Core-Level spectroscopy

Experiments and first-principles calculations

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Outline

- What is core-level spectroscopy

  XPS, XAS, XES, EELS, AES, XMCD

- How to analyze these experimental spectra with WIEN2k

  XSPEC, TELNES, others

- Examples
  - Various kinds of semiconductors
  - Ultra dilute dopants in functional materials
  - Dilute magnetic material

References

Nature Materials **2** (2003) 541.

Phys. Rev. B70 (2004) 045103

J. Am. Ceram. Soc. **88** (2005) 2013.

J. Phys.: Condens. Matter **21** (2009) 104211.

Solid State Comm. **151** (2011) 1749.

How do you know electronic structure?

- You can obtain theoretical (E-k) band structure and density of states with first-principles calc. such as WIEN2k.

- How do you know them experimentally?

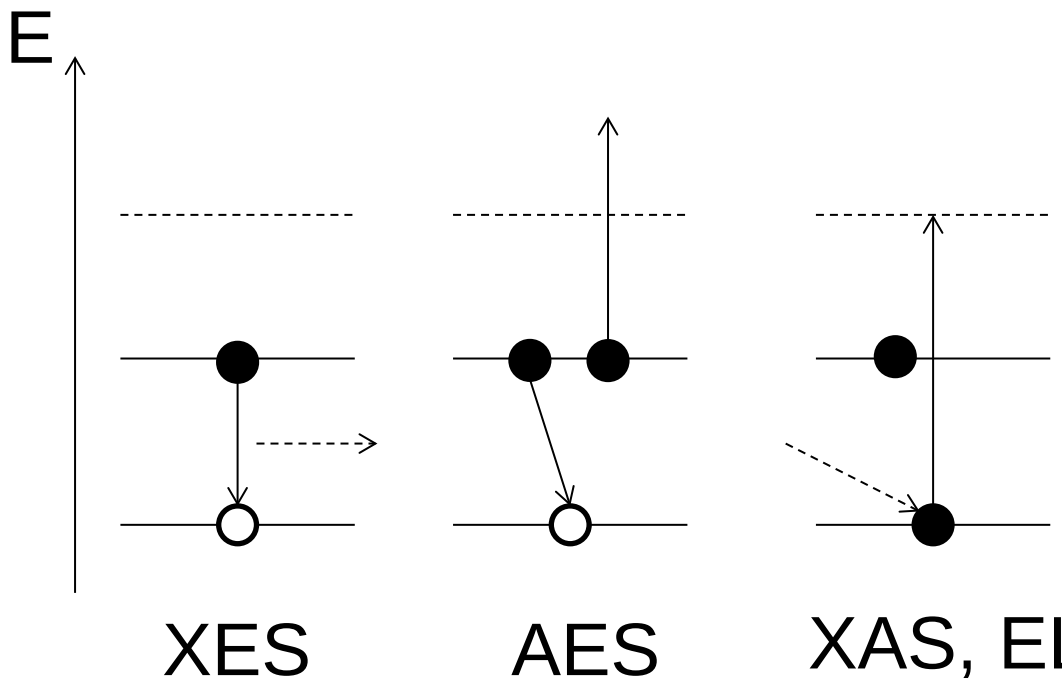
Core-Level spectroscopy

What is core-level spectroscopy?

Spectrum by electronic transition of core electrons

1) from core to unoccupied or ionized states

2) from outer to inner shells



Direct comparison with theoretical electronic structure is possible.

Theoretical spectrum -within IPA-

Transition probability

$$P \propto |\langle \psi_f | h | \psi_i \rangle|^2$$

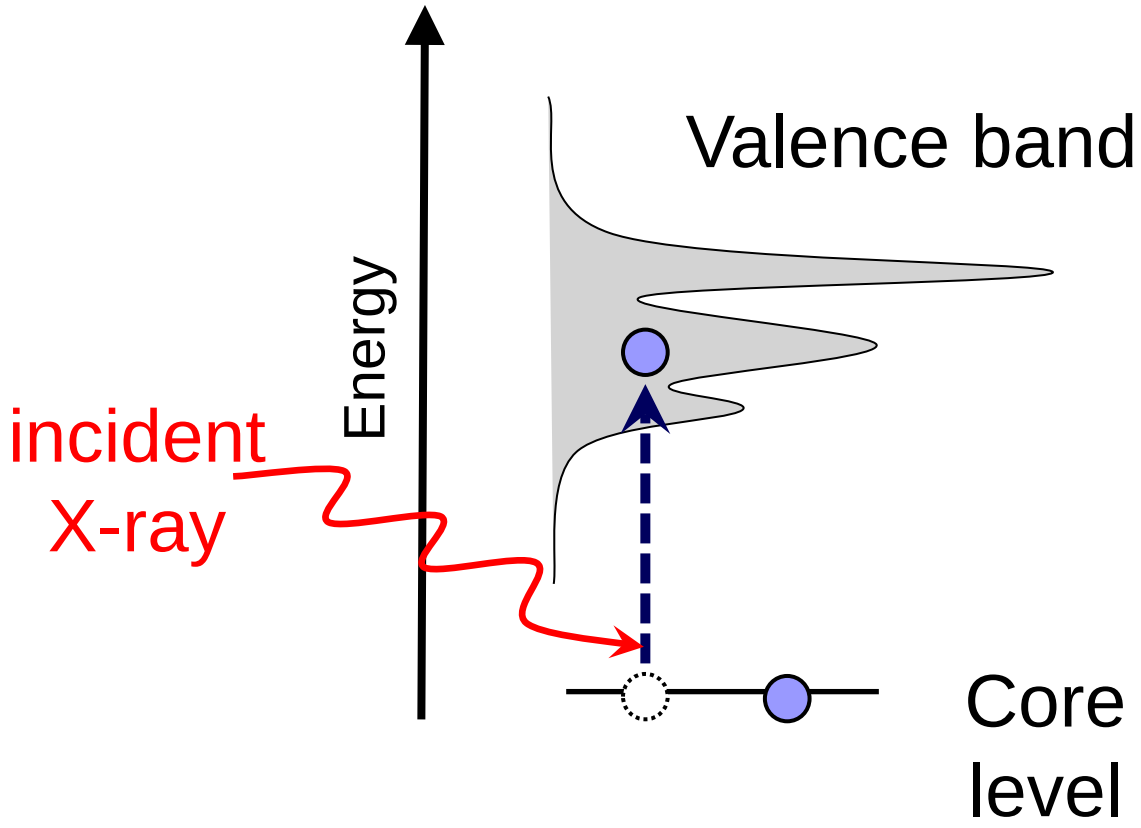
final state wave function

initial state wave function

- Selection rule for light emission and absorption from the Fermi's golden rule: h->**r**

$$\Delta l = \pm 1$$

XAS (X-ray absorption spectrum)



Electric dipole

Selection rule

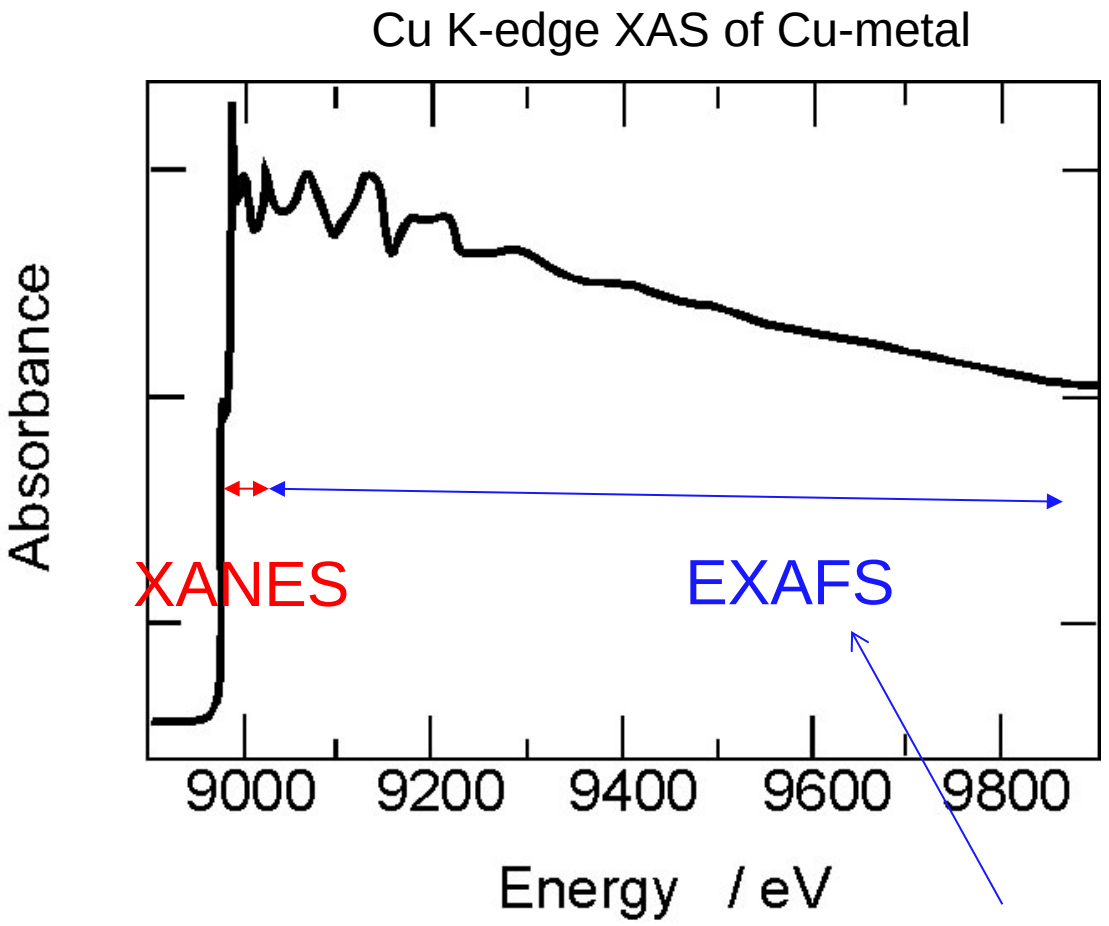
$\Delta l = \pm 1$

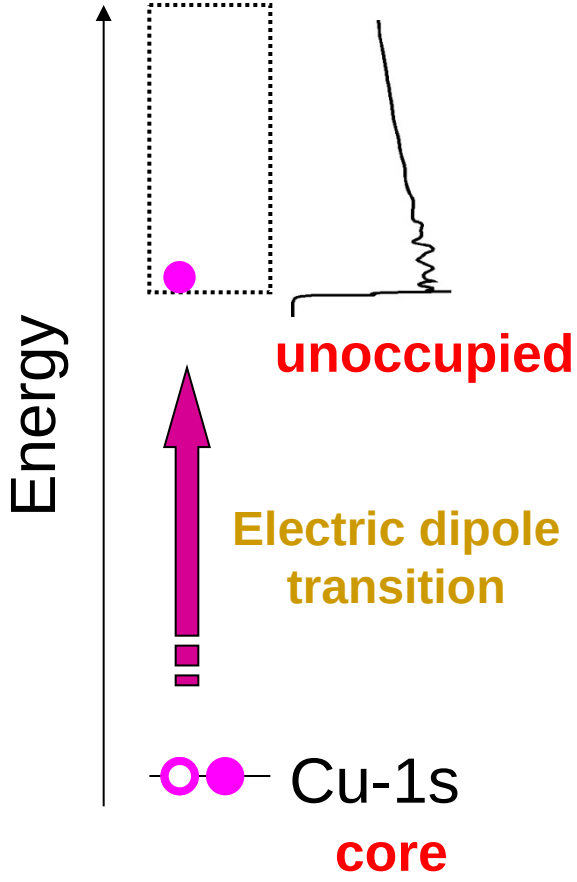
e.g., s->p, p->s,d

Spectral profile is a reflection of partial density of state in unoccupied state

Run XSPEC

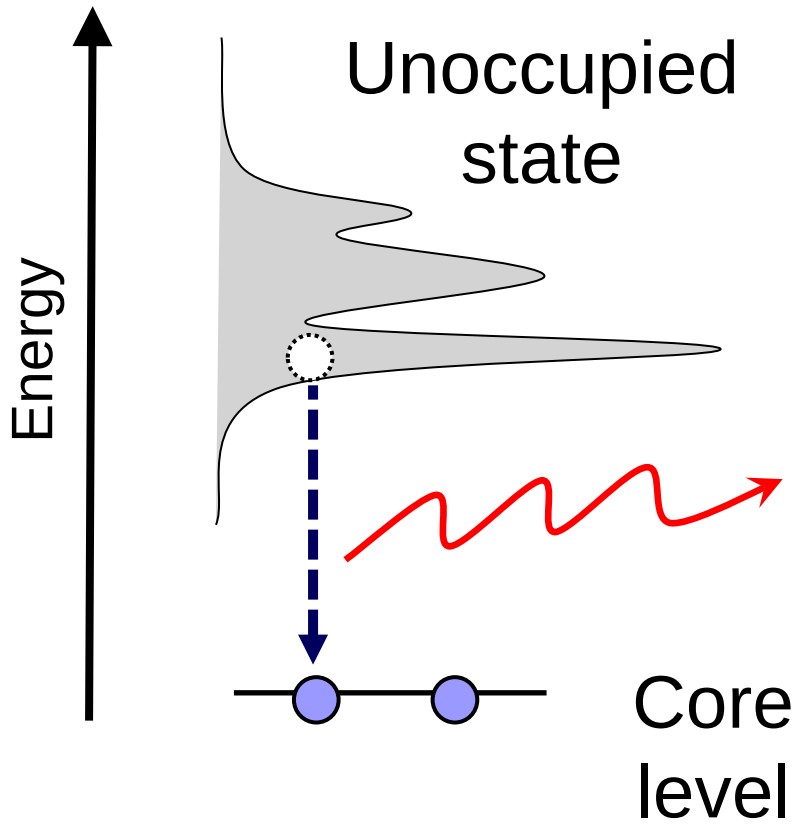
X-ray absorption near-edge structure (XANES)





Extended X-ray absorption fine structure

XES (X-ray emission spectrum)



Electric dipole

Selection rule

$\Delta l = \pm 1$

e.g., s->p, p->s,d

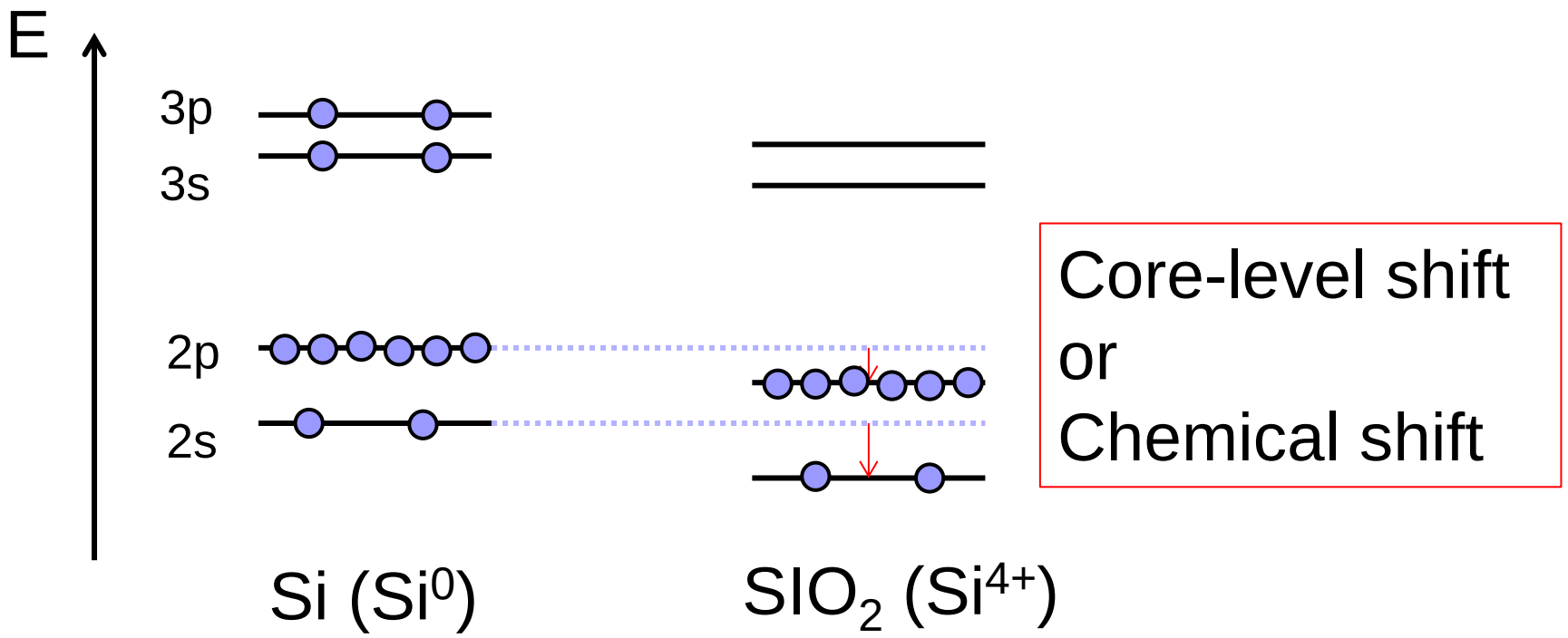
Spectral profile is a reflection of partial density of state in unoccupied state

Run XSPEC

XPS (X-ray photoemission spectrum)

- Core-level shift

$$E_{bin} = |h\nu - E_{kin} - \varphi|$$



look at the eigenvalue or the number of electrons in MT
(Slater's transition state method (1/2 core hole))

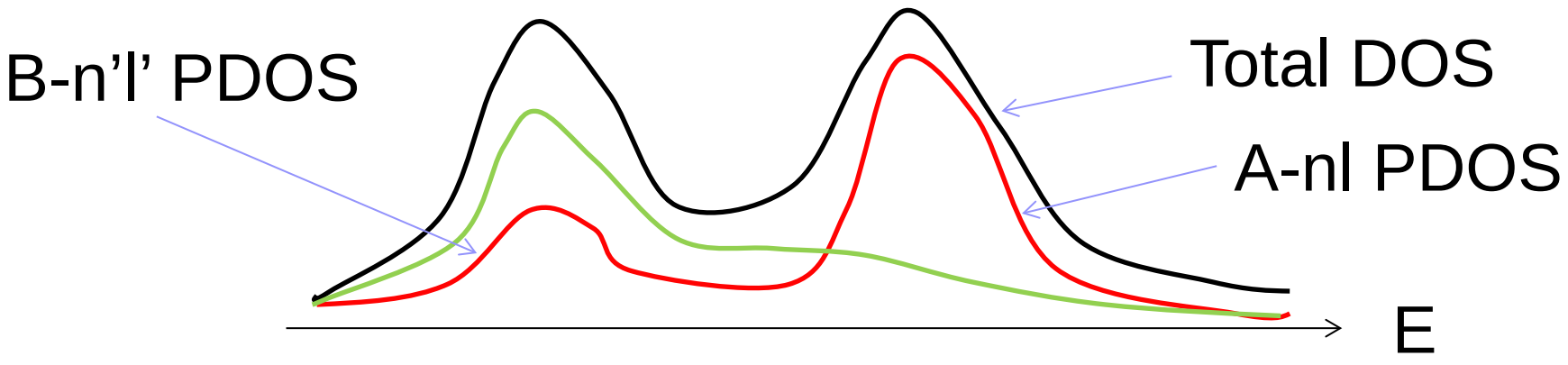
XPS (X-ray photoemission spectrum)

Valence XPS (not a core-level spectrum)

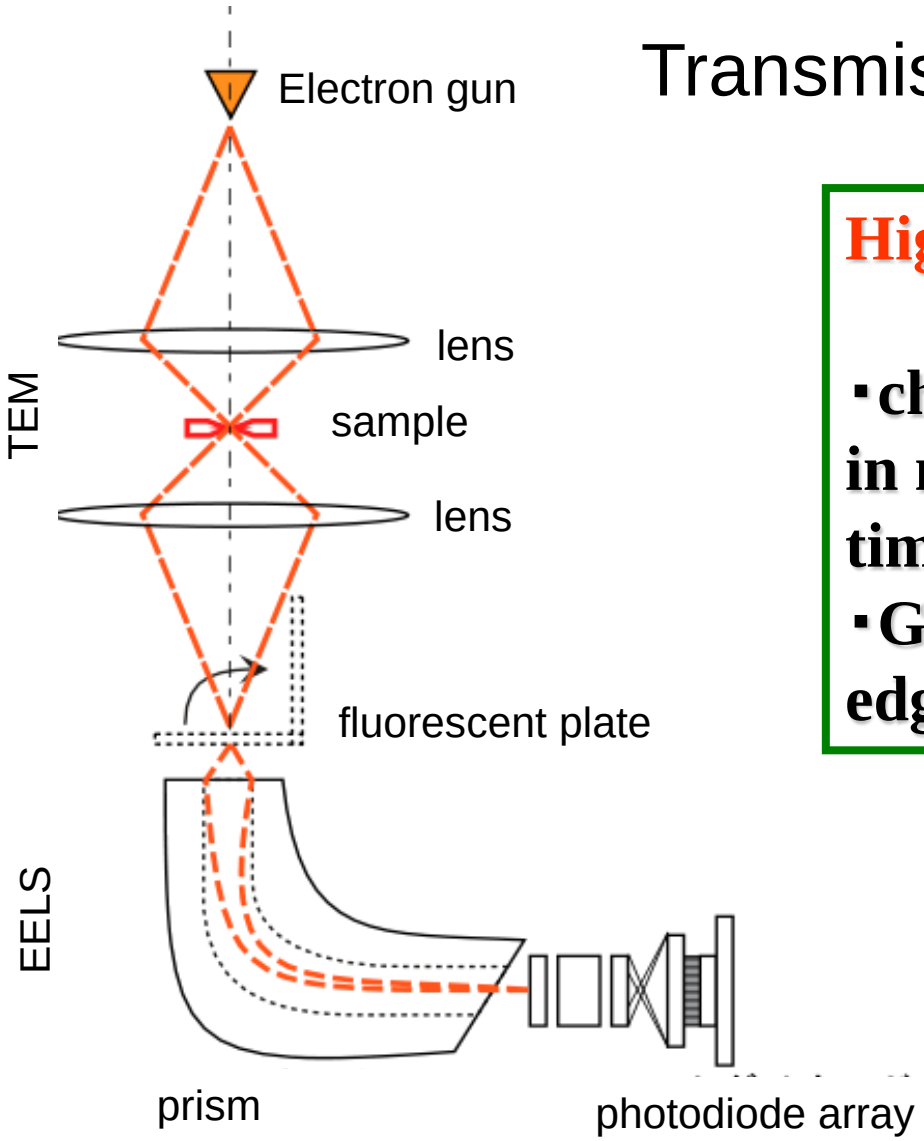
$$I(E) = \sum_i P_i D_i(E)$$

Ionization probability for ith component

Partial density of state ith component



ELNES with TEM



Transmission Electron Microprobe

High spatial resolution

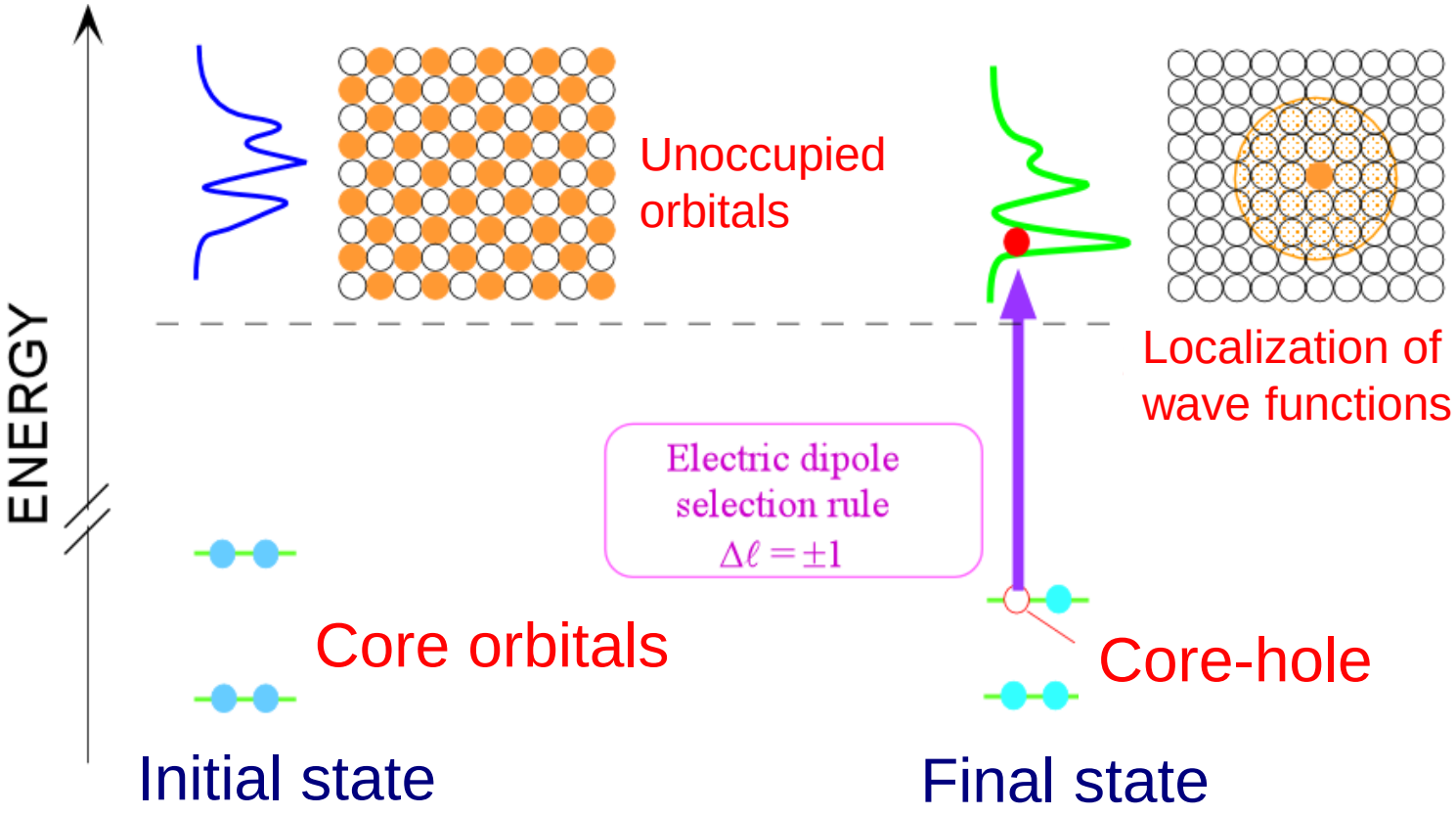
- **chemical state analysis is possible in nano-meter scale within a short time**
- **Good for light elements and L-edge of 3d transition metal**

Final state rule

- Final state determine the spectral shape!
- In the X-ray absorption process, core-hole exists in the final states, which must be considered in the calculation.
- In the X-ray emission process, holes exist in valence state, which can be well screened. Then we do not care much on this effect in the calc.

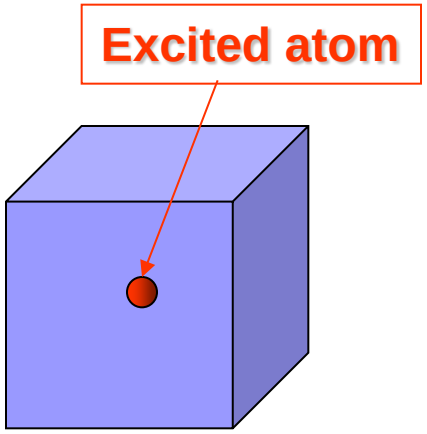
Core-hole effect

After the electron excitation, core-hole is created at the final state of X-ray absorption. Due to this core-hole, wave function is localized



XANES analysis with WIEN2k

- Approx. 100 atoms super-cell
（reduce the interaction among core-hole）



- Calculate both initial and final states
(introduce core-hole effect）

- Transition probability is obtained as a product of partial density of state and radial part of transision probability for corresponding atomic orbitals

- Transition energy from the difference in total electronic energy between initial and final states

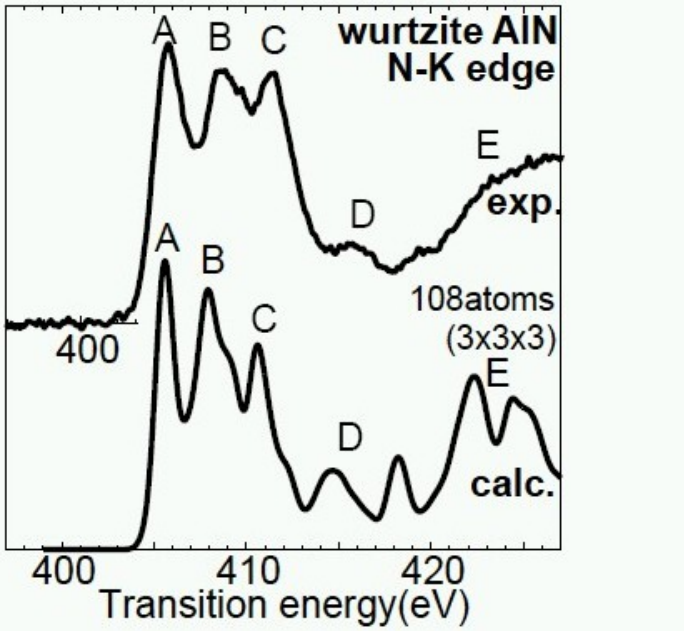
Flow of XANES analysis with WIEN2k

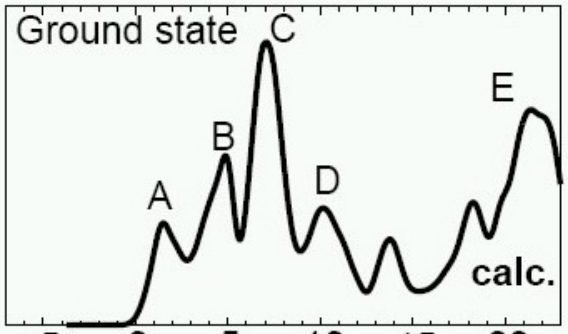
- Create super-cell (x supercell)
- Create core-hole (case.inc)
- Add one electron (excited electron) (case.in2)
- Do scf calc.
- Go into “XSPEC” in “Tasks”
- Increase bands in unoccupied states (case.in1)
- Remove added electron (case.in2)
- Non-scf calc. (x lapw1, x lapw2 –qtl)
- Prepare input for XSPEC (case.inxs)
- Do XSPEC -> you can get theoretical XANES

Example

- III-V nitrides and ZnO

N K-edge of AlN





Relative energy from conduction band bottom (eV)

Core-hole effect

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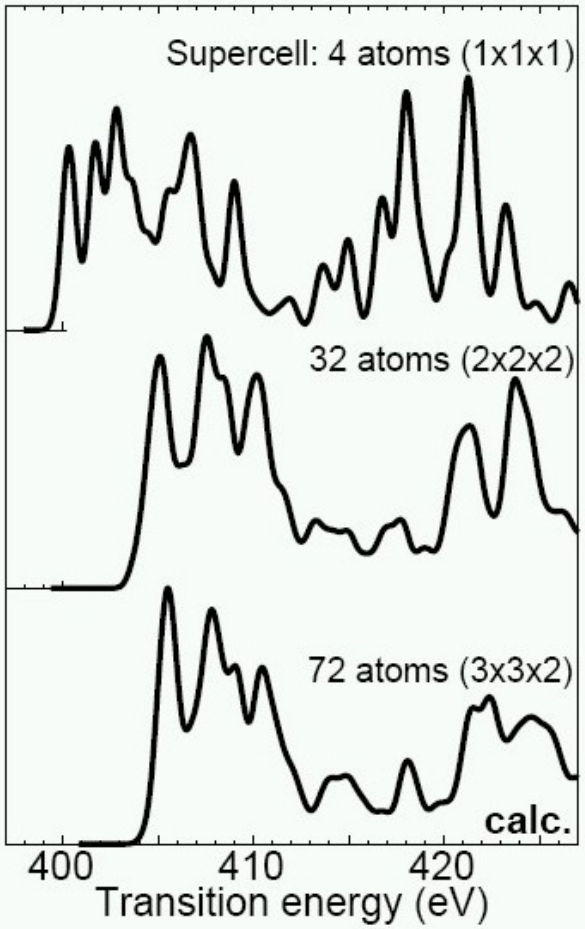
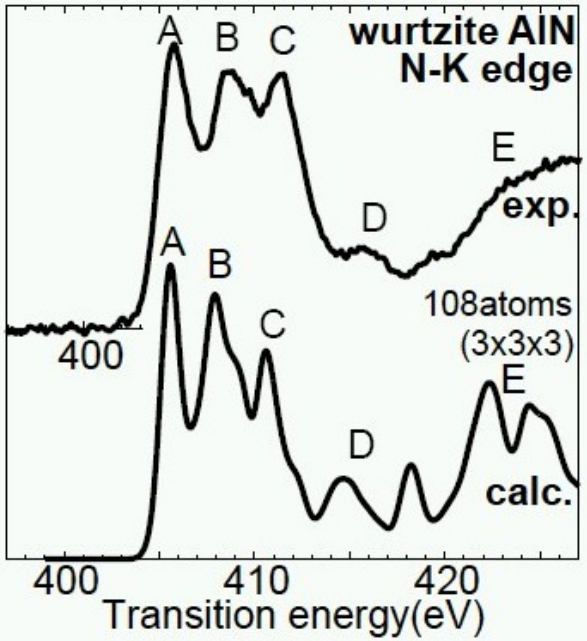
N K-edge of AlN





In the smaller super-cell, large interaction appears among core-holes

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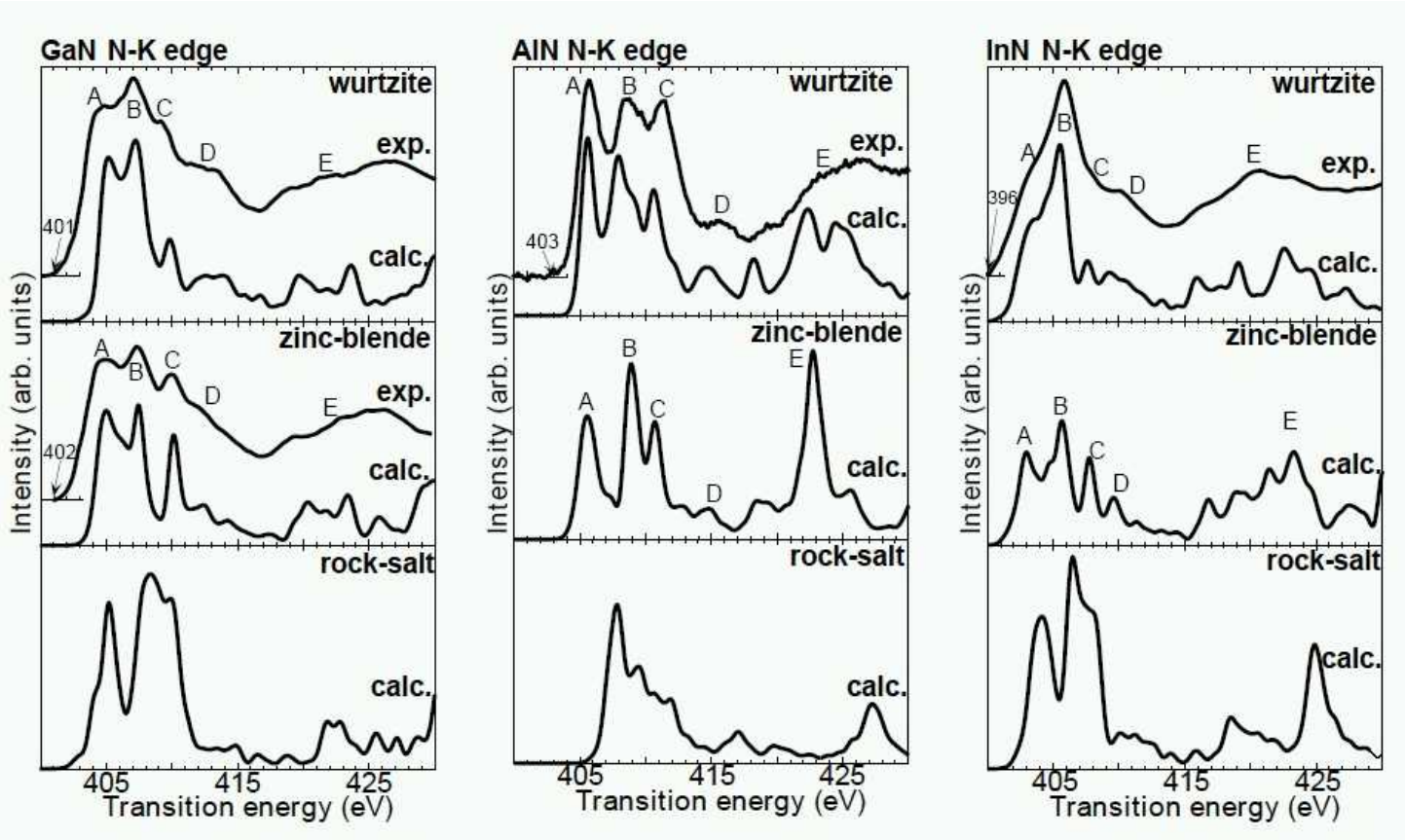
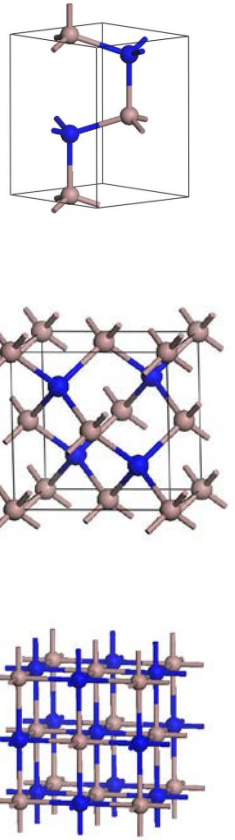
N K-edges of GaN, AlN, InN





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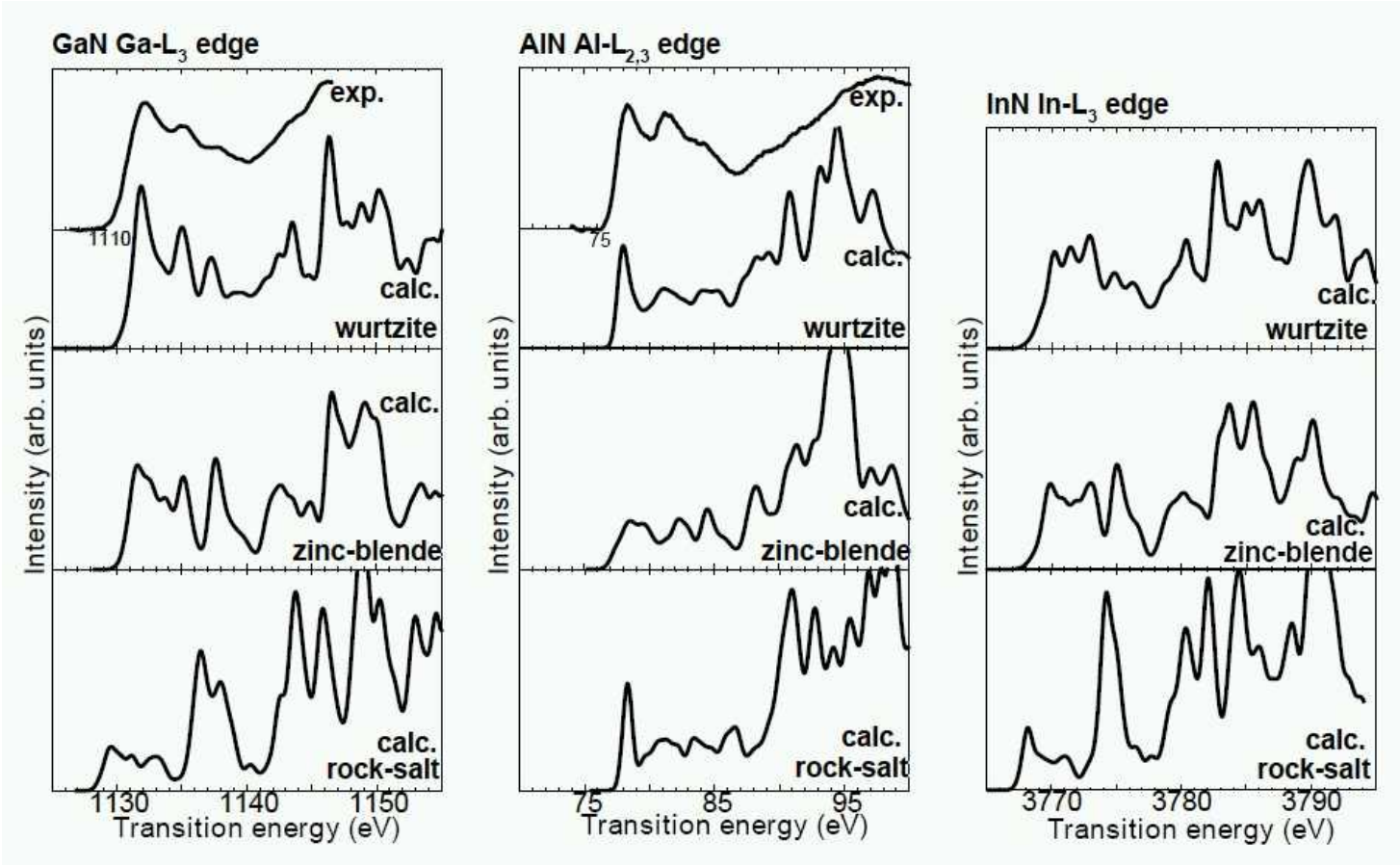
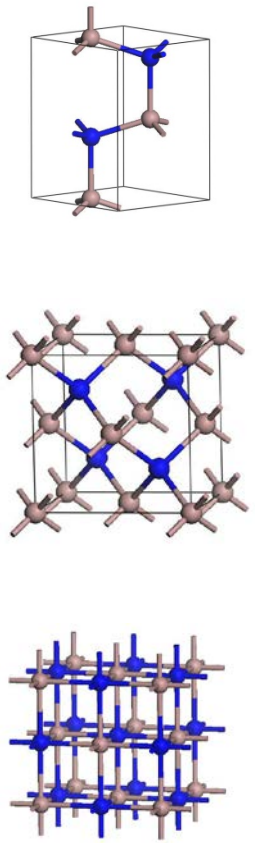
Cation L edges of GaN, AlN, InN





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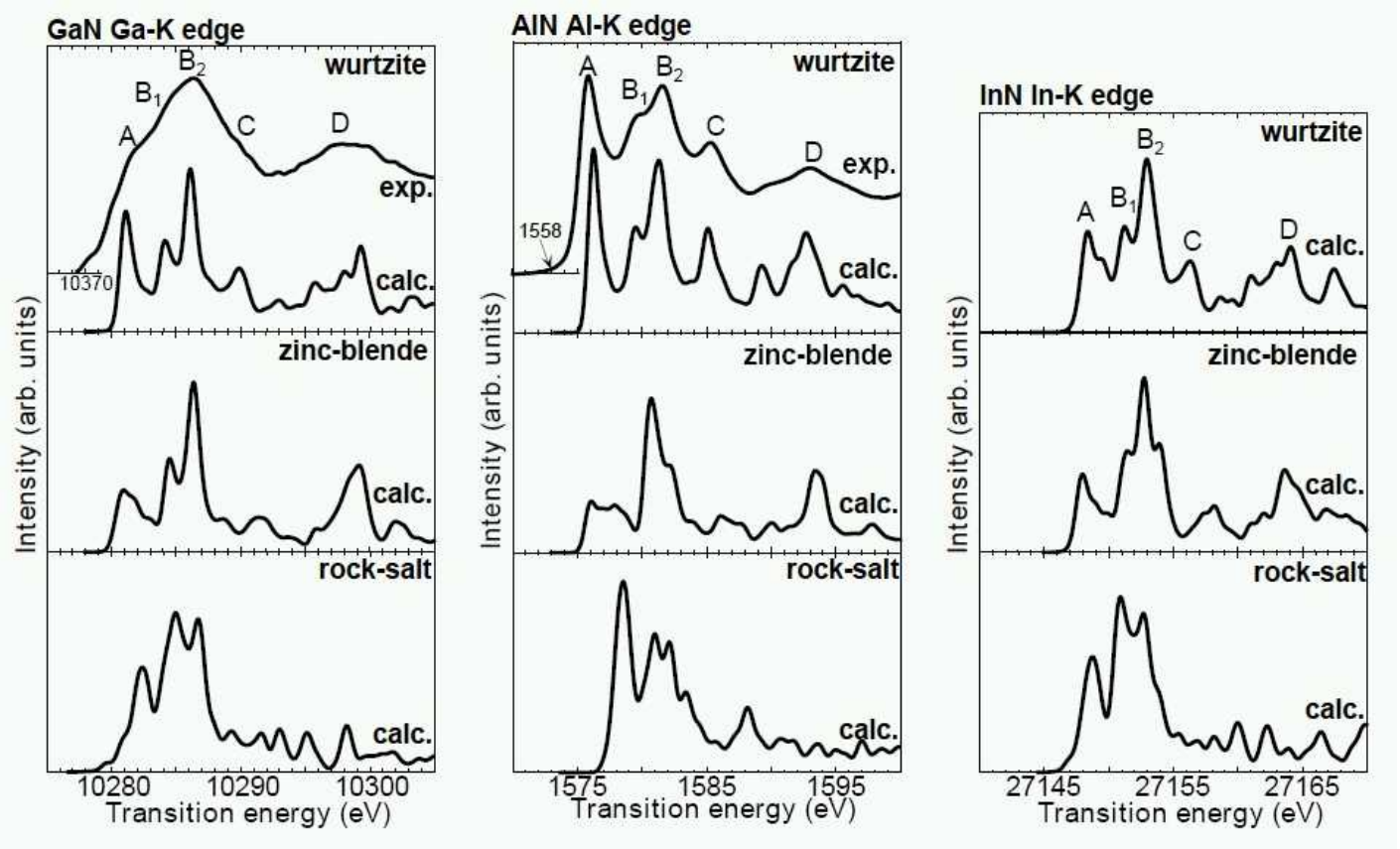
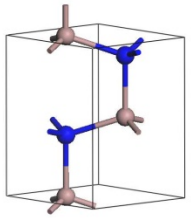
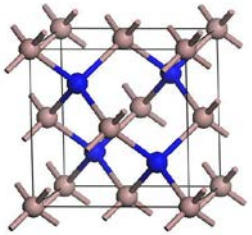
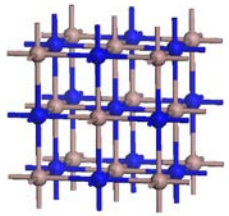
Cation K edges of GaN, AlN, InN









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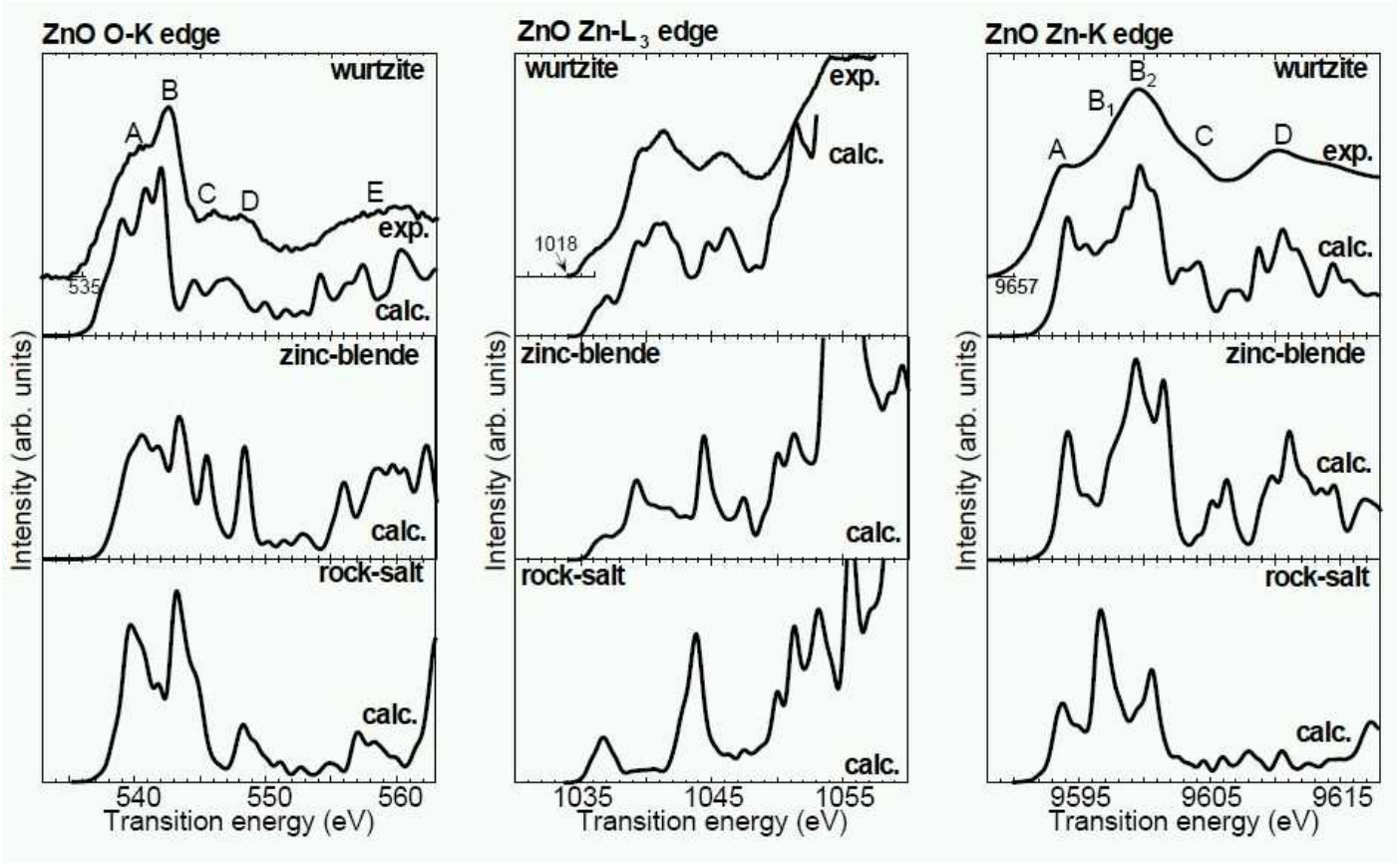
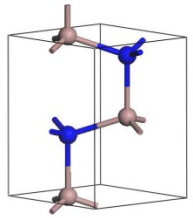
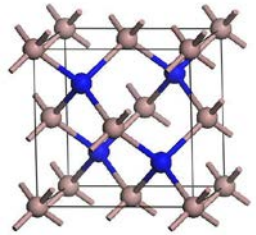
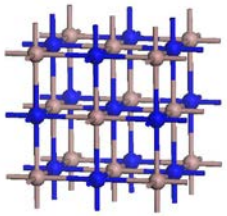
w-, zb-, rs-ZnO









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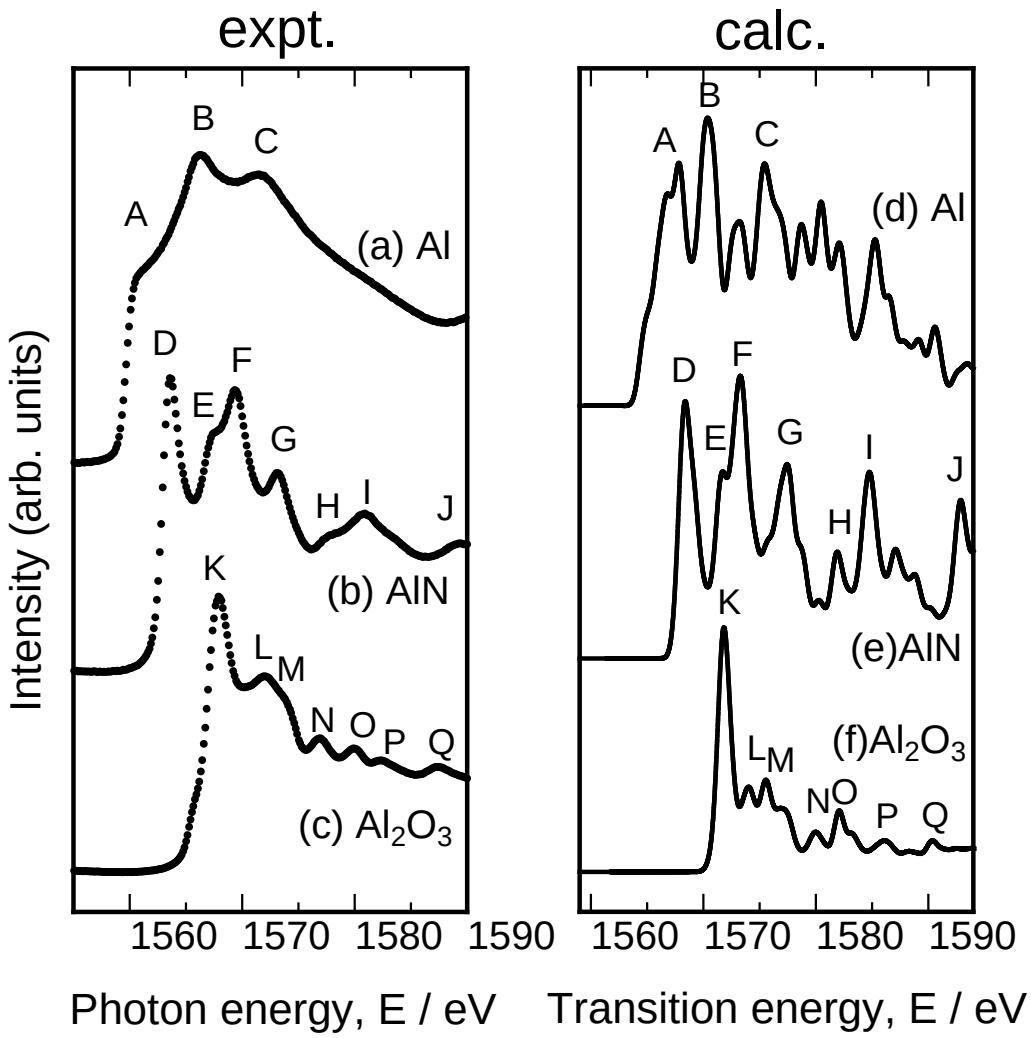
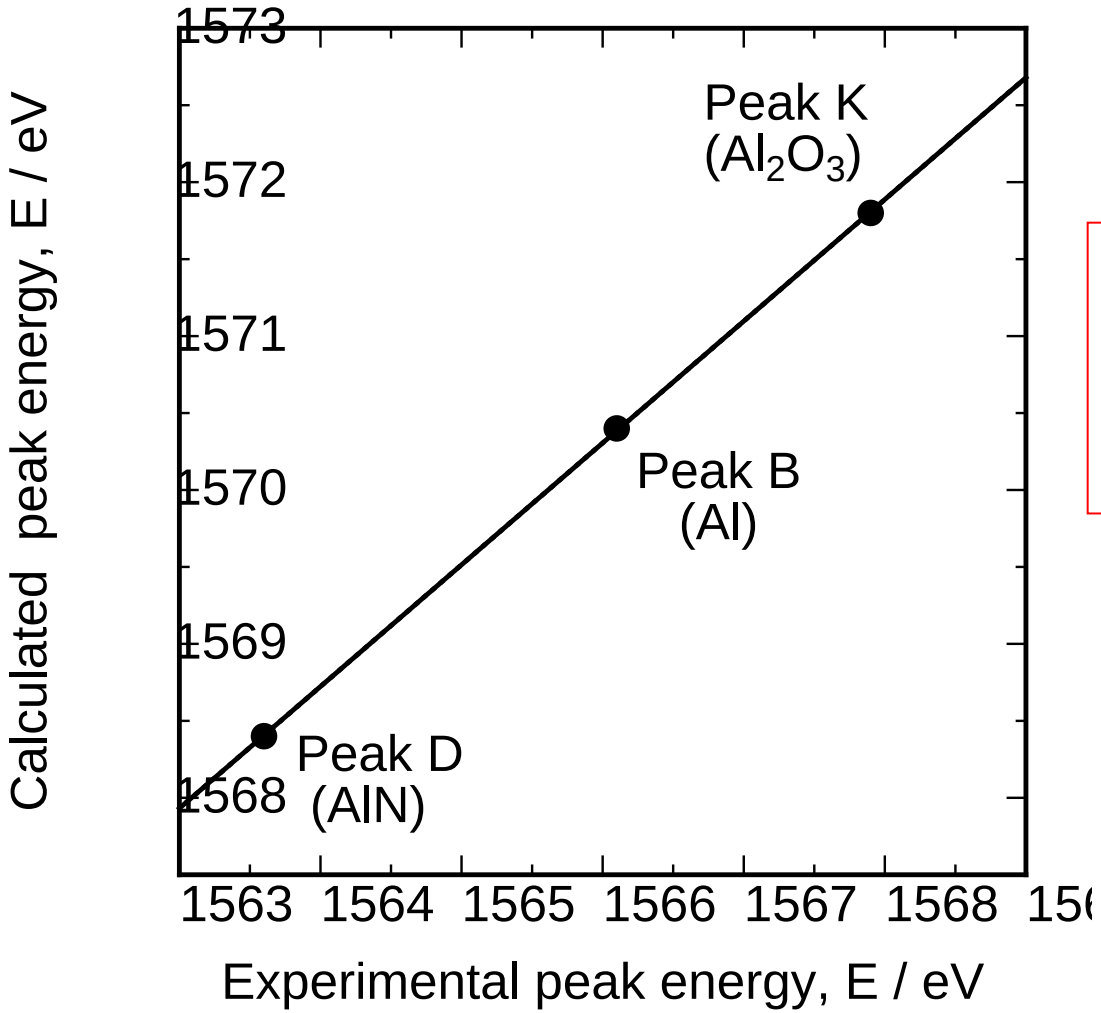
Al K-edges of Al, AlN, Al_2O_3



Good Agreement, both in shape and energy!

Mater. Trans. 45 (2004) 2031

Chemical shift (Al K-edge)



Chemical shift can be determined!

Mater. Trans. 45 (2004) 2031

Angle dependence of XANES

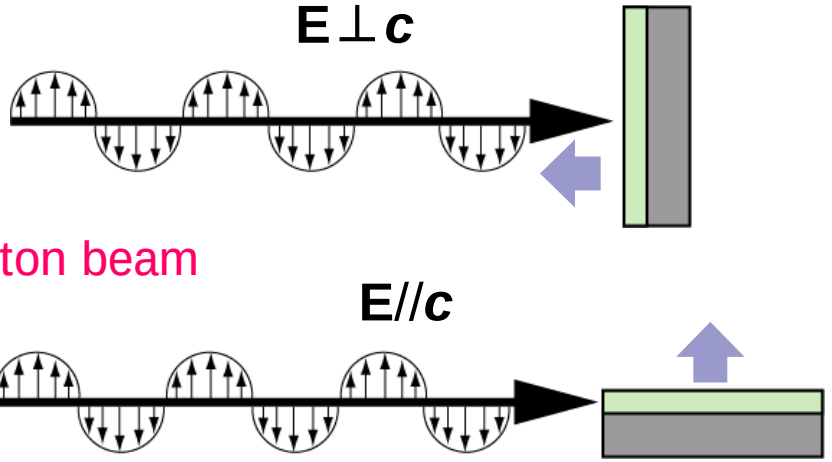
s→p

dipole transition

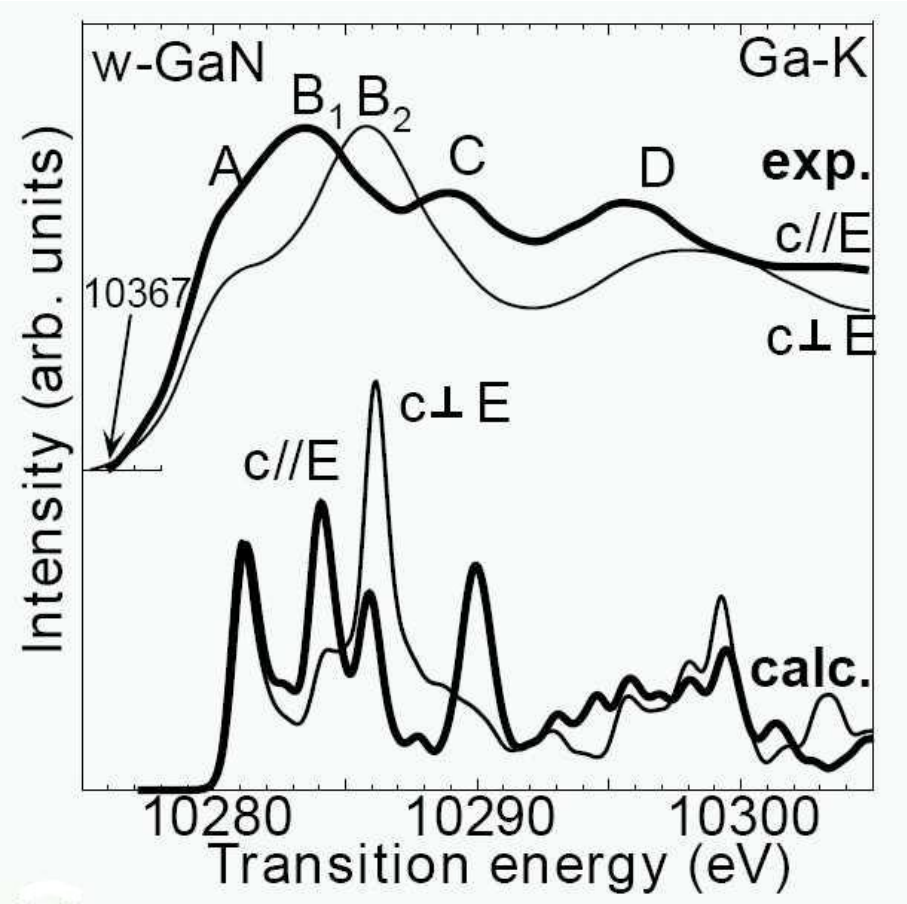
$$\left|\left\langle \Psi_{f,p}\left|\vec{r}\right|\Psi_{i,s}\right\rangle\right|^2$$

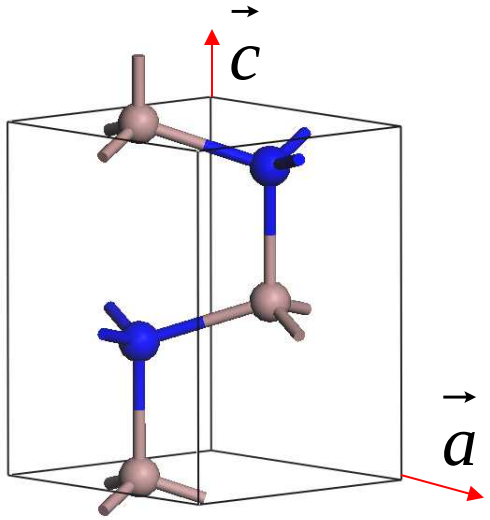
$$\left|\left\langle \Psi_{f,p_x}\left|\vec{x}\right|\Psi_{i,s}\right\rangle\right|^2 \qquad \left|\left\langle \Psi_{f,p_y}\left|\vec{y}\right|\Psi_{i,s}\right\rangle\right|^2 \qquad \left|\left\langle \Psi_{f,p_z}\left|\vec{z}\right|\Psi_{i,s}\right\rangle\right|^2$$

Incident photon beam



Angle dependence of XANES (Ga-K of GaN)





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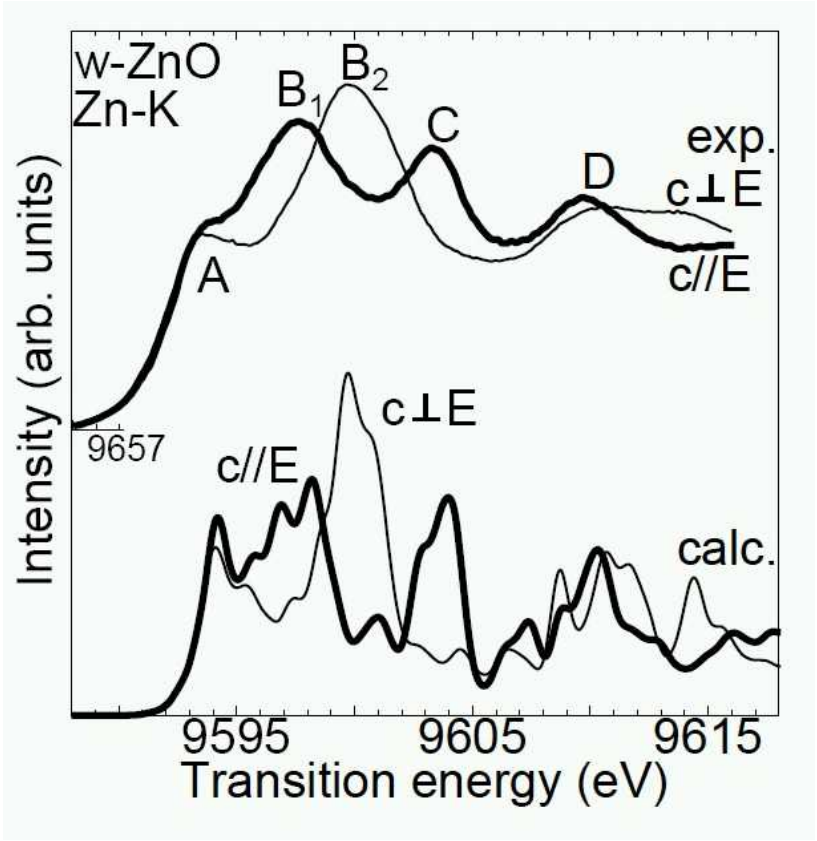
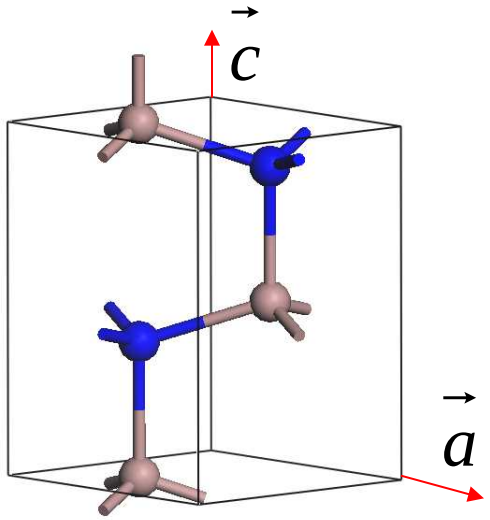
Angle dependence of XANES (Zn-K of ZnO)





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xspec input file

XES

```
NbC: C K      (Title)
2             ( atom)
1             (n core)
0             (l core)
0,0.5,0.5     (split, int1, int2)
-20,0.1,3     (EMIN,DE,EMAX in eV)
EMIS          (type of spectrum)
0.35          (S)
0.25          (gamma0)
0.3           (W)
AUTO          (band ranges AUTO or MAN
-7.21         (E0 in eV)
-10.04        (E1 in eV)
-13.37        (E2 in eV)
```

XAS

```
NbC: C K      (Title)
2             (atom)
1             (n core)
0             (l core)
0,0.5,0.5     (split, int1, int2)
-2,0.1,30     (EMIN,DE,EMAX in eV)
 ABS  (type of spectrum)
0.5           (S)
0.25          (gamma0)
```

Details in user guide

EELS in wien2k (**telnes2** program)

- Within the dipole approximation the momentum transfer vector in non-relativistic EELS playes the same role as polarization vector in XAS
- ***telnes2*** program also handles non-dipole transitions and relativistic corrections

See details in users guide

When independent particles approximation does not work

we have to go

Beyond independent particles approximation

summary

- standard calculations (optical and X-ray spectra) always operate within independent particles approximation
    - Band details matter (band gap problem)
    - No electron-hole correlation
        - Core hole helps for K edges in XAS but not for L23
- Going beyond IPA is expensive but possible