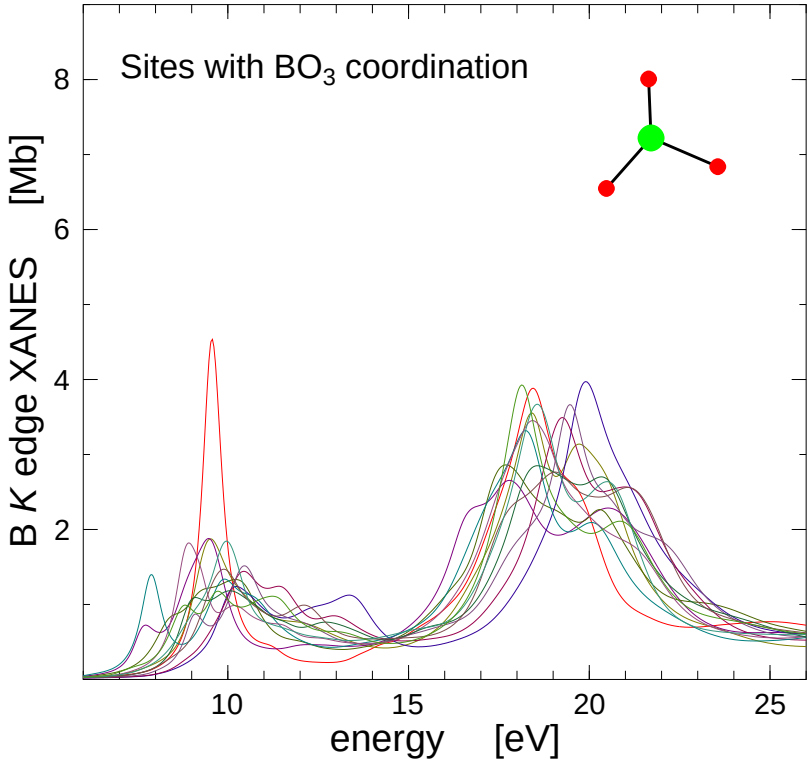
Minerals with borons in both BO_3 and BO_4 units

Minerals with both BO_3 and BO_4

name	formula	BO_3	BO_4
boracite	$Mg_3ClB_7O_{13}$	1	6
borax	$Na_2B_4O_5(OH)_4 \cdot 8(H_2O)$	1	1
colemanite	$CaB_3O_4(OH)_3 \cdot H_2O$	1	2
howlite	$Ca_2SiB_5O_9(OH)_5$	1	4
kernite	$Na_2B_4O_6(OH)_2 \cdot 3(H_2O)$	2	2
kurnakovite	$MgB_3O_3(OH)_5 \cdot 5(H_2O)$	1	2
meyerhofferite	$Ca_2B_6O_6(OH)_{10} \cdot 2(H_2O)$	1	2
probertite	$NaCaB_5O_7(OH)_4 \cdot 3(H_2O)$	2	3
tincalconite	$Na_2B_4O_5(OH)_4 \cdot 3(H_2O)$	1	1
ulexite	$NaCaB_5O_6(OH)_6 \cdot 5(H_2O)$	2	3

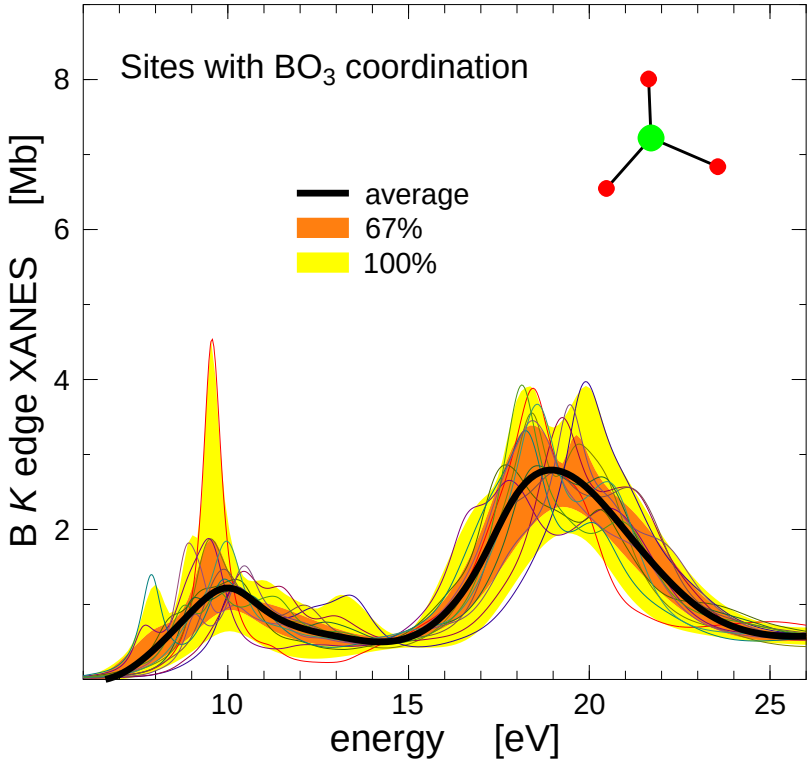
- Spectra generated at inequivalent sites of the same system are aligned one to another by the theory

Spectra of borons in BO_3 units



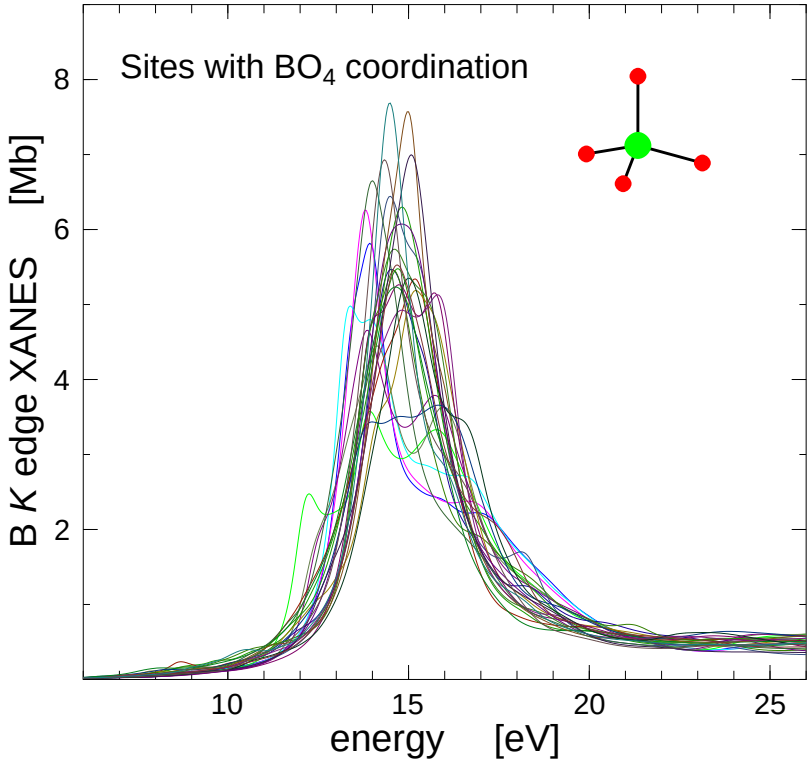
- 13 sites, 10 minerals

Spectra of borons in BO_3 units



- 13 sites, 10 minerals
- Confidence intervals — either 67% or 100% of all curves fall within these limits

Spectra of borons in BO_4 units



- 26 sites, 10 minerals

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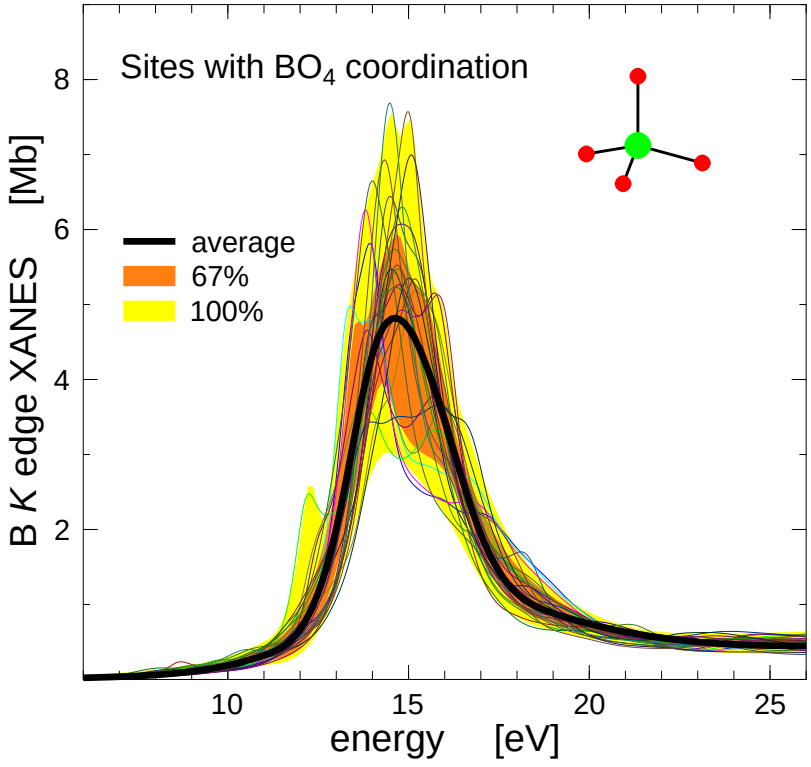

- 26 sites, 10 minerals
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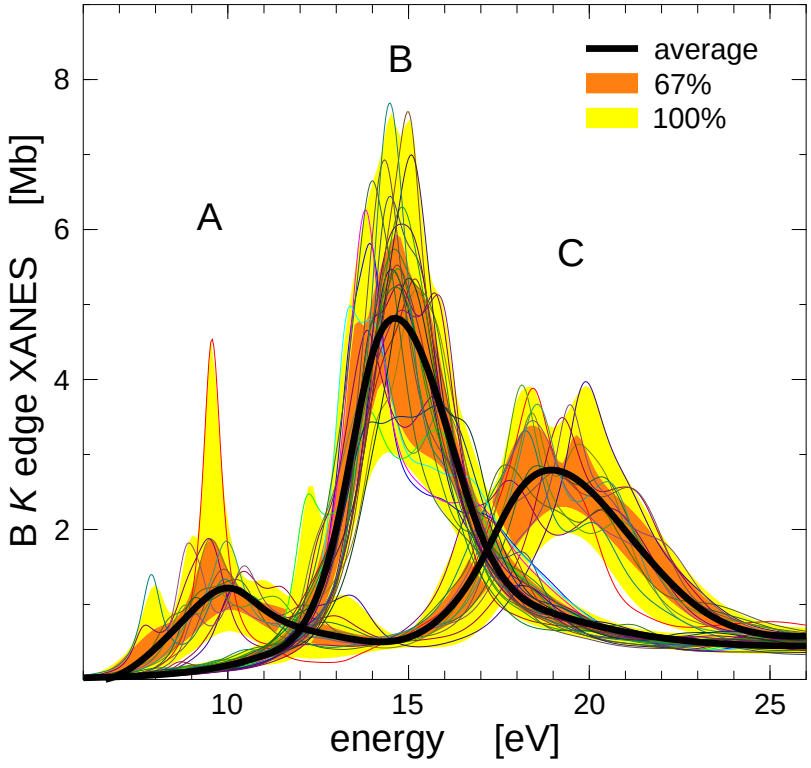
Markers of BO_3 and BO_4



- Features characteristic for BO_3 or BO_4 coordinations well separated

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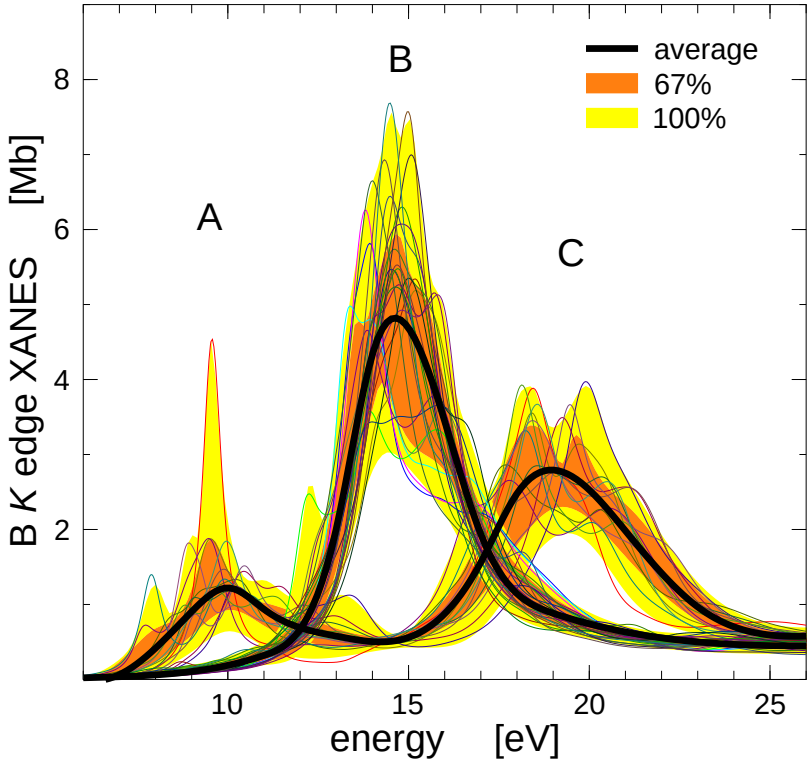

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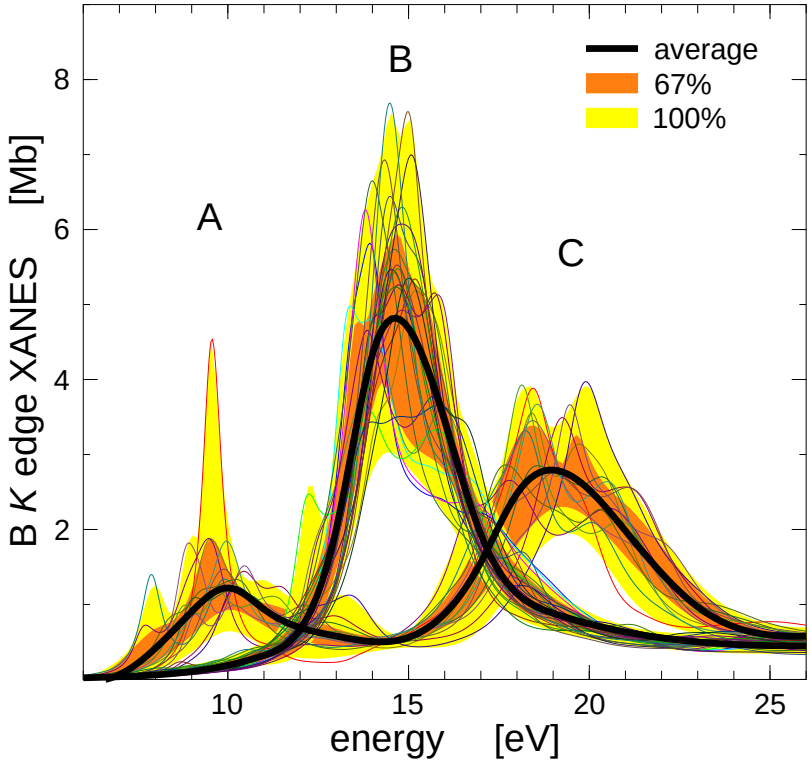
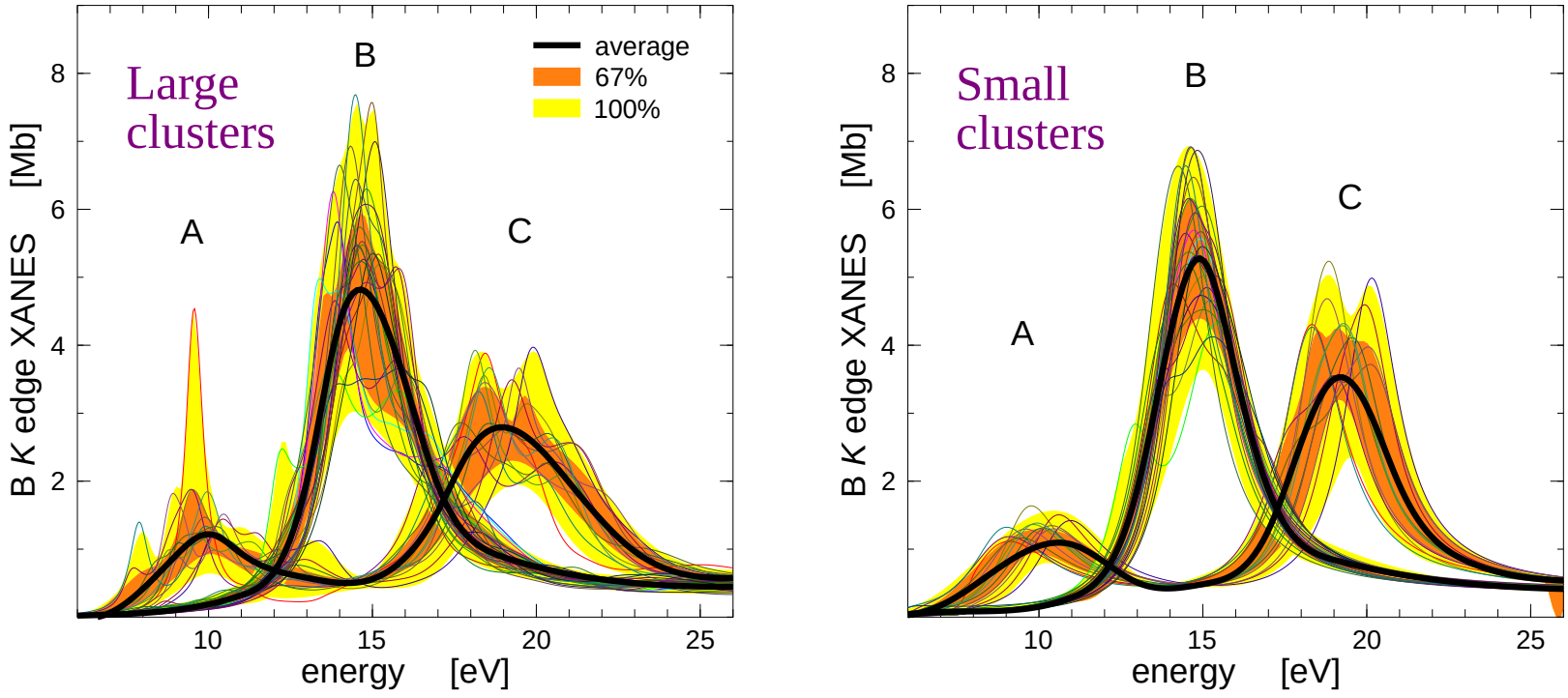
- Similar picture obtained no matter what scattering potential is used

Markers of BO_3 and BO_4



- Features characteristic for BO_3 or BO_4 coordinations well separated
- Similar picture obtained no matter what scattering potential is used
- B K edge is well-suited for structural studies

Short-range order is dominant



- Clusters of 140 atoms and of 4 or 5 atoms yield similar picture

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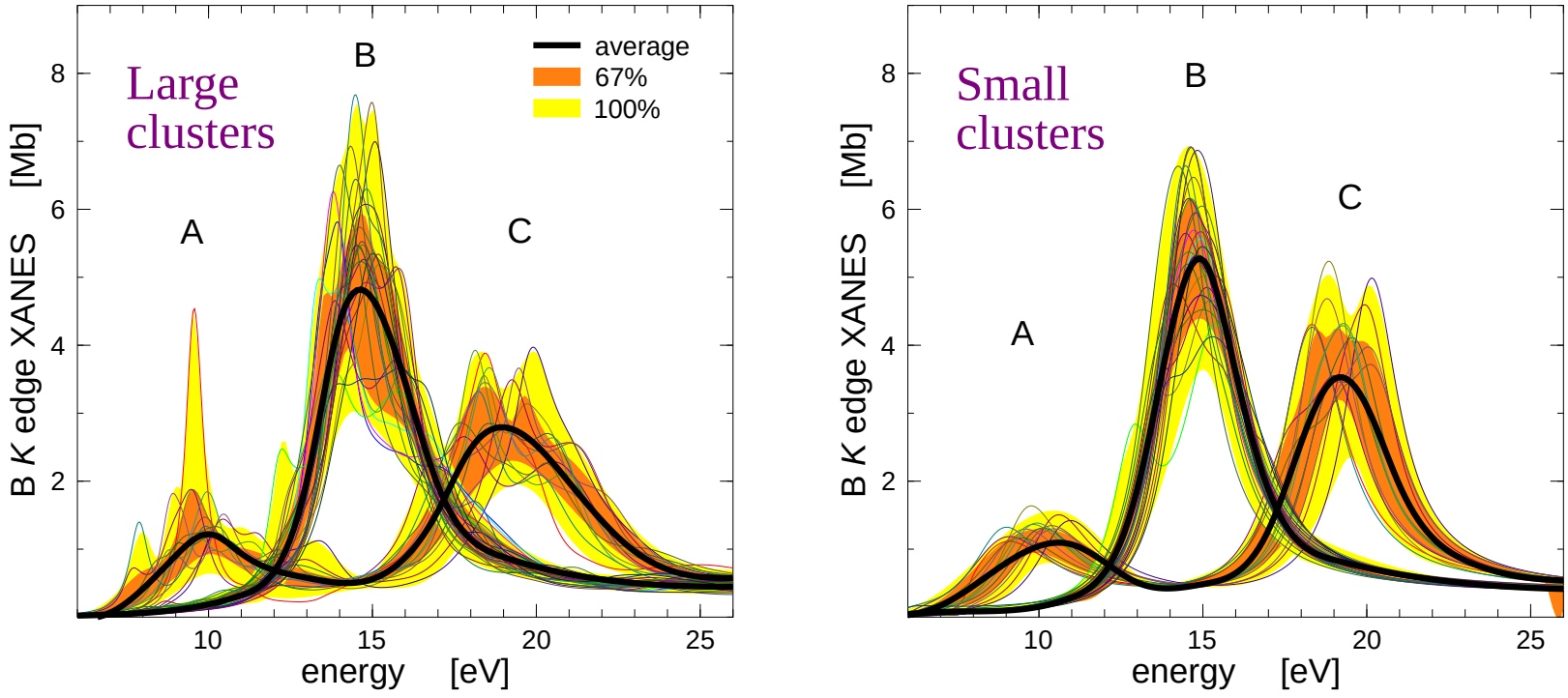

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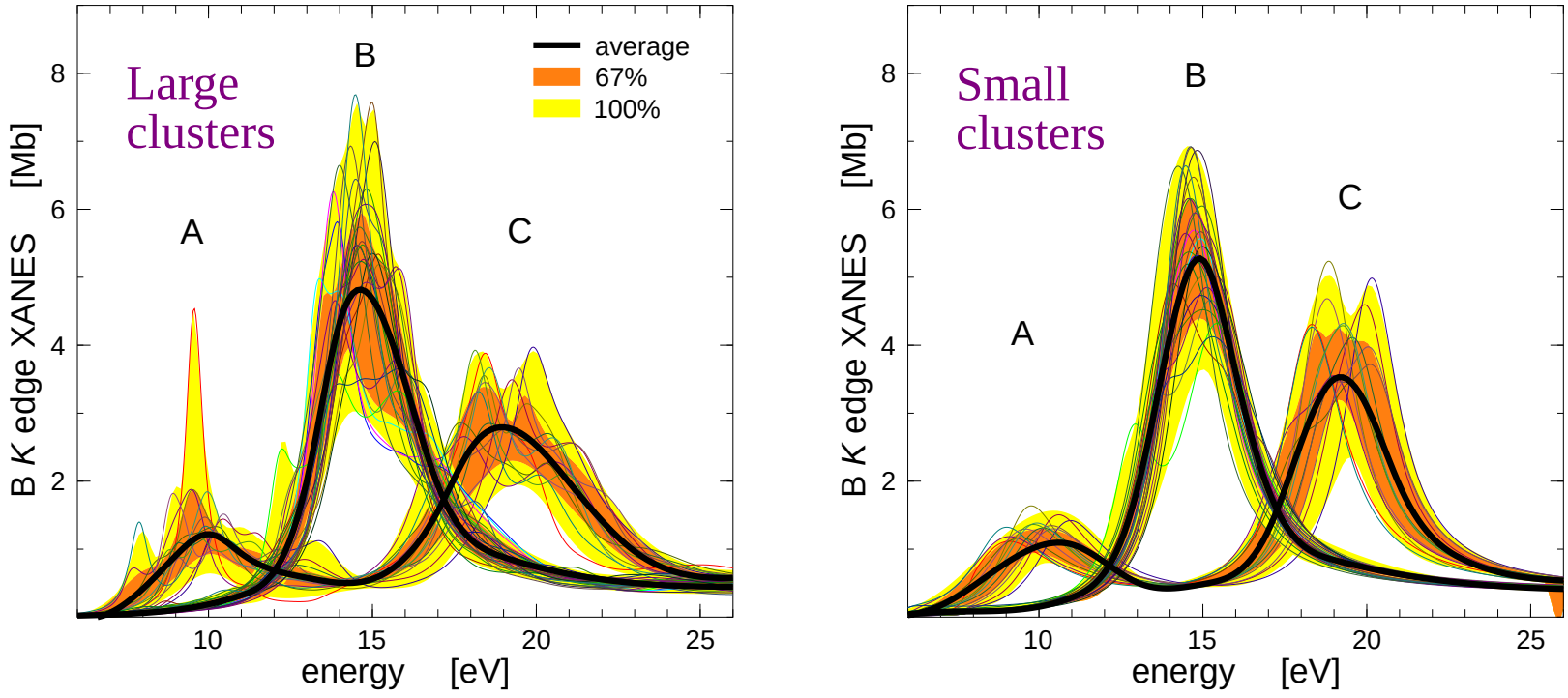
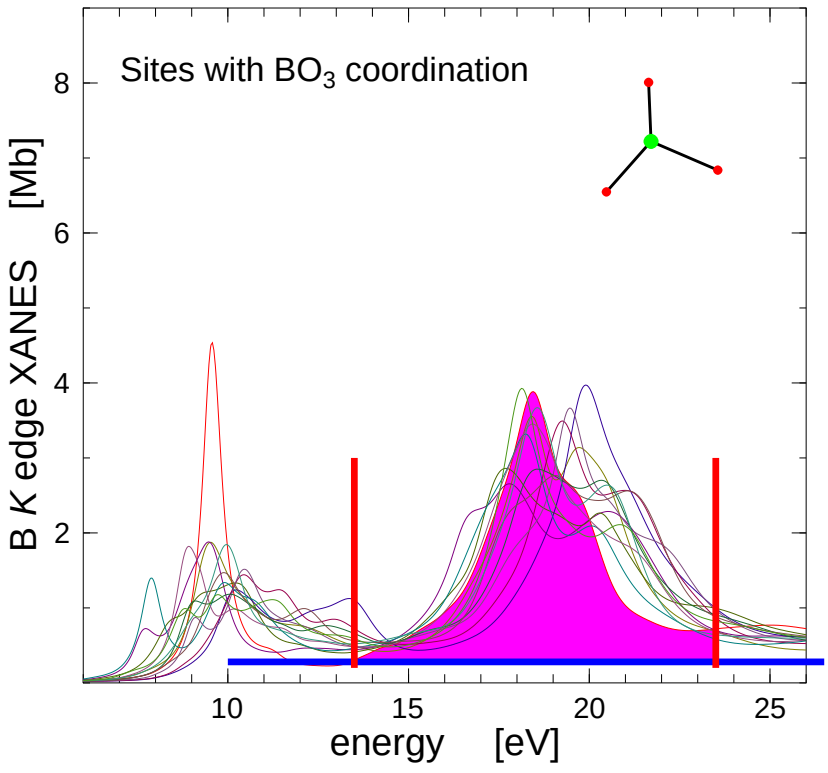


- Clusters of 140 atoms and of 4 or 5 atoms yield similar picture
- XANES shape is governed by short-range order
- Results may be transferred from crystal to glasses

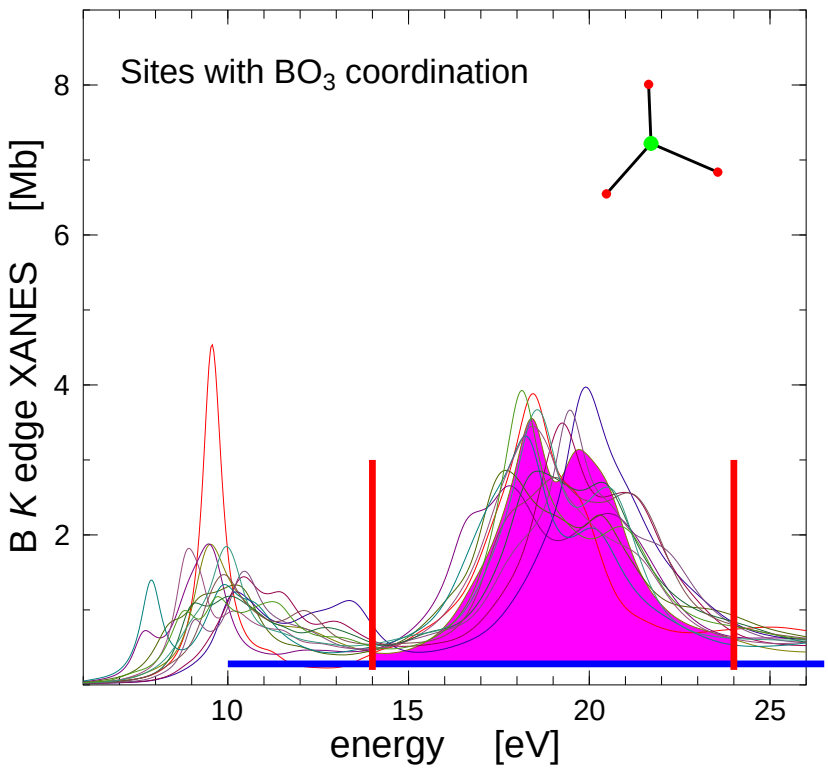
Trying to make quantitative estimates

Variations in peak areas (BO_3)



- Measuring peak area over a 10 eV range

Variations in peak areas (BO_3)



- Measuring peak area over a 10 eV range
- For each peak, find deviation of its area from the average

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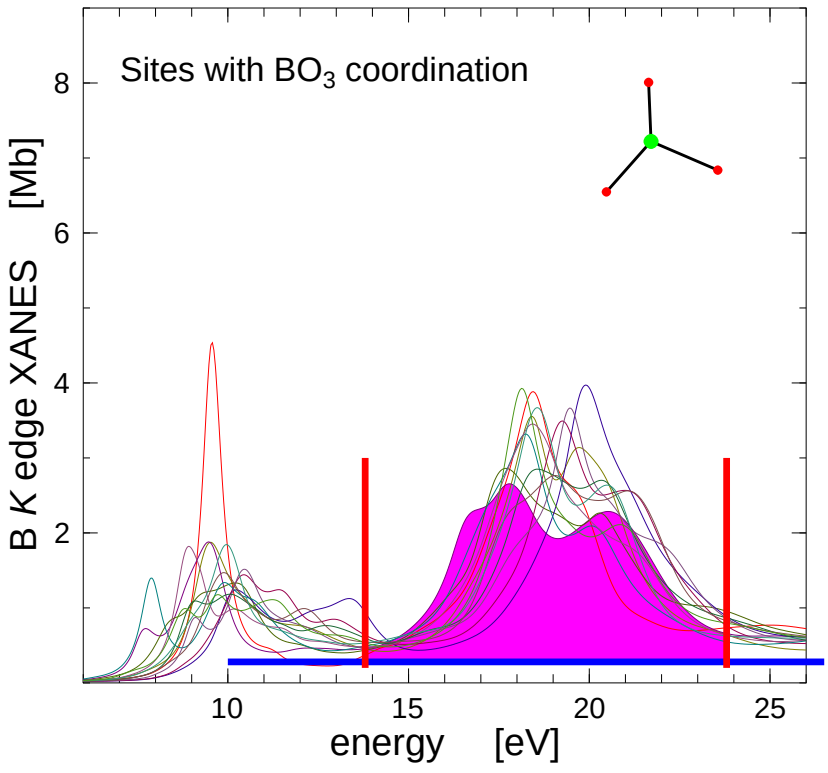

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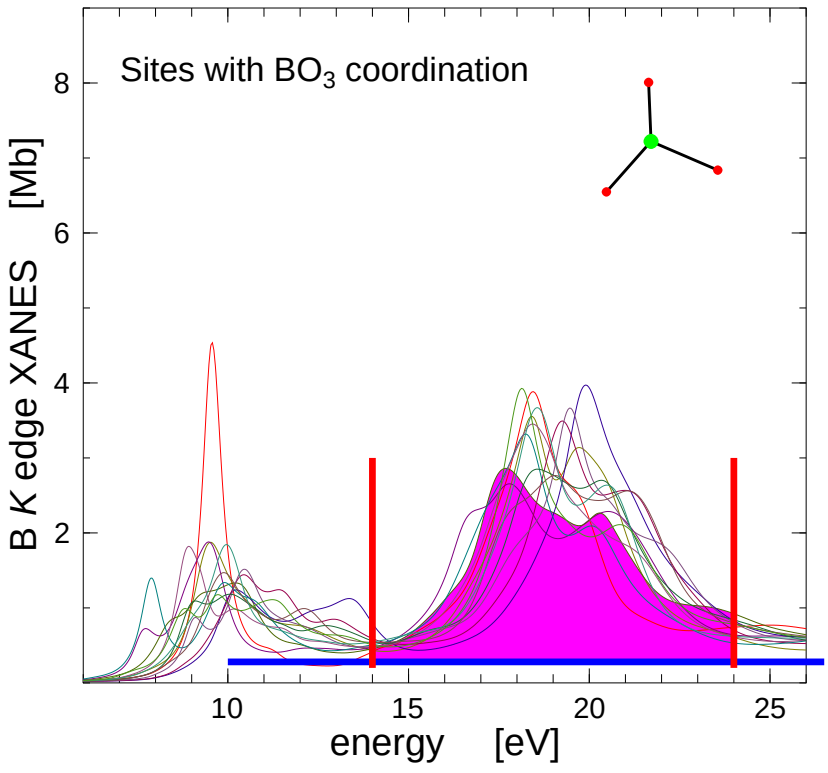

- Measuring peak area over a 10 eV range
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- For 67% percents of peaks, their areas deviate from the average by less than 4%

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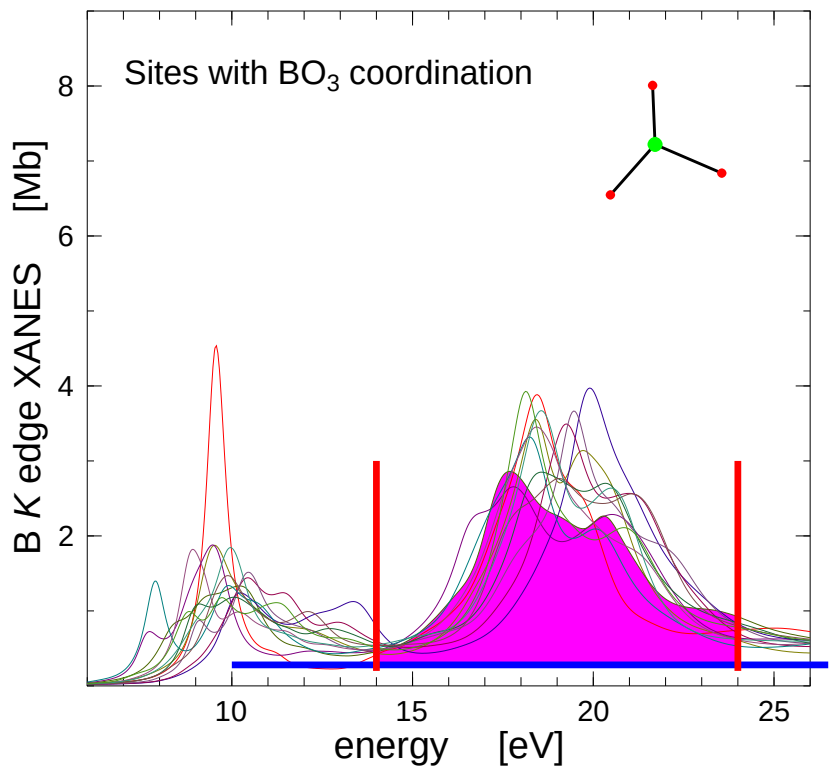

- Measuring peak area over a 10 eV range
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- Maximum deviation from the average is about 12%

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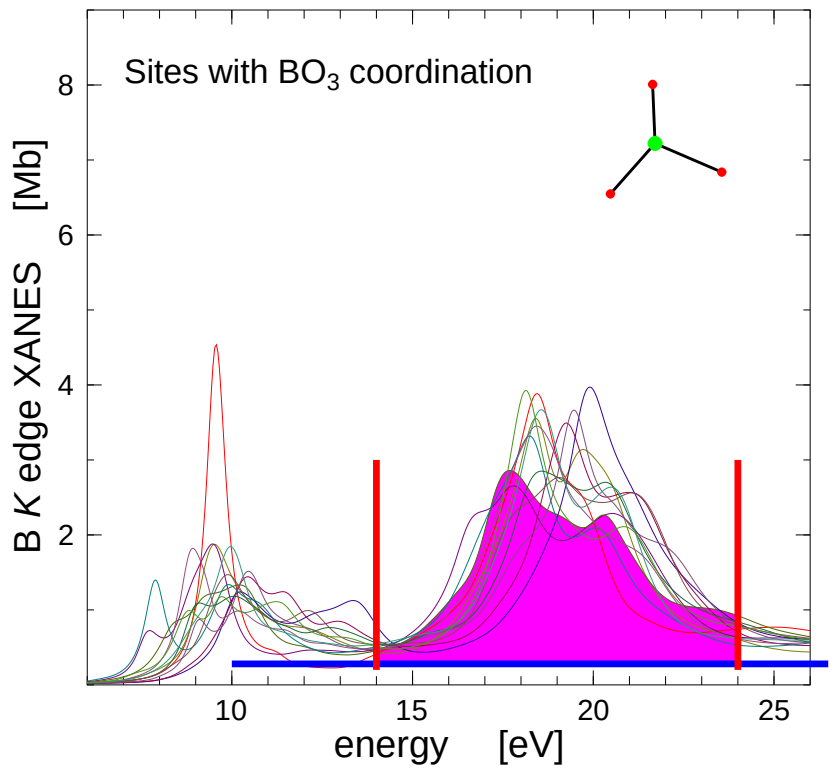
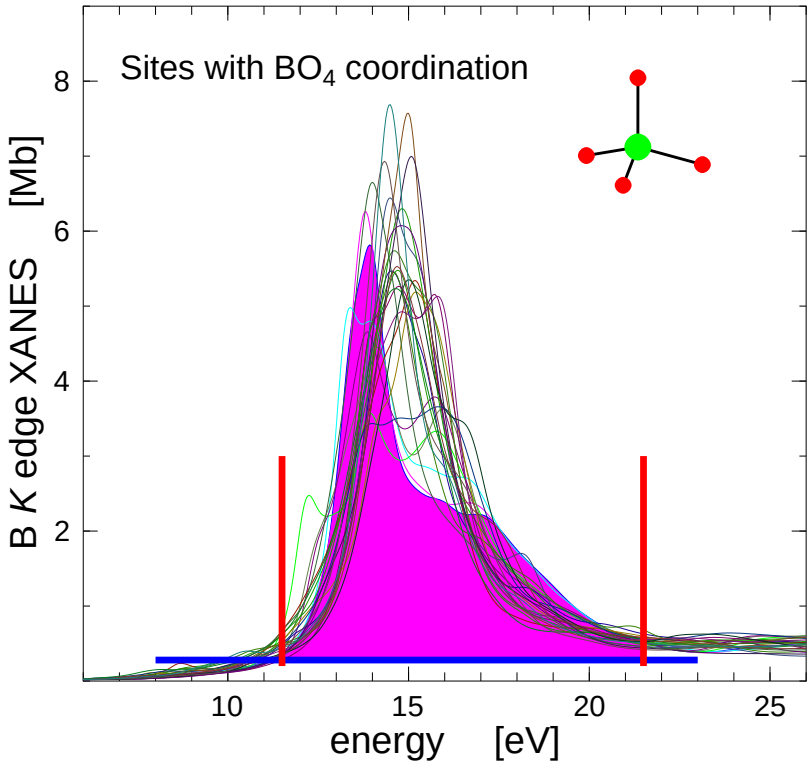


- Measuring peak area over a 10 eV range
- For each peak, find deviation of its area from the average
- For 67% percents of peaks, their areas deviate from the average by less than 4%
- Maximum deviation from the average is about 12%
- Choice of scattering potential and other “technical” parameters does not matter

Variations in peak areas BO_4



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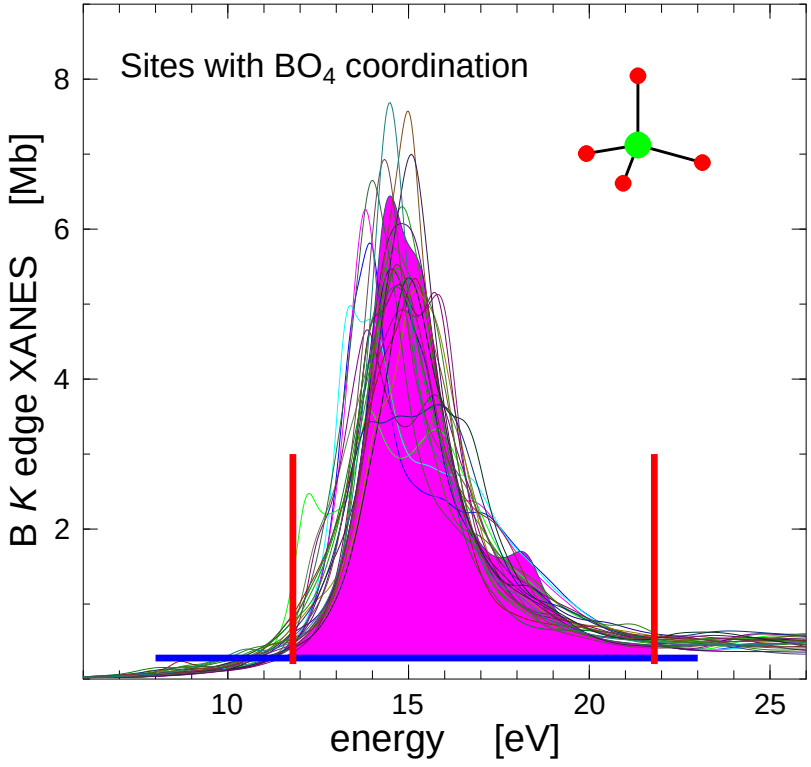
Variations in peak areas BO_4



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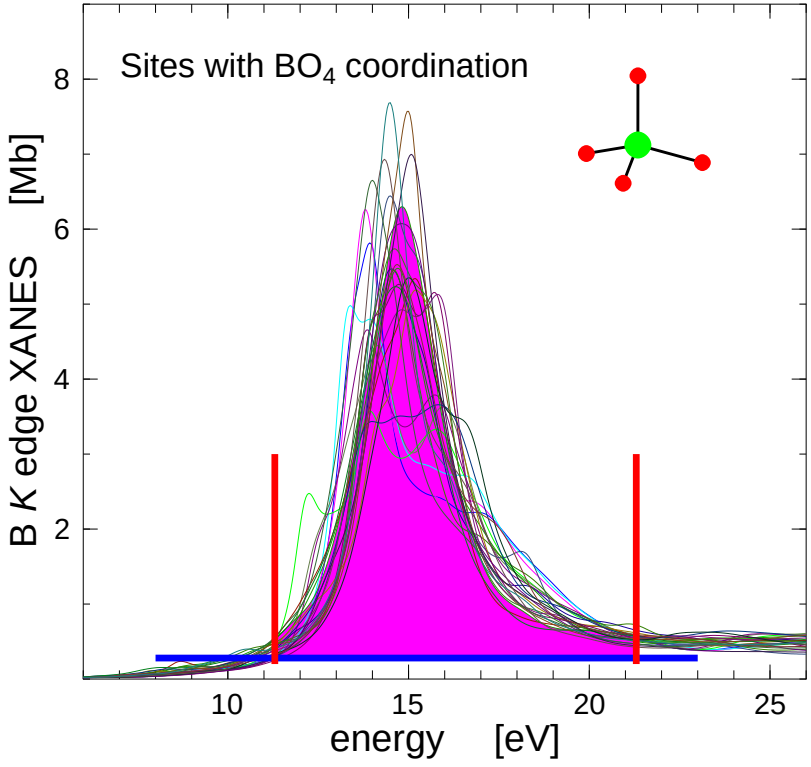
Variations in peak areas BO_4



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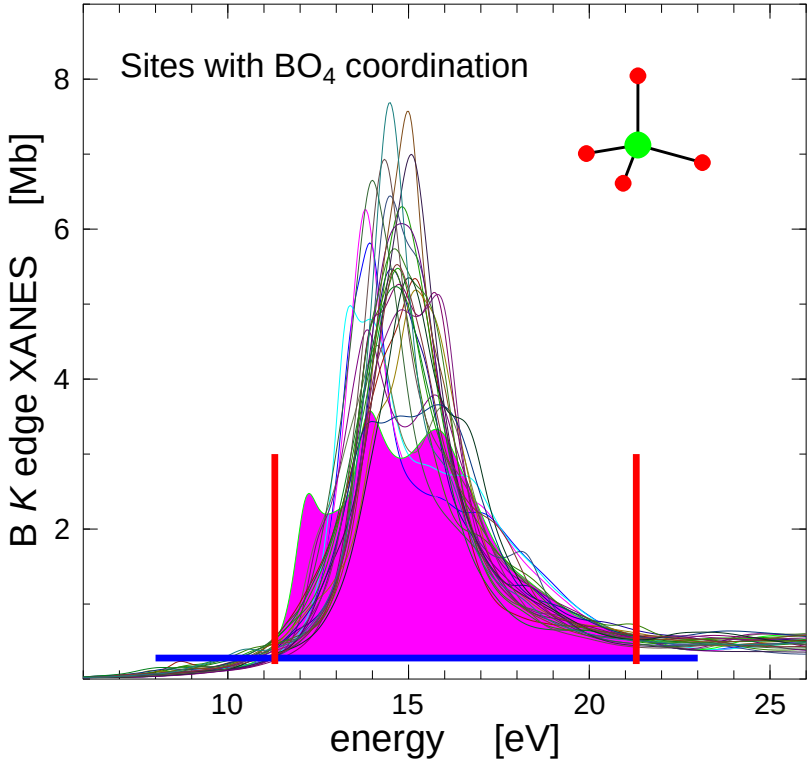
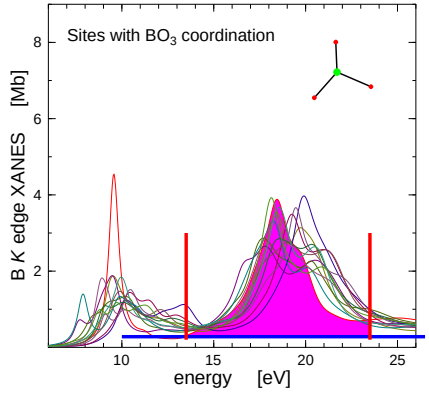
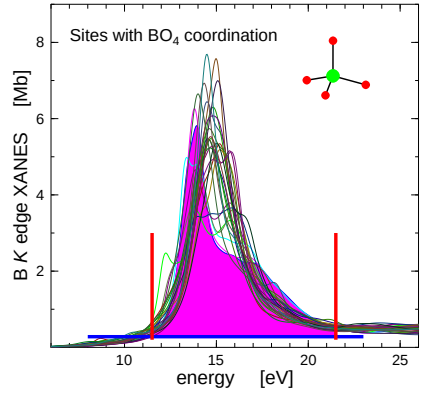


- Measuring peak area
- Find deviations from the average
- Statistics similar as in the case of BO_3 sites
- Standard deviation of the area is 4%, maximum deviation from the average is 12%

Quantifying ratio of BO_3 and BO_4





- Area of the main peak depends only on the number of nearest oxygens

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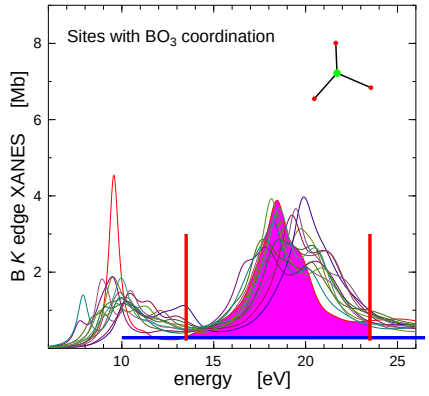

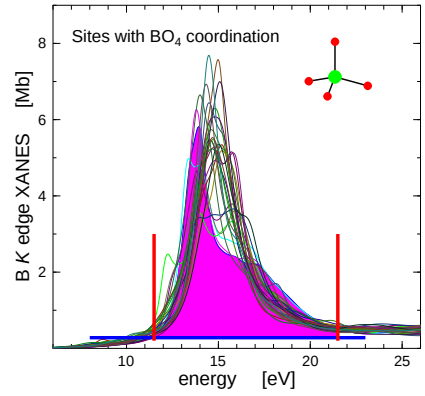

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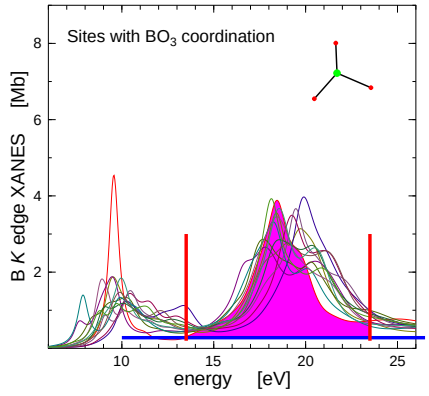

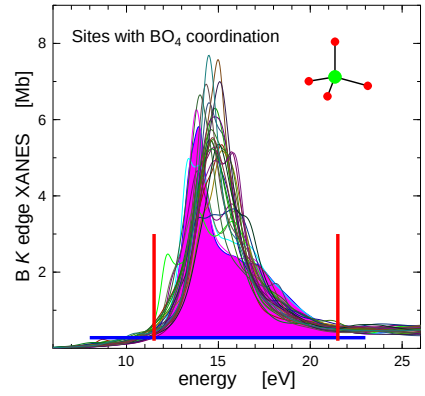

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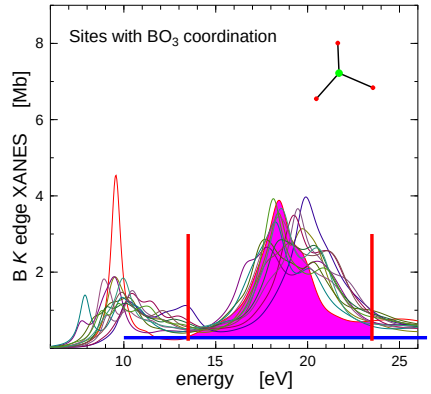
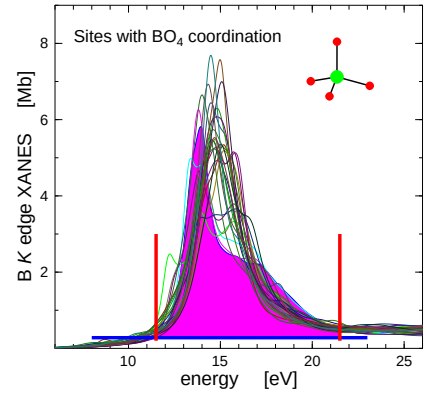
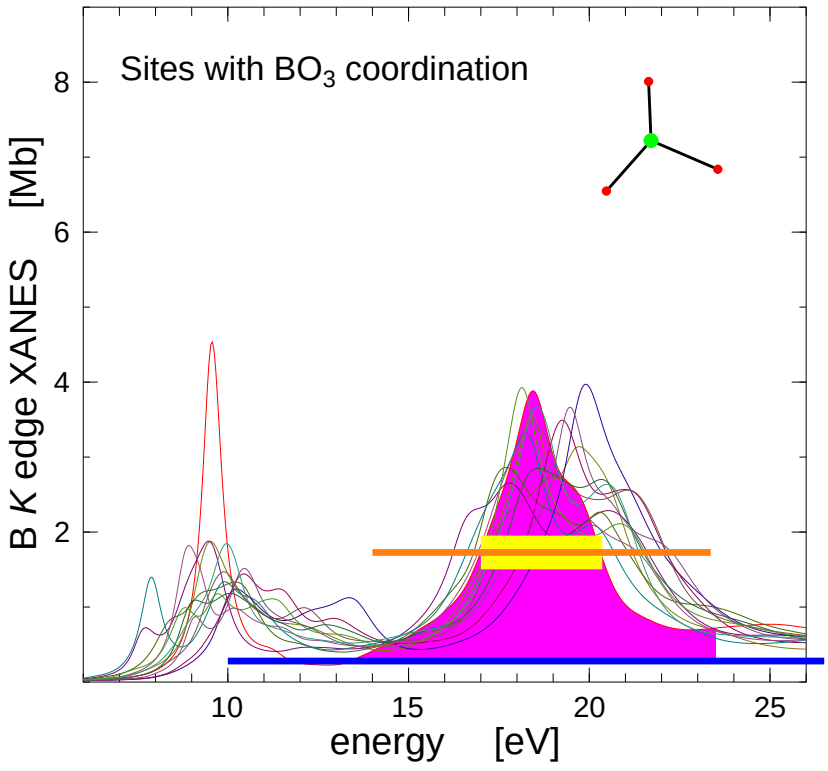




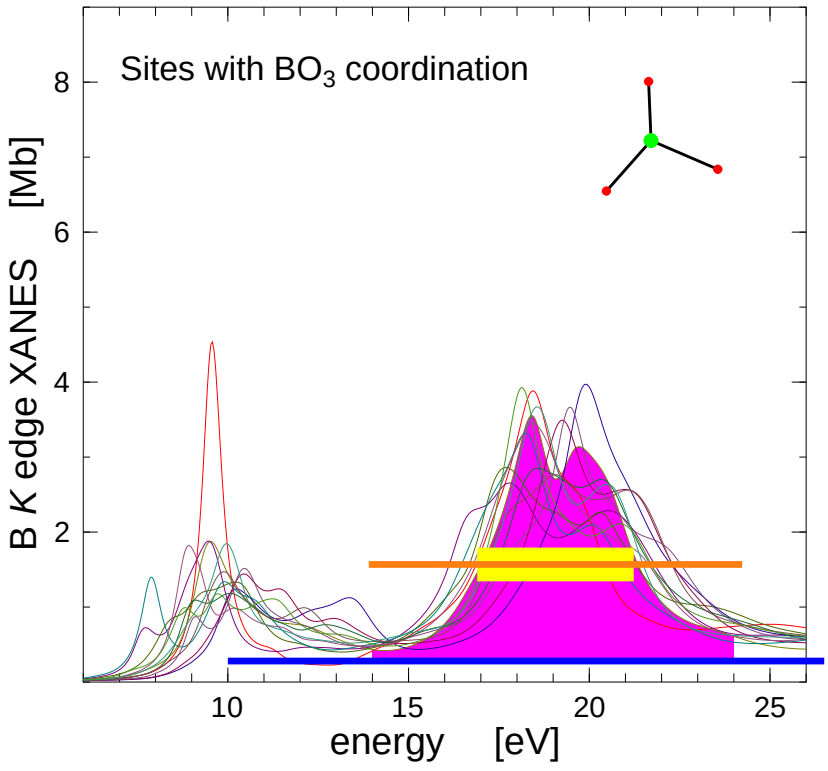
- Area of the main peak depends only on the number of nearest oxygens (it does not depend on compound, distances, middle-range order etc.)
- Ratio of areas of main peaks is a measure of the ratio of three-fold and four-fold boron sites
- Normalization: Area of main spectral peak at a BO_3 site constitutes $\sim$75% of area of main spectral peak at a BO_4 site

Widths of main peaks — BO_3 sites



- Measuring width of the peak at 40% of its maximum height

Widths of main peaks — BO_3 sites



- Measuring width of the peak at 40% of its maximum height (full width at 0.4 of maximum)

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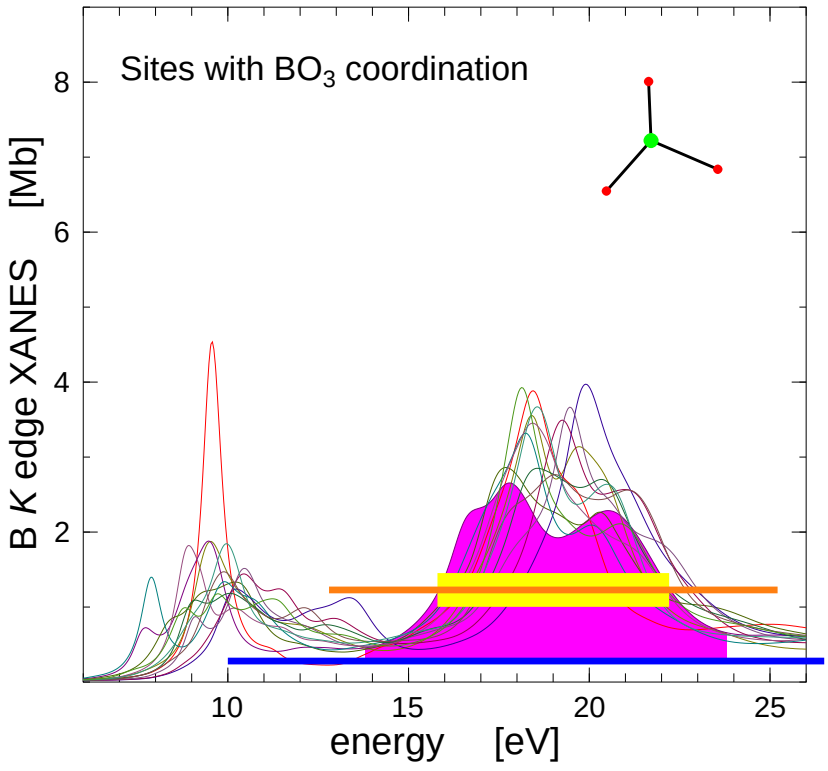

- Measuring width of the peak at 40% of its maximum height (full width at 0.4 of maximum)
- Searching for any systematic dependence

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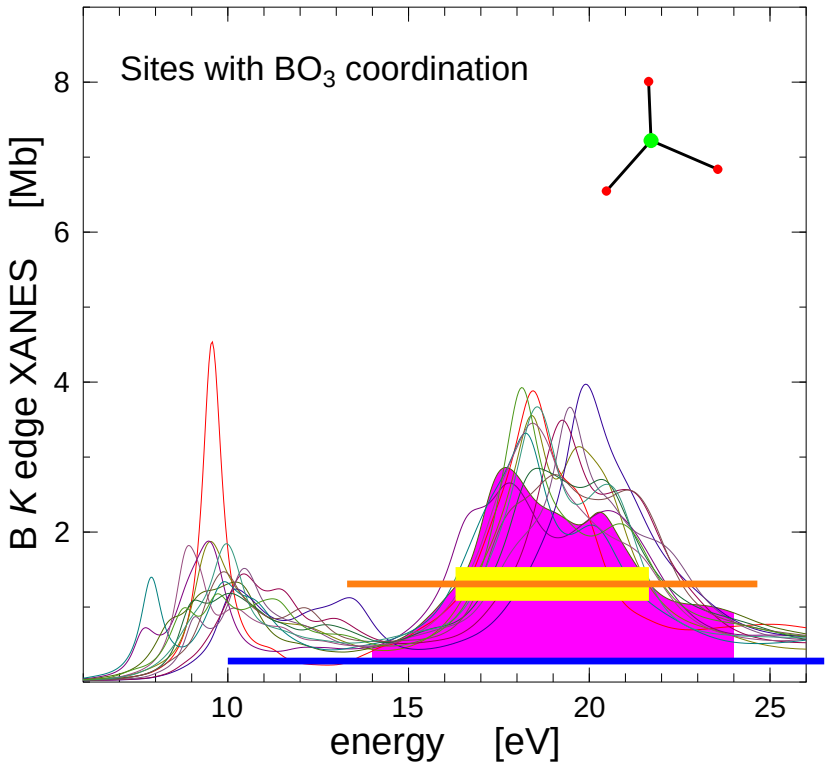

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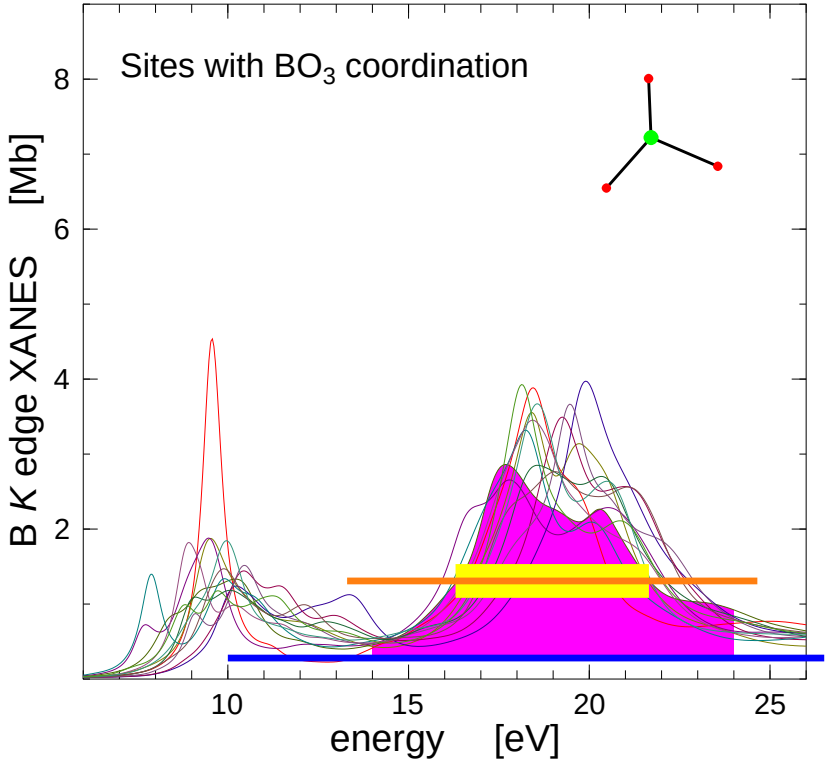
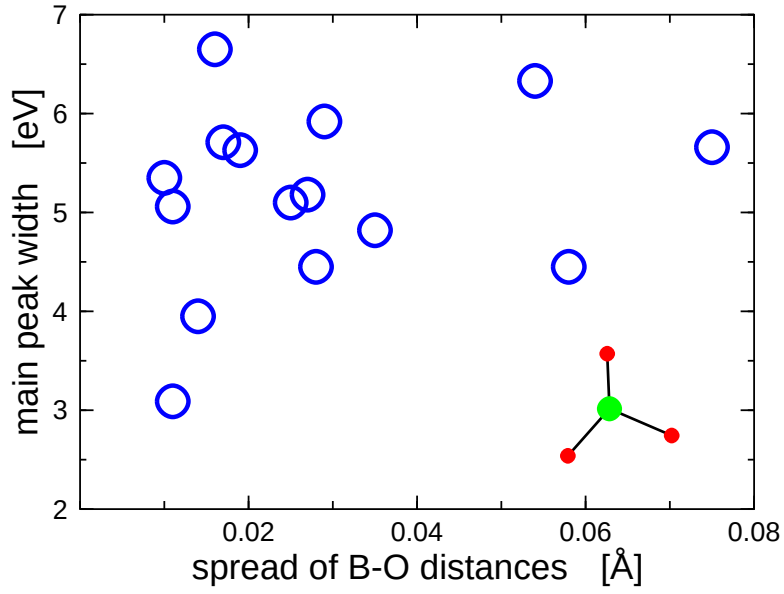
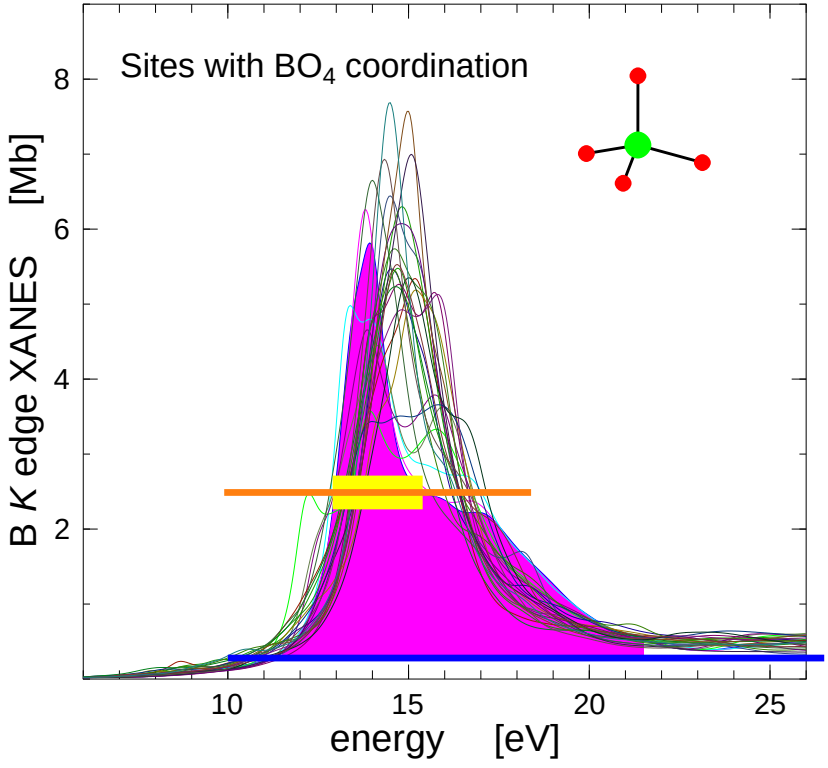




- No obvious relation between the spread of B–O distances and the width of the main peak

Widths of main peaks — BO_4 sites



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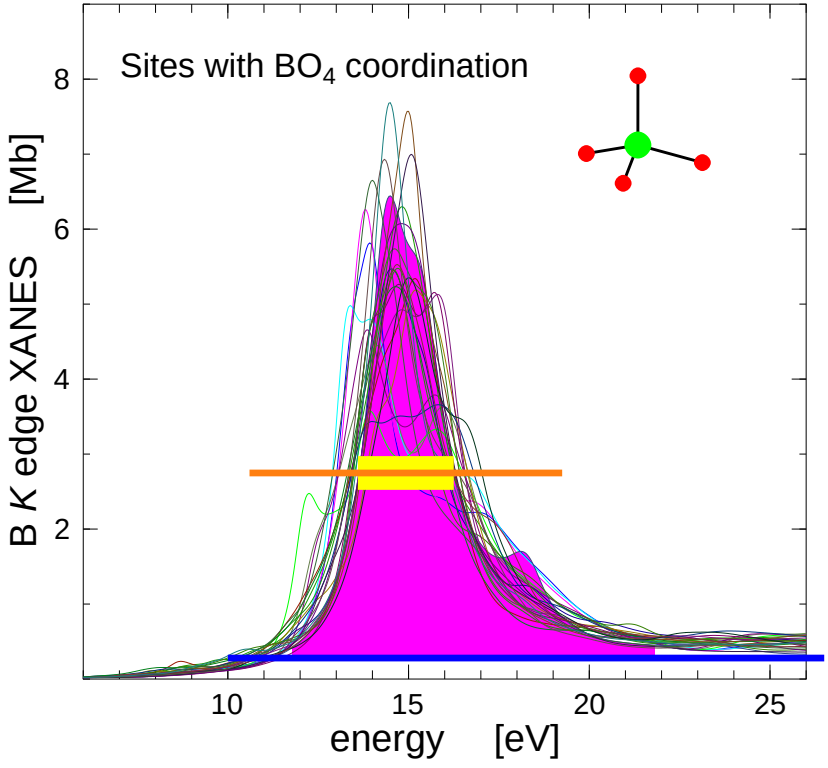

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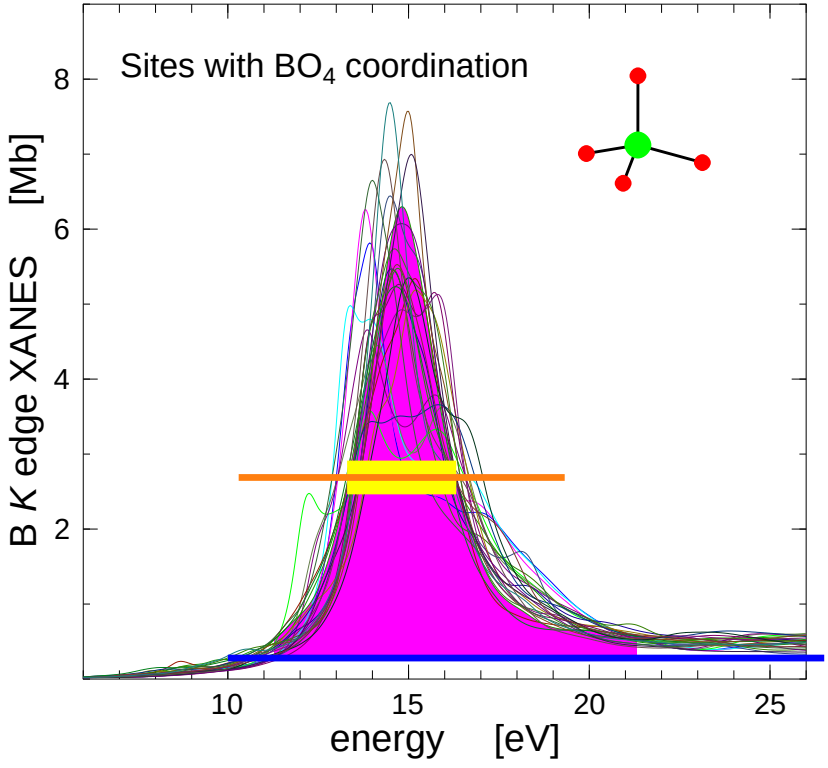

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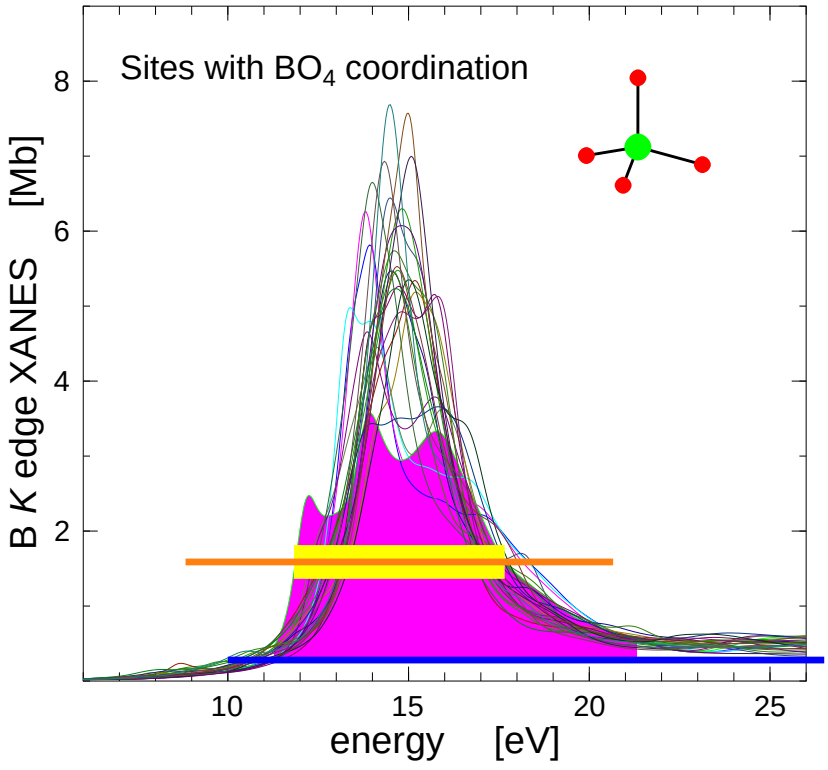

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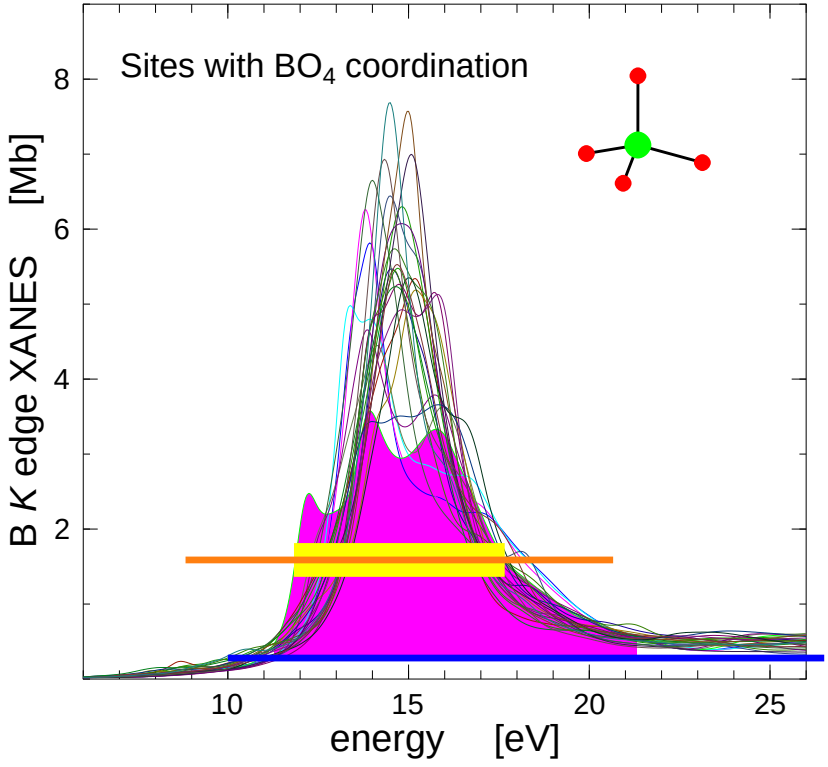
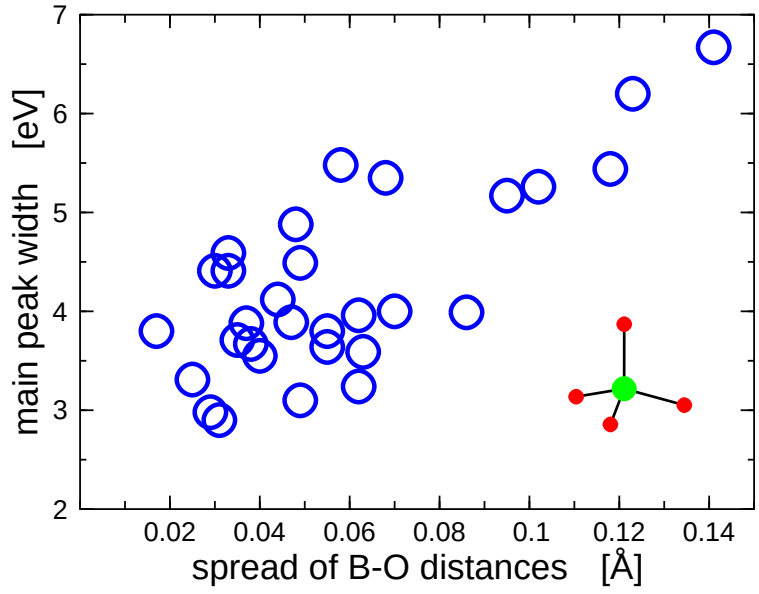
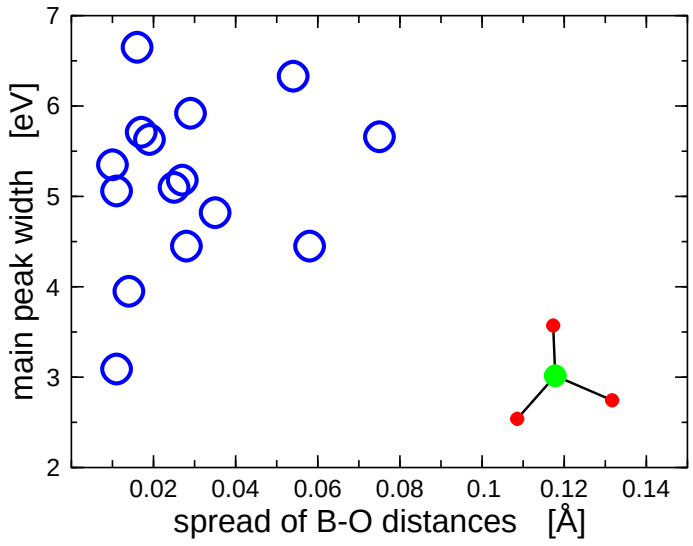
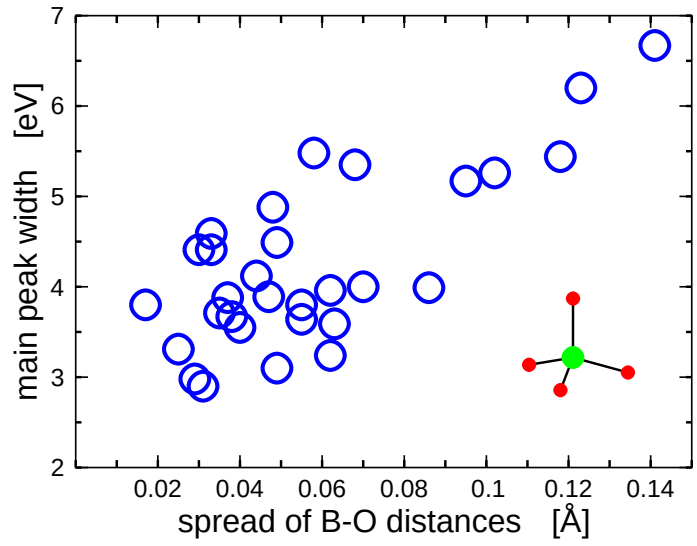




- There is *some relation* between spread of the B–O distances in the BO_4 tetrahedron and the width of the main peak

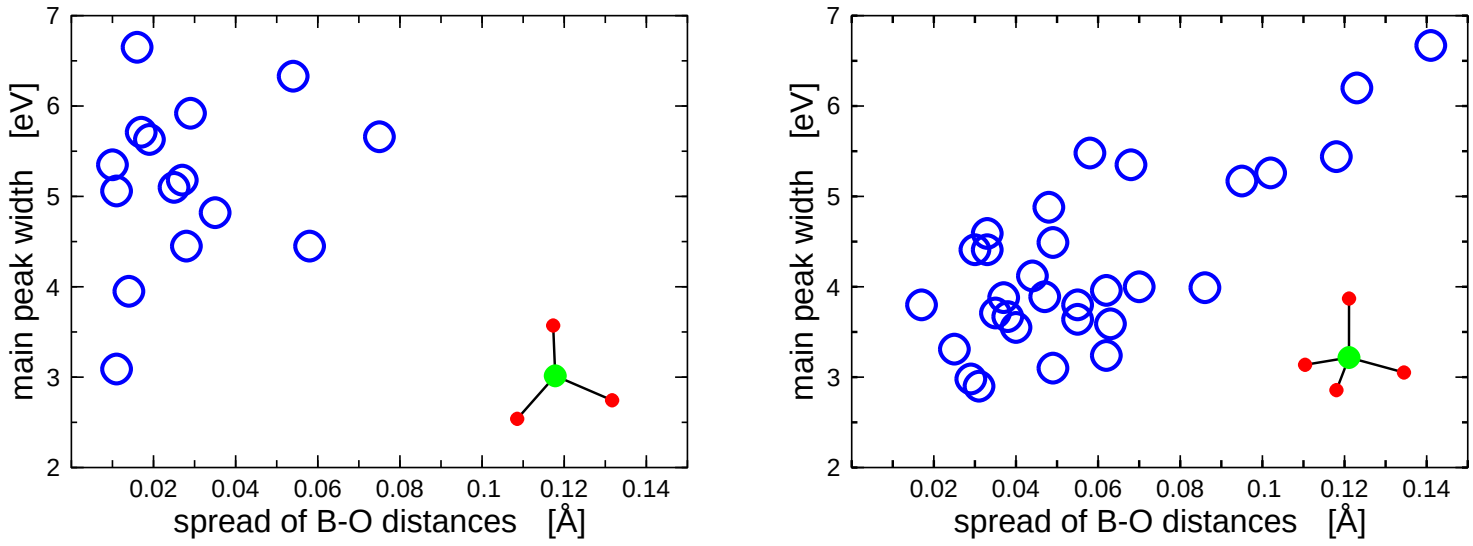
Peak widths and spread of distances





- Peaks related to BO_3 and BO_4 units behave differently in this respect

Peak widths and spread of distances



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- Even for spectra at BO_4 sites, there are significant deviations from the statistical relation

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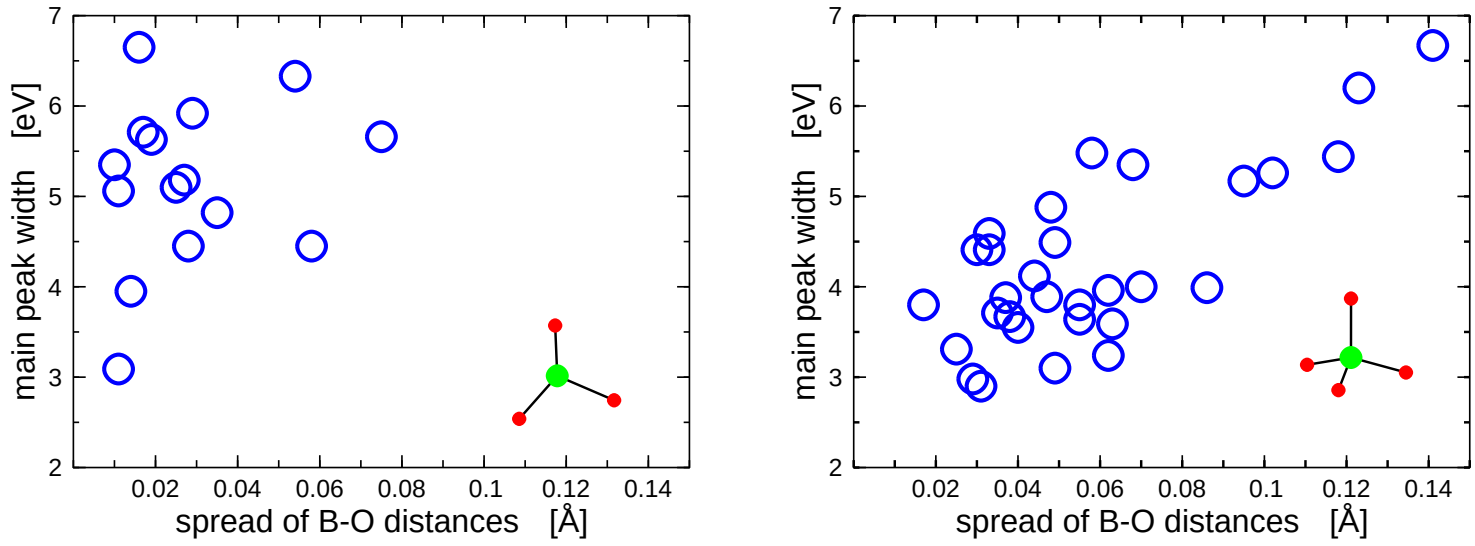

- Peaks related to BO_3 and BO_4 units behave differently in this respect
- Even for spectra at BO_4 sites, there are significant deviations from the statistical relation
- Exceptionally large spread of B–O distances yields exceptionally broad peak

The end is getting near. . .

Summary

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- Areas of main peaks depend only on the number of nearest oxygens — can be used for quantifying ratio of borons in BO_3 or BO_4 units
- Width of main peak at BO_4 site is related to the spread of B–O distances (with a significant statistical noise for typical situations)