Applications of FLAPW Method: HiLAPW

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OUTLINE

- **Typical Applications**
  - **Electric Field Gradient**
  - **Atomic Force and Phonon**
  - **X-ray Absorption Spectroscopy Spectra**
- **Summary**

Electric Field Gradient

- **Definition of EFG**

$$V_{ij} = \frac{\partial V(\mathbf{r})}{\partial i \partial j} \quad (i, j = x, y, z)$$

- **Maximum Term**

$$q = V_{ZZ}$$

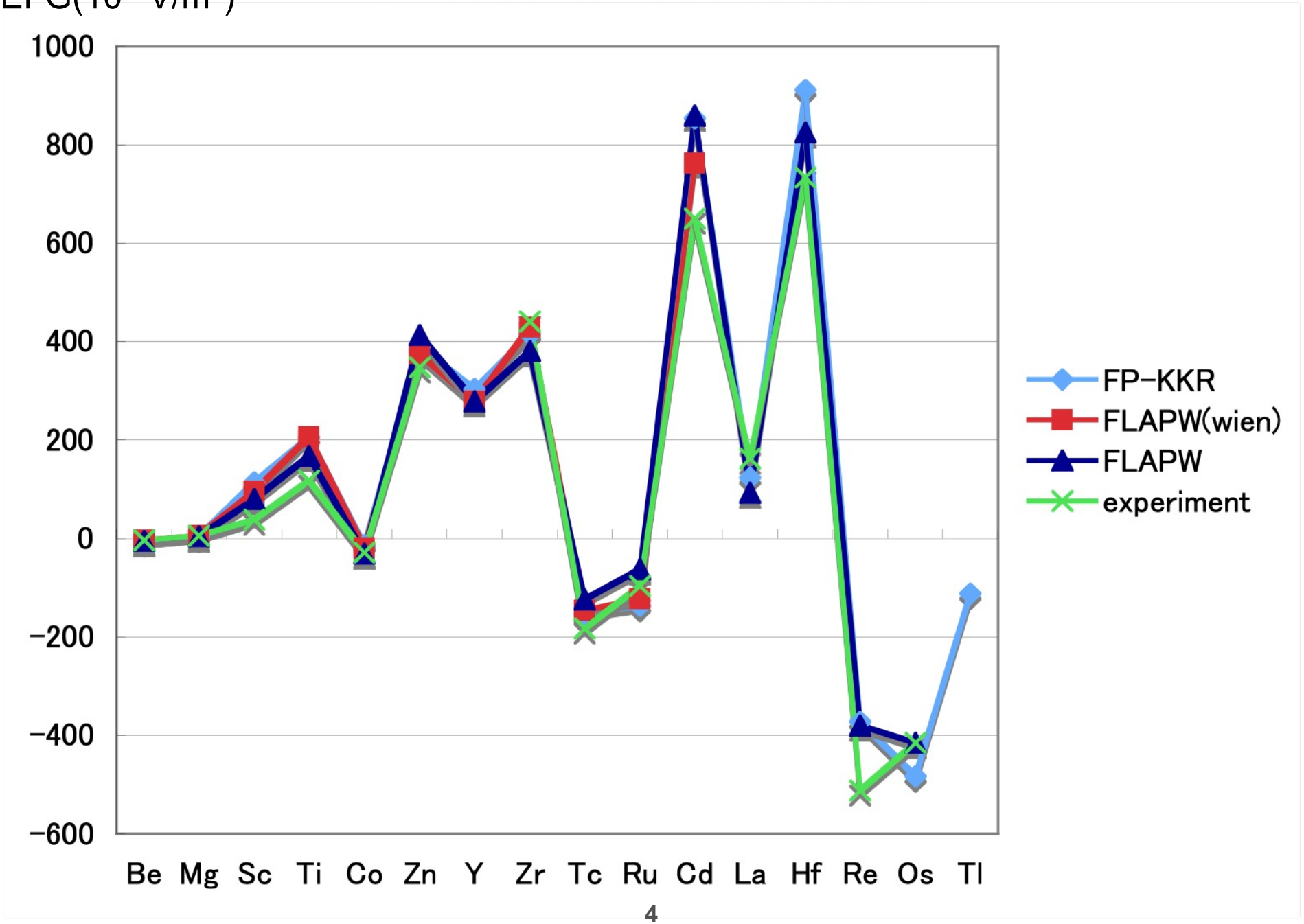
- **Asymmetric Parameter**

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

- **Nuclear Magnetic Resonance Measurements**

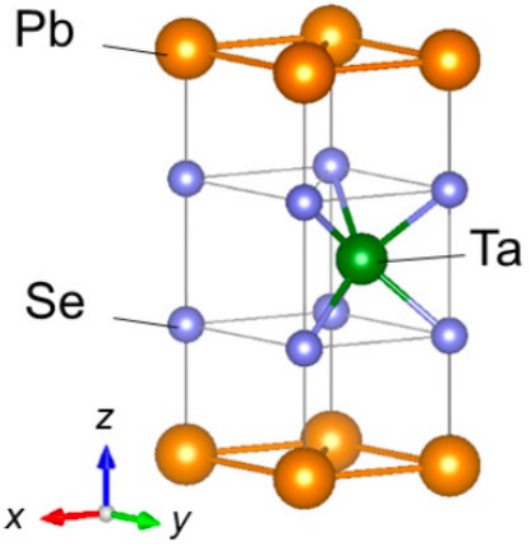
$$\nu_Q = \frac{3eqQ}{2I(2I-1)h}$$ **Quadruple coupling frequency**

EFG in HCP Metals

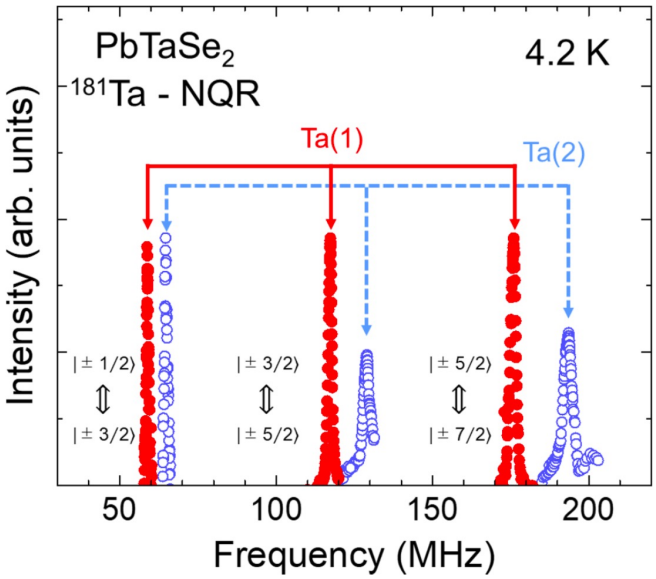


EFG at Ta in $PbTaSe_2$

PRB **102**, 214504 (2020)



P-6m2 structure



^{181}Ta NQR spectra

	ν_Q (MHz)	η
Experiment		
Ta(1) site	58.7 ± 0.5	0.00–0.02
Ta(2) site	64.5 ± 0.5	0.03–0.04
DFT calculation		
$P\bar{6}m2$	57.78	0.00
$P6_3/mmc$	46.39	0.00

Reference: EFG

- **EFG Calculations by FLAPW**
  - **PRL 54, 1192 (1985)** **Li_3N**
  - **PRB 37, 2792 (1988)** **hcp metals**
  - **PRB 102, 214504 (2020)** **$PbTaSe_2$**
- **EFG Calculations by FP-KKR**
  - **M. Ogura, PhD Thesis, Osaka University (2004)**
- **Review on EFG in NMR**
  - **Solid State Physics Vol. 5, pp. 321.**

Atomic Forces

$$\boldsymbol{F}_\alpha = \boldsymbol{F}_\alpha^{\mathrm{Hellmann-Feynman}} + \boldsymbol{F}_\alpha^{\mathrm{Pulay}}$$

$$\boldsymbol{F}_\alpha^{\mathrm{Pulay}} = -\sum_i^{\mathrm{occ.}} \left[\langle \frac{\delta\psi_i}{\delta \boldsymbol{R}_\alpha} | \mathcal{H} | \psi_i \rangle + \langle \psi_i | \mathcal{H} | \frac{\delta\psi_i}{\delta \boldsymbol{R}_\alpha} \rangle \right]$$

$$\langle \frac{\delta\phi^{\mathrm{APW}}_{\boldsymbol{k}+\boldsymbol{K}}}{\delta \boldsymbol{R}_\alpha} | \mathcal{H} | \psi_i \rangle = i(\boldsymbol{k}+\boldsymbol{K}) \langle \phi^{\mathrm{APW}}_{\boldsymbol{k}+\boldsymbol{K}} | \mathcal{H} | \psi_i \rangle$$

$$\delta C_{\boldsymbol{k}+\boldsymbol{K},i} = -\langle \phi^{\mathrm{APW}}_{\boldsymbol{k}+\boldsymbol{K}} | \mathcal{H} - \varepsilon_i | \psi_i \rangle \delta t$$

"Augmented-Plane-Wave Force Calculations for Transition-Metal Systems",
Interatomic Potentials and Structural Stability,
ed. K. Terakura and H. Akai, (Springer-Verlag, 1993) p. 33.

Phonon Calculation

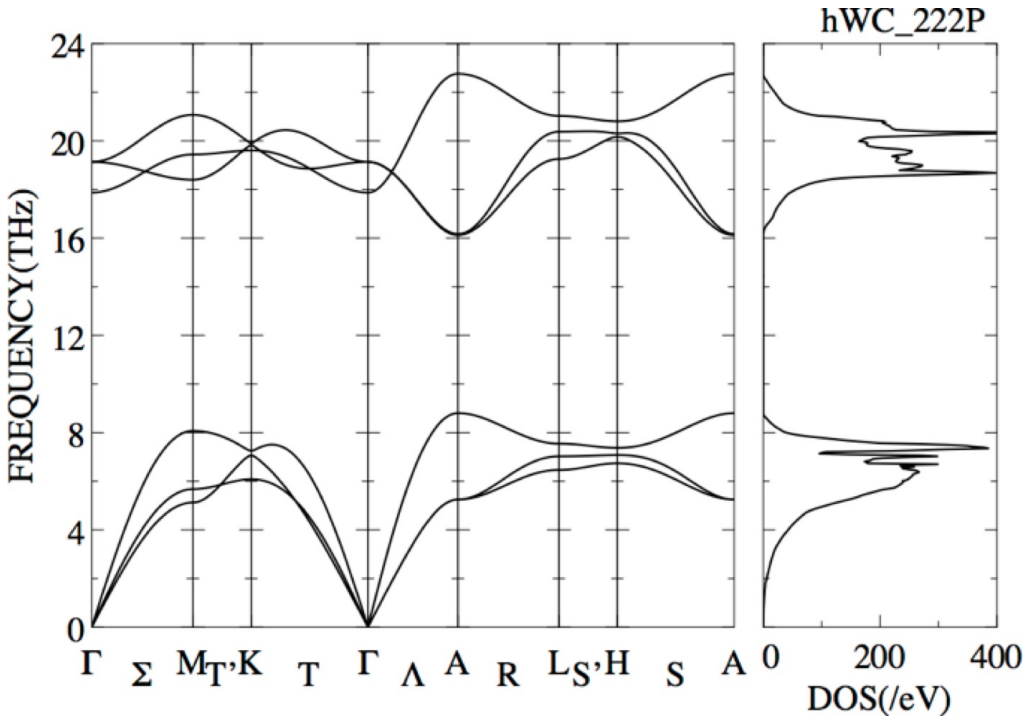
- **Equations of Motion** $M_\nu \ddot{u}_{n\nu\alpha} = -\sum_{n'\nu'\beta} \frac{\partial^2 E}{\partial u_{n\nu\alpha} \partial u_{n'\nu'\beta}} u_{n'\nu'\beta}$
- **Displacements** $u_{n\nu\alpha} = (M_\nu)^{-\frac{1}{2}} C_{\nu\alpha} e^{i(\mathbf{q}\cdot\mathbf{R}_n - \omega(\mathbf{q})t)}$
- **Dynamical Matrix**

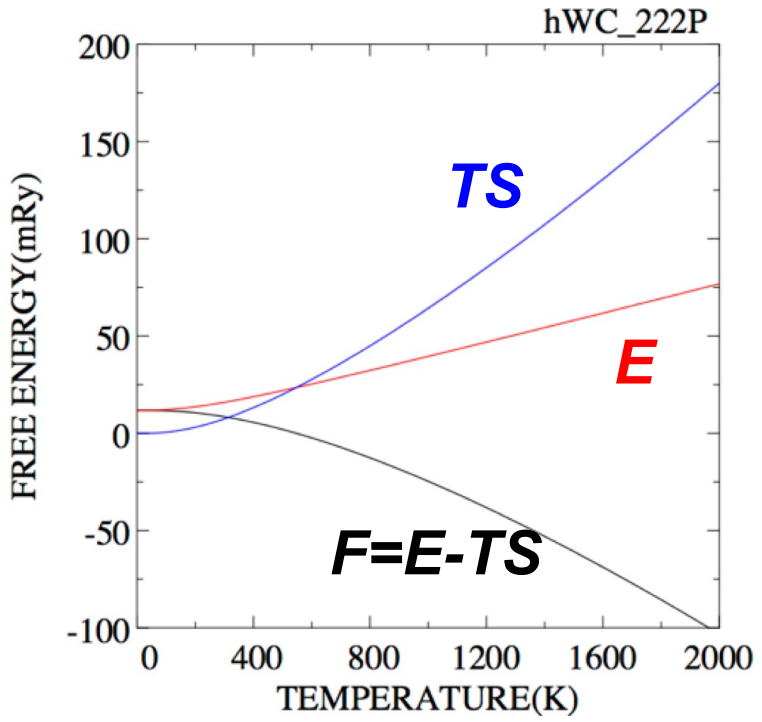
$$D_{\nu\alpha,\nu'\beta}(\mathbf{q}) = (M_\nu M_{\nu'})^{-\frac{1}{2}} \sum_{n'} \frac{\partial^2 E}{\partial u_{0\nu\alpha} \partial u_{n'\nu'\beta}} e^{i\mathbf{q}\cdot\mathbf{R}_{n'}}$$

$$\approx -(M_\nu M_{\nu'})^{-\frac{1}{2}} \frac{F_{0\nu\alpha}}{u_{0\nu'\beta}} \qquad \begin{cases} u_{n\nu\alpha} = u_{0\nu\alpha} e^{i\mathbf{q}\cdot\mathbf{R}_n} \\ F_{n\nu\alpha} = -\dfrac{\partial E}{\partial u_{n\nu\alpha}} \end{cases}$$

$$\mathbf{D}(\mathbf{q})\mathbf{C} = \mathbf{C}\omega^2(\mathbf{q}) \quad \Rightarrow \quad \textbf{Phonon modes}$$

Phonon Calculation of WC





$$E = \sum_{n,\boldsymbol{q}} \hbar\omega_n(\boldsymbol{q}) \left[\frac{1}{2} + (e^{\beta\hbar\omega_n(\boldsymbol{q})} - 1)^{-1} \right]$$

$$F = \sum_{n,\boldsymbol{q}} \left[\frac{\hbar\omega_n(\boldsymbol{q})}{2} + \beta^{-1} \ln\left(1 - e^{-\beta\hbar\omega_n(\boldsymbol{q})}\right) \right]$$

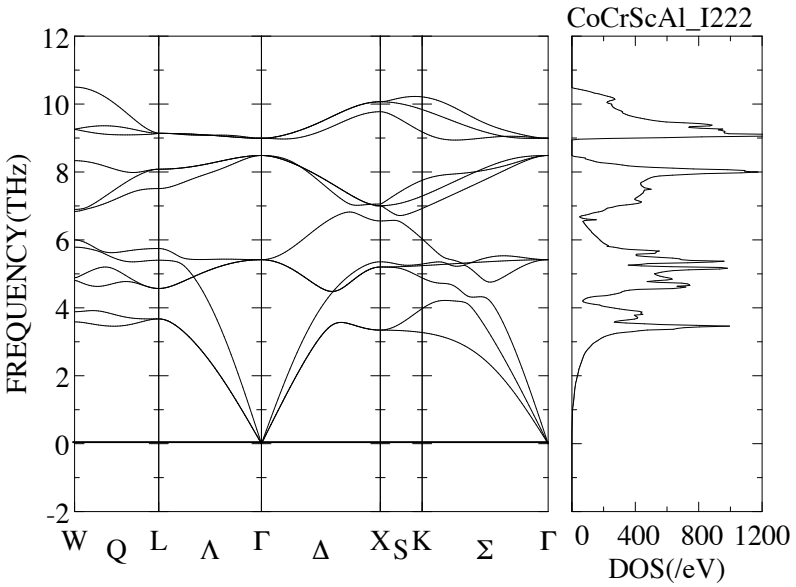
Structural Stability of CoCrScAl

➢ **Elastic stability**

		Born-Cauchy conditions (GPa)
Bulk modulus :	$K=(C_{11}+2C_{12})/2$	116.1 > 0
Shear modulus :	$Cs=(C_{11}-C_{12})/2$	61.9 > 0
	C_{44}	103 > 0

Elastically stable

➢ **Dynamical stability**



No soft mode

Dynamically stable

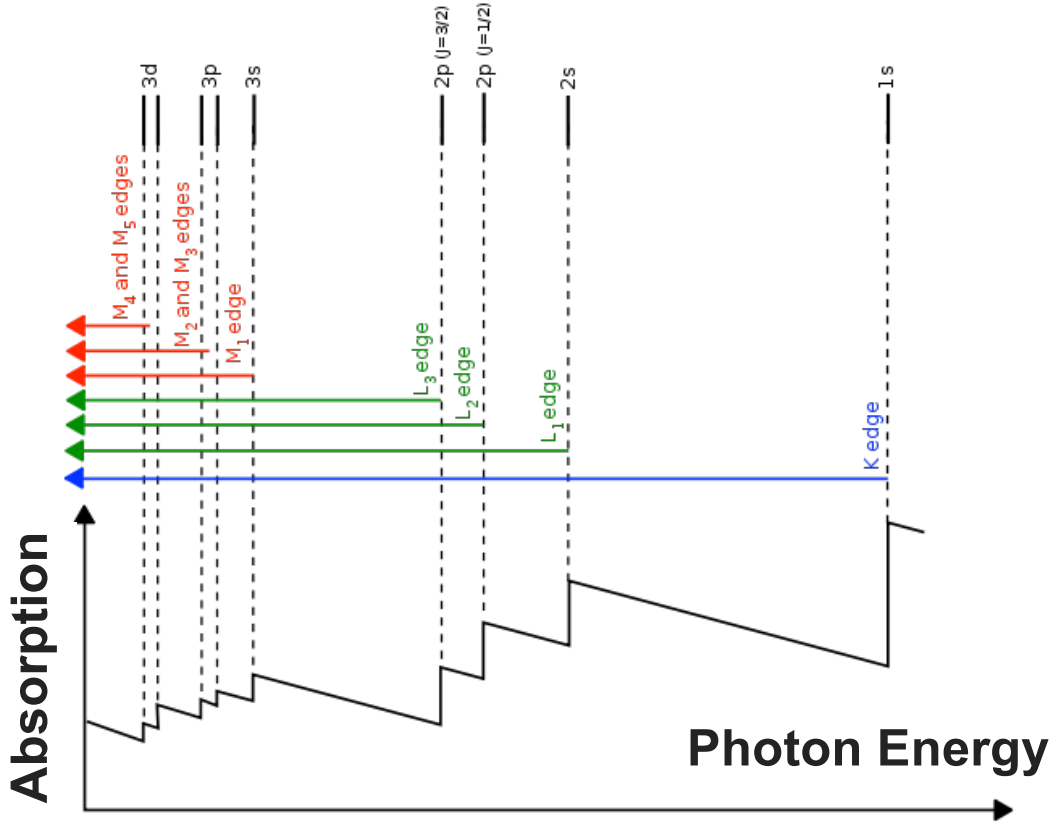
F. Kuroda, unpublished

Refereces: Atomic Forces by FLAPW

- **Soler, Williams, PRB40, 1560 (1989); PRB42, 9728 (1990); PRB47, 6784 (1993).**
- **Yu, Singh, Krakauer, PRB43, 6411 (1991); PRB45, 8671 (1992).**
- **Goedecker, Maschke, PRB45, 1597 (1992).**
- **T. Oguchi, "Interatomic Potentials and Structural Stability", ed. by K. Terakura and H. Akai, (Springer-Verlag, 1993) p. 33.**
- **D. J. Singh, "Planewaves, pseudopotentials and the LAPW method" (Kluwer Academic, Boston, 1994).**

X-ray Absorption Spectroscopy (XAS)

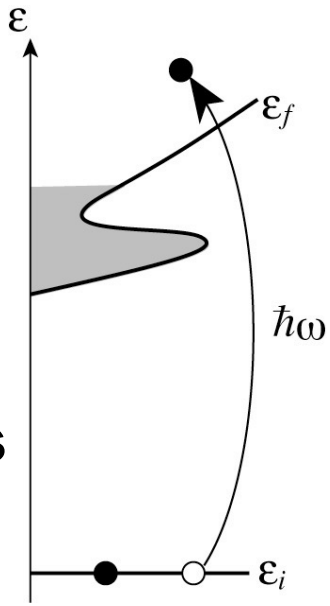
- **X-ray absorption: electronic transitions by photon from inner core states to empty states**
  - **suitable for studying valence states with specific element, orbital and symmetry by tuning the photon energy and polarization**



Fundamentals of XAS

- **Transition Probability by Fermi Golden Rule**

$$W(\omega) = \frac{2\pi}{\hbar} \sum_{f,i} |\langle f|\hat{F}|i\rangle|^2 \delta(\varepsilon_f - \varepsilon_i - \hbar\omega)$$



- **Rigorous Theory**

ε_i ε_f **Total energies of initial and final states**

$|i\rangle$ $|f\rangle$ **Many-body initial and final states**

$\hat{F}$ **Perturbation by photon in many-body hamiltonian**

- **Quasi-particle (One-electron) Approach**

ε_i ε_f **Orbital energies of initial and final states**

$|i\rangle$ $|f\rangle$ **One-electron initial and final states**

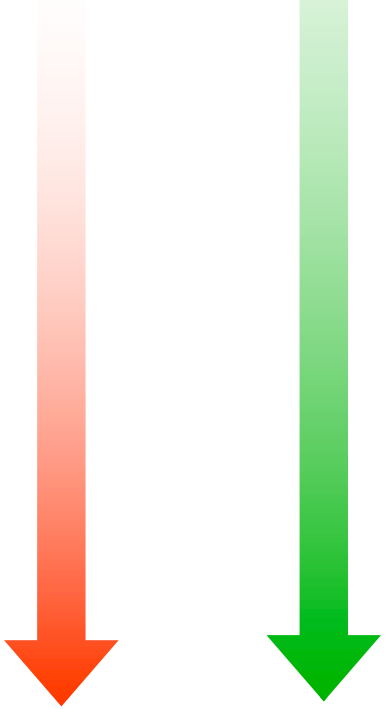
$\hat{F}$ **Perturbation by photon in one-electron hamiltonian**

Theoretical Approaches

- Quasi-particle Approaches
  - Ground-state calculation
  - Core-hole calculation
  - Perturbation calculation (GW, ...)
  - .....
- ΔSCF Approach
  - (Excited State) – (Ground State)
- Many Body Approaches

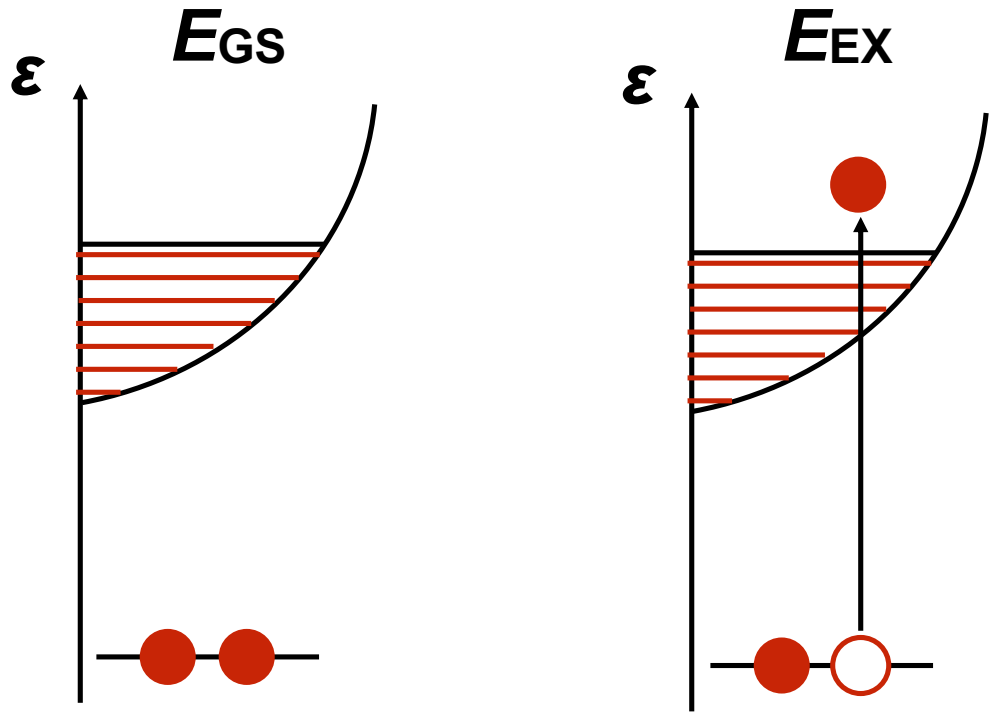
spectrum shape
polarization dependence

excitation energy

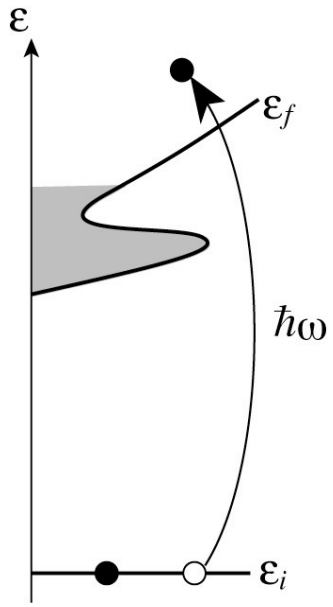


ΔSCF

- **Self-Consistent-Field (SCF) DFT Calculation**
  - **Grand state: E_{GS}**
  - **Excited state: E_{EX}**
- **Excitation Energy = E_{EX} - E_{GS}**

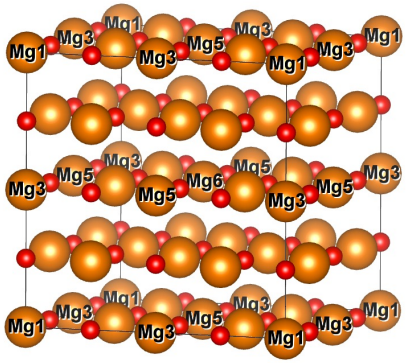
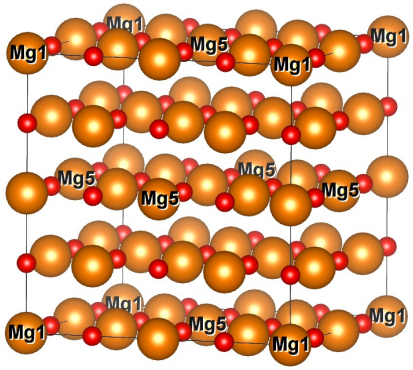
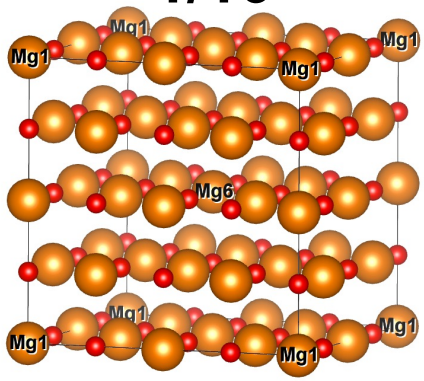
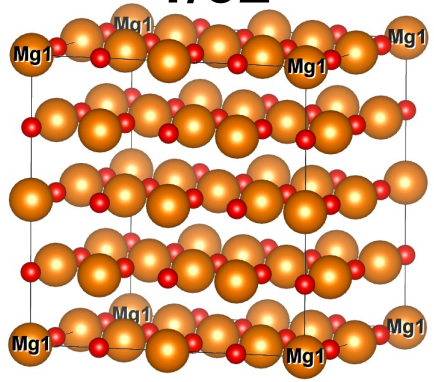


Supercell Model



- Core hole: well localized
- Excited electron: usually delocalized
  - Hybridization with neighbors
  - Electrostatic fields due to holes and excited electrons at neighboring sites

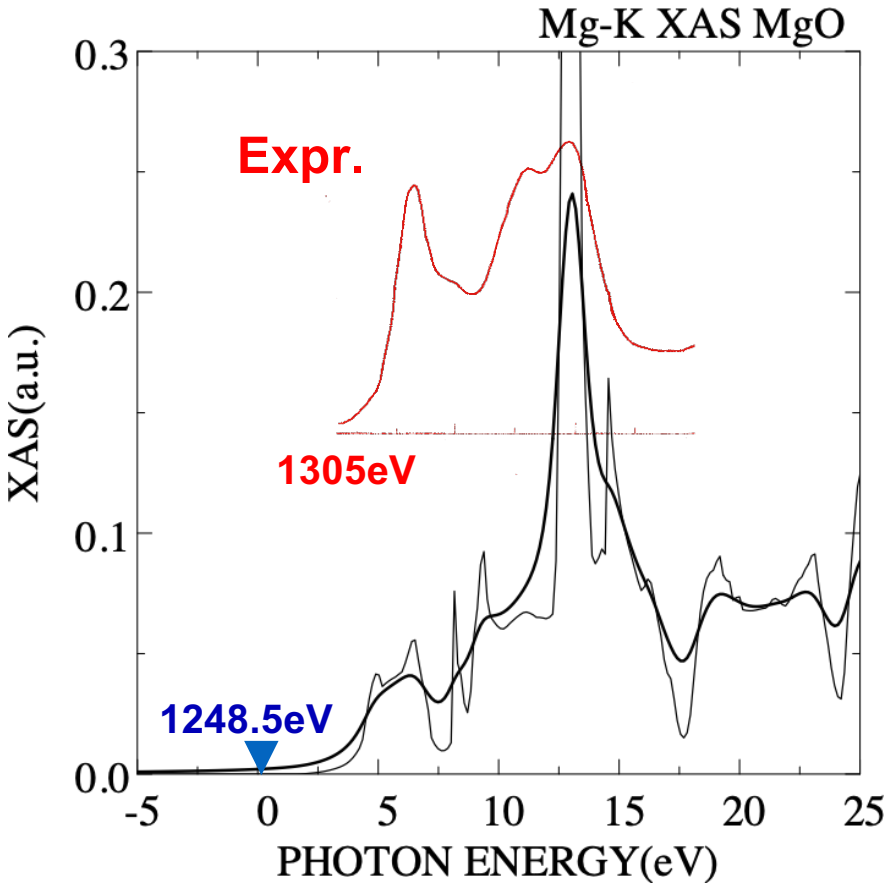
hole concentration

1/4	1/8	1/16	1/32
			
$(MgO)_4$	$(MgO)_8$	$(MgO)_{16}$	$(MgO)_{32}$
$4^3=64$	$8^3=512$	$16^3=4096$	$32^3=32768$

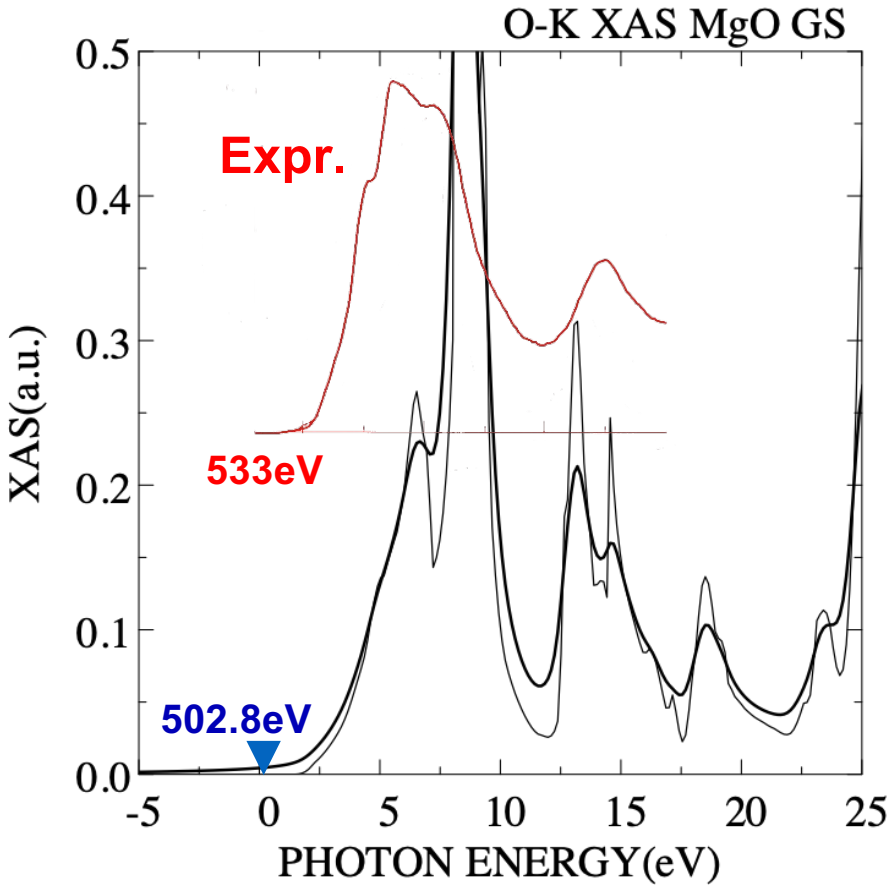
XAS of MgO

Grand-State Approximation

Mg K-edge (E1: 1s → 3p)

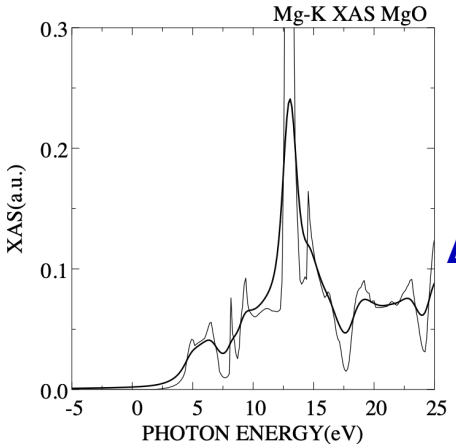


O K-edge (E1: 1s → 2p)

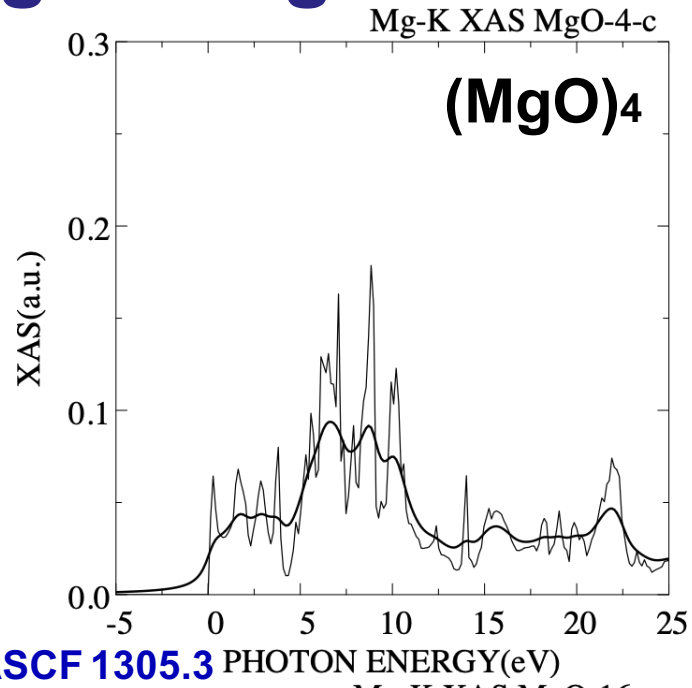


Thick lines: broadened by Lorentzian

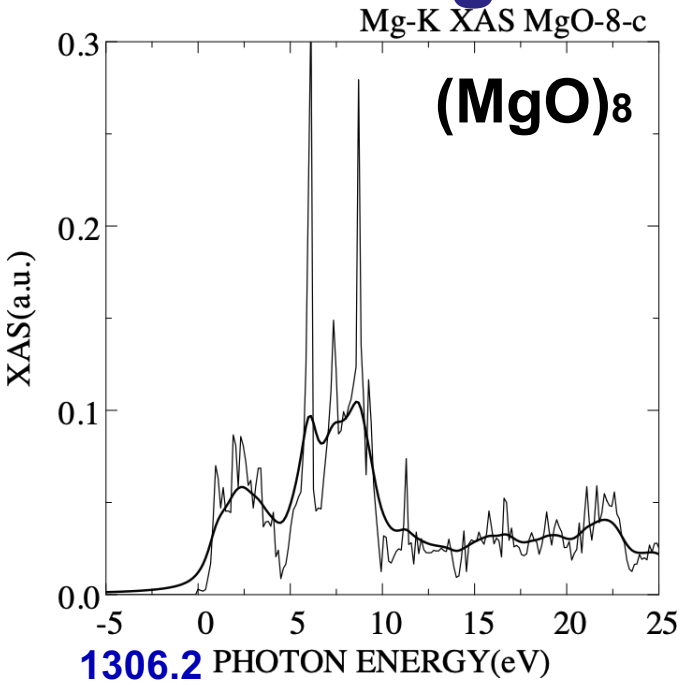
Mg K-Edge of MgO with Core Hole in Mg-1s



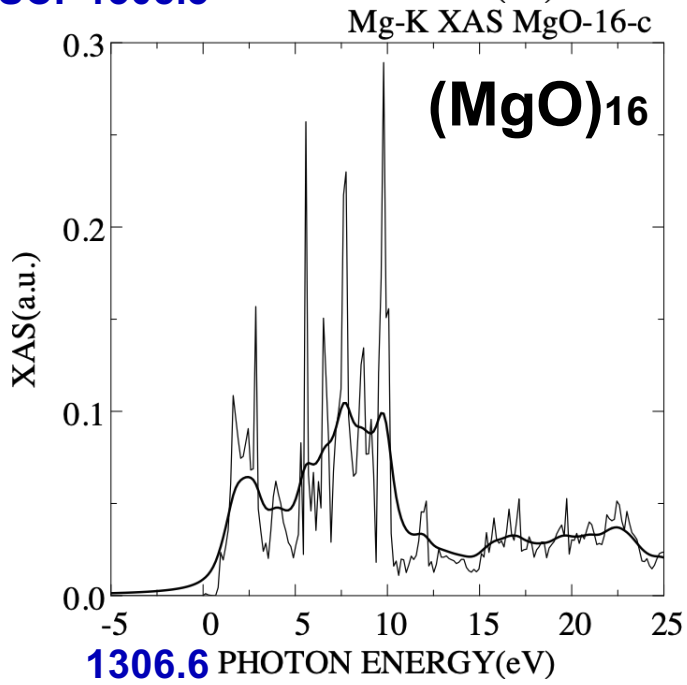
G.S.



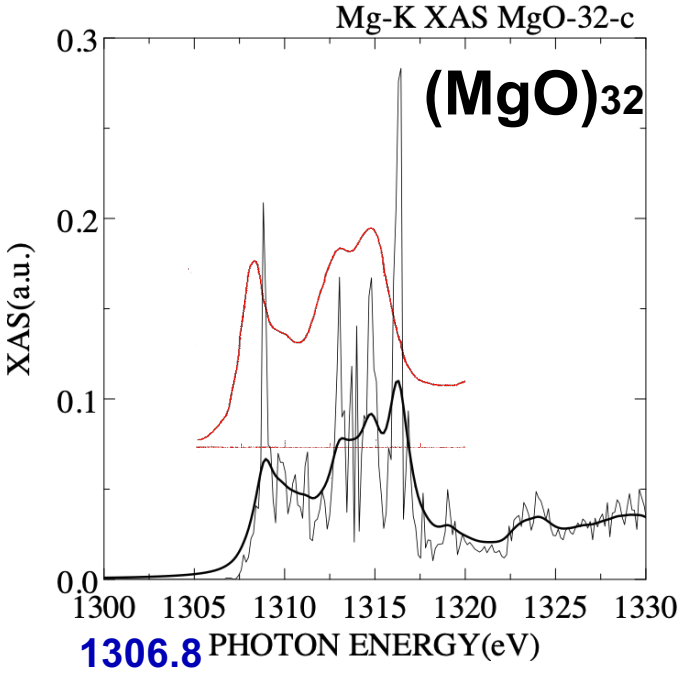
ΔSCF 1305.3



1306.2

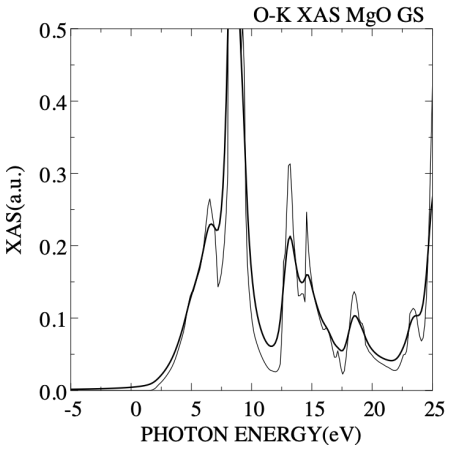


1306.6



1306.8

O K-Edge of MgO with Core Hole in O-1s



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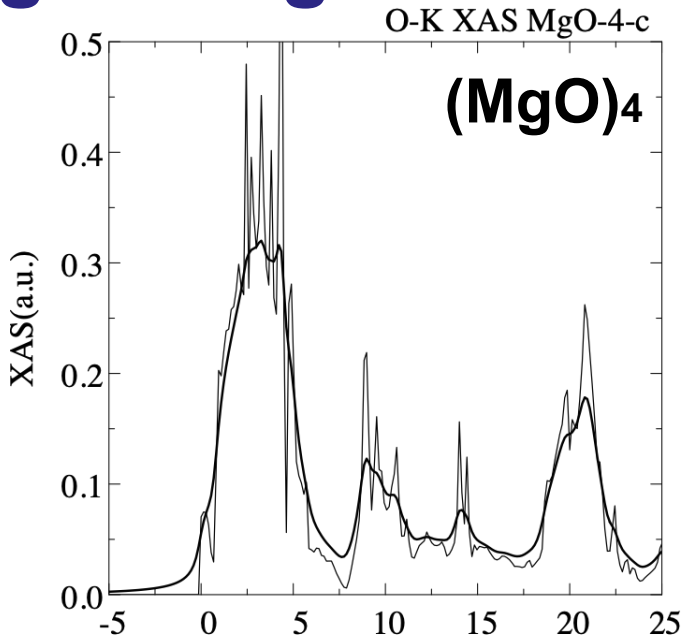
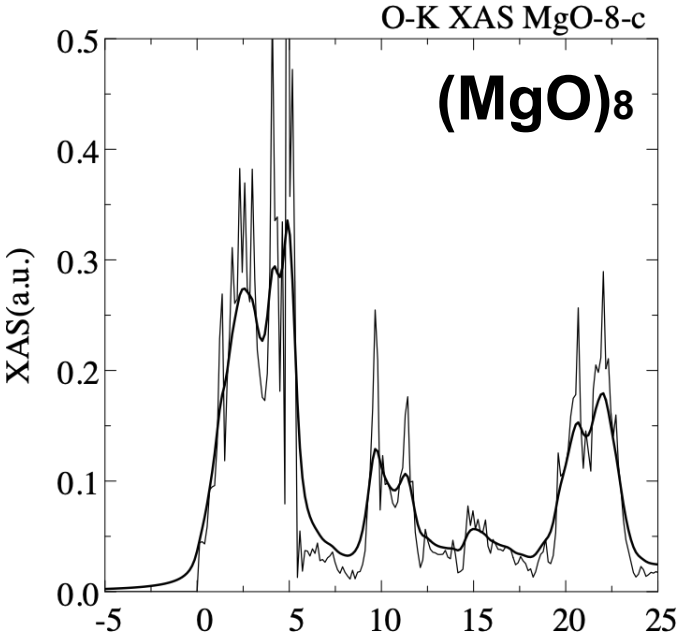
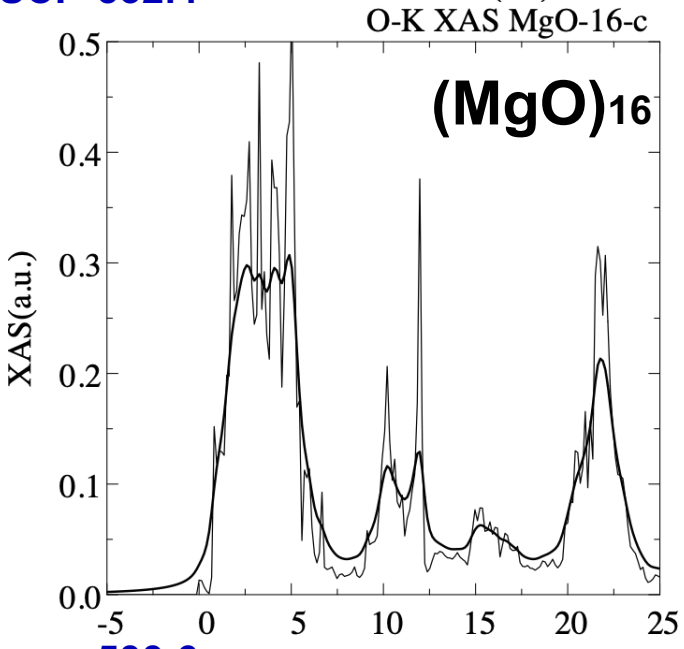


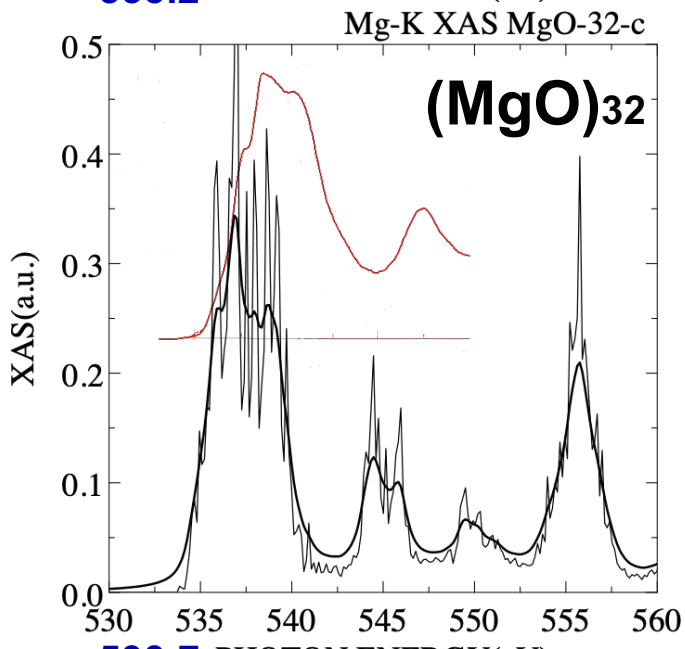
ΔSCF 532.4



533.2



533.6



533.7

Summary

- **XAS calculations with core hole**
  - **Better shape of the spectra**
  - **Better excitation energy in the ΔSCF sense**
- **Test calculations at *K* edges of MgO**

- **Further test**
  - ➢ **Different edges (L, M, N, …)**
  - ➢ **Different materials (magnetic, …)**
  - ➢ **Effects on polarization (MCD, LD, …) …..**