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XAFS Spectroscopy
X-ray absorption fine structure

K.Asakura, ICAT Hokudai

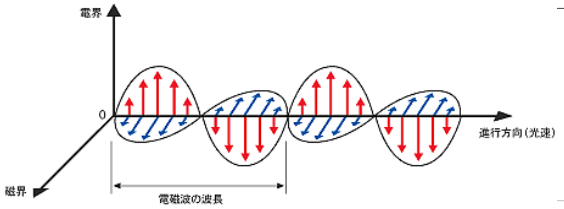
X線とは

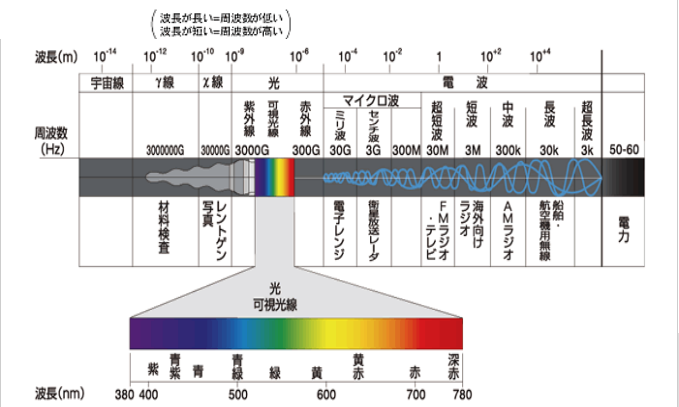
X線とは波長の短い電磁波(横波)である.

$$\lambda(nm) = 1239.852/E(eV)$$

マックスウェル方程式対照表

	ガウス単位系	SI 単位系
クーロン - ガウスの法則	$\mathrm{div}\,\mathbf{D} = 4\pi\rho$	$\mathrm{div}\,\mathbf{D}_{SI} = \rho_{SI}$
アンペールの法則	$\mathrm{rot}\,\mathbf{H} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t}$	$\mathrm{rot}\,\mathbf{H}_{SI} = \mathbf{j}_{SI} + \frac{\partial \mathbf{D}_{SI}}{\partial t}$
磁気単極不存在の法則	$\mathrm{div}\,\mathbf{B} = 0$	$\mathrm{div}\,\mathbf{B}_{SI} = 0$
ファラディーの法則	$\mathrm{rot}\,\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}$	$\mathrm{rot}\,\mathbf{E}_{SI} = -\frac{\partial \mathbf{B}_{SI}}{\partial t}$
ローレンツ力	$\mathbf{F} = q\mathbf{E} + \frac{q}{c}\mathbf{v} \times \mathbf{B}$	$\mathbf{F} = q\mathbf{E} + q\mathbf{v} \times \mathbf{B}$





X線と物質との相互作用

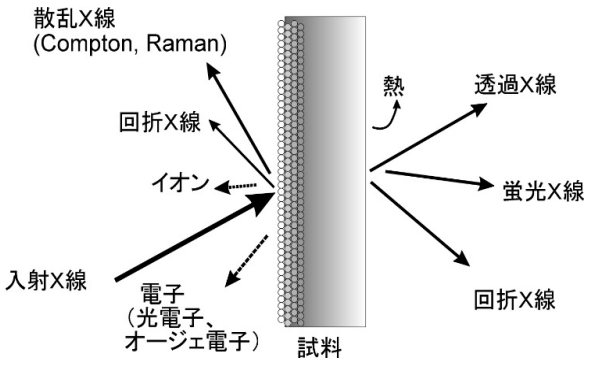


図1.3 X線の吸収によって引き起こされる様々な現象.

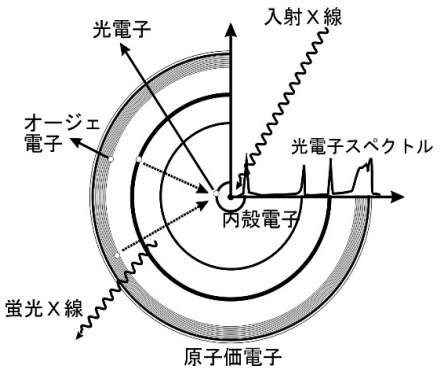
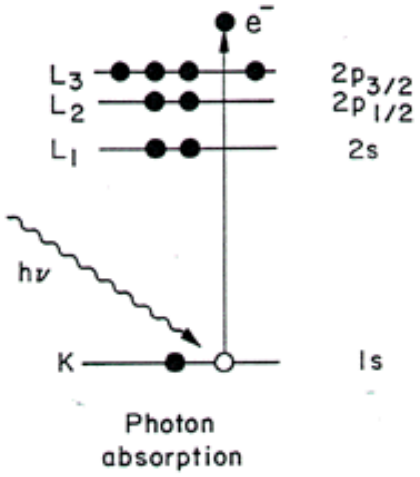
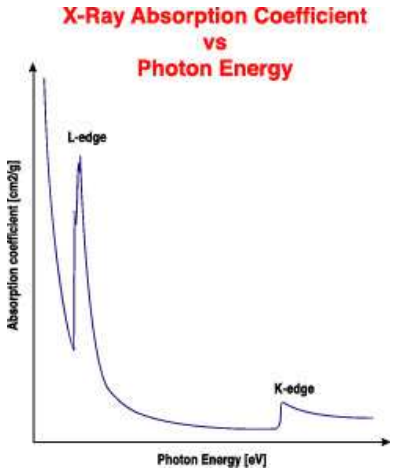


図1.4 1個の原子内でのX線吸収現象.

Core-shell electron and absorption edge



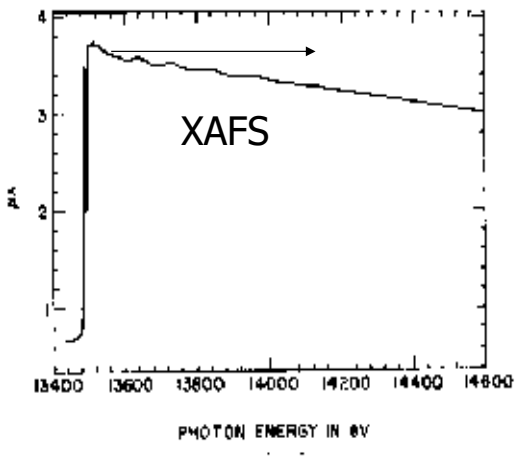


What is XAFS?

XAFS=(X-ray absorption fine structure)

K-edge XAFS

There is an oscillatory structure in the high energy region.



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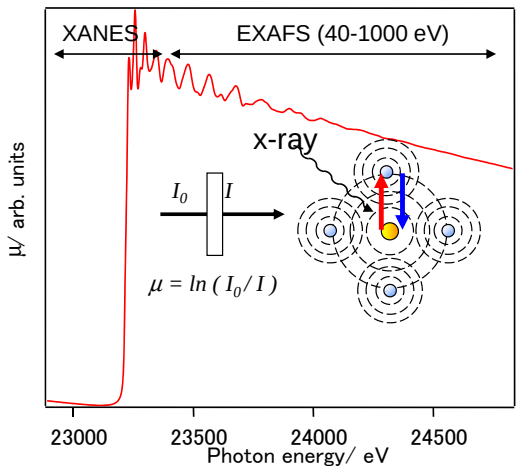
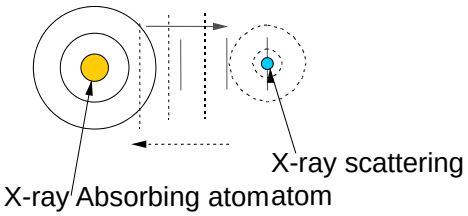
Principle of XAFS





✓Electron is not only particle but wave

There should be interference between outgoing and scattered electron

✓The interference depends on the distance between the two atoms

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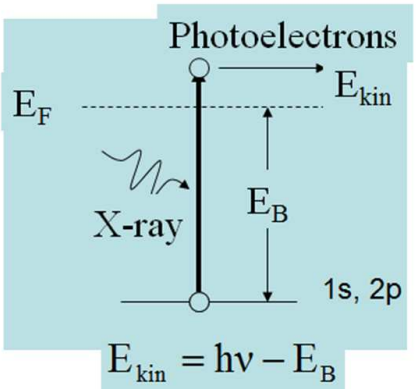
Photoelectron is wave



$$k = \frac{2\pi}{\lambda}$$

$$E_{kin} = \frac{\hbar^2 k^2}{2m} = h\nu - E_B$$

Path difference , $d = \lambda = \frac{2\pi}{k}$

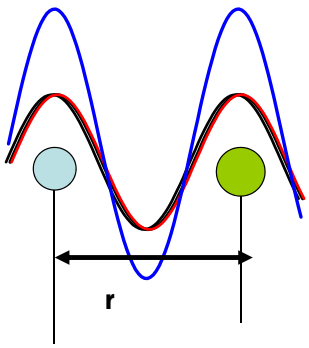
$$d \cdot k = 2kr = 2\pi$$

or $\chi(k) = \sin(2kr)$

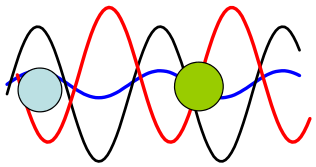
Scattering of electron and interference

$$\frac{\hbar^2 k^2}{2m} = E - E_0$$

K: wave vector、
$\hbar$: Plank Const
E：Photon energy E0:threshold

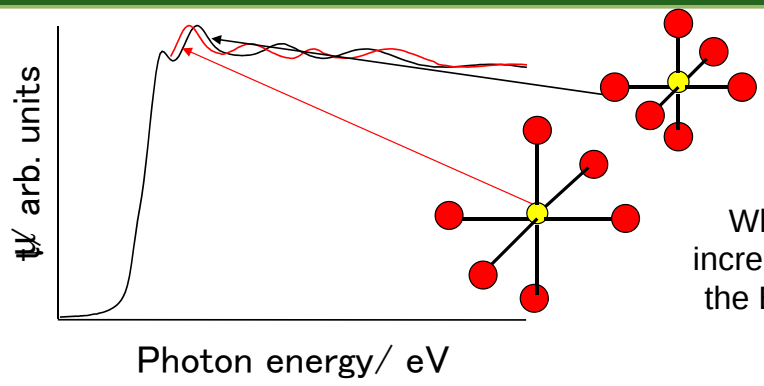


Enhancement

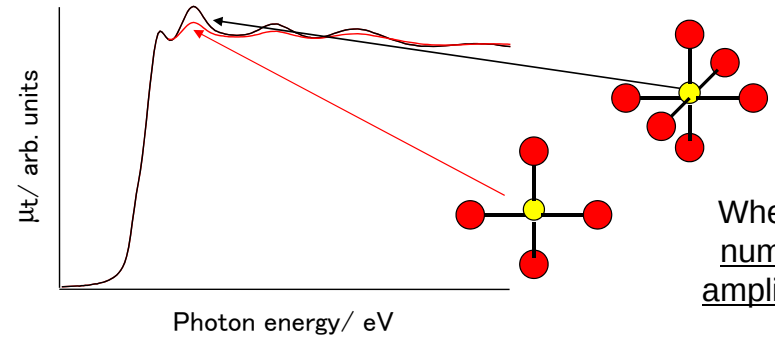


suppression

EXAFS gives you bond distance and coordination number



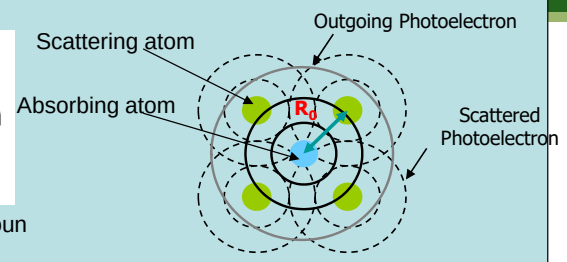
When the bond length increases, the frequency of the EXAFS oscillation will higher



When the coordination number increases, the amplitude also increases

The EXAFS equation

1. leaving the absorbing atom
2. scattering from the neighbor atom
3. returning to the absorbing atom



XAFS oscillation | Absorbance | Smooth backgroun

$$\chi(k) = \frac{\mu(E) - \mu_s(E)}{\mu_0(E)} = S_0^2 \sum_i \frac{N_i F_i(k_i)}{k_i r_i^2} e^{-2k_i^2\sigma_i^2} \sin(2k_i r_i + \phi_i(k_i))$$

Edge-jump

$$k = \sqrt{2m_e(E - E_0)/\hbar}$$

Theorptically or empirically derived Parameters

F_i : Backscattering amblitude $* e^{-2r_i/\lambda(k_i)}$

ϕ_i : Phase shift

Curve-Fitting Parameters

N_i Coordination number

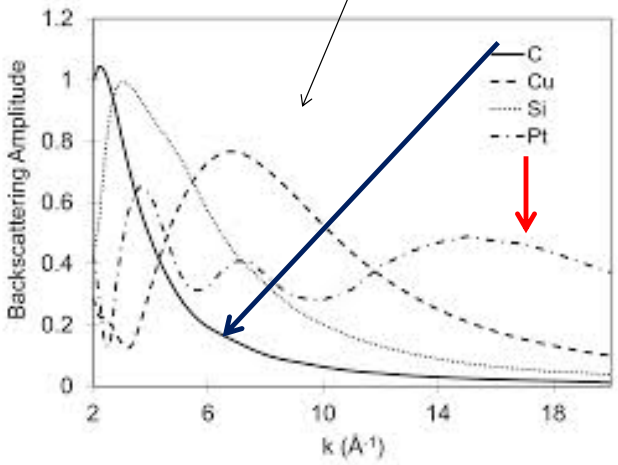
σ_i^2 DW factor

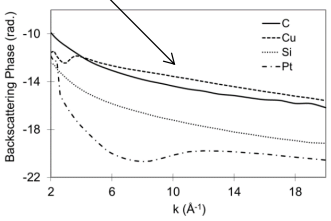
E_0 energy shift

r distance

Backscattering amplitude depends on Z (原子番号)

$$\chi(k) = \frac{\mu(E) - \mu_s(E)}{\mu_0(E)} = S_0^2 \sum_i \frac{N_i F_i(k_i)}{k_i r_i^2} e^{-2k_i^2\sigma_i^2} \sin(2k_i r_i + \phi_i(k_i))$$





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You can get following information from EXAFS

1. **Bond distance**
2. **Coodination number**
3. **Disorder in the bond length**
4. **Kind of coordinating atom**

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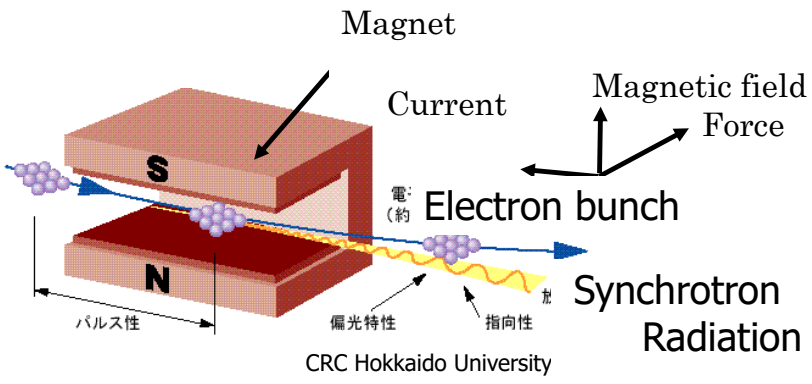
The feature of EXAFS

1. No crystallinity is necessary
    1. Local diffraction of electron
2. In-situ measurement
    1. X-ray penetrates
3. Element specific
4. High sensitivity
    1. A few %
5. But you need Synchrotron Radiation

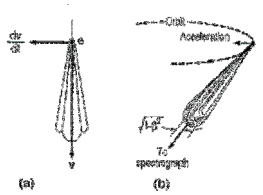
Synchrotron Radiation

Electron having a near light speed emits the strongly collimated light when it is bent.



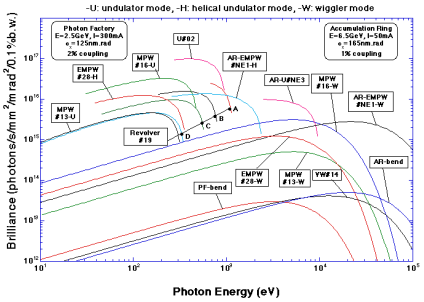
Features of synchrotron radiation

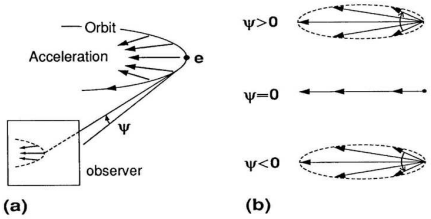
1. **Collimated**
2. **Wide energy spectrum**
3. **Pulse**
4. **Linearly polarized**
5. **Strong light**



$$\beta = v/c$$

$$\gamma = 1/\sqrt{1-\beta^2}$$

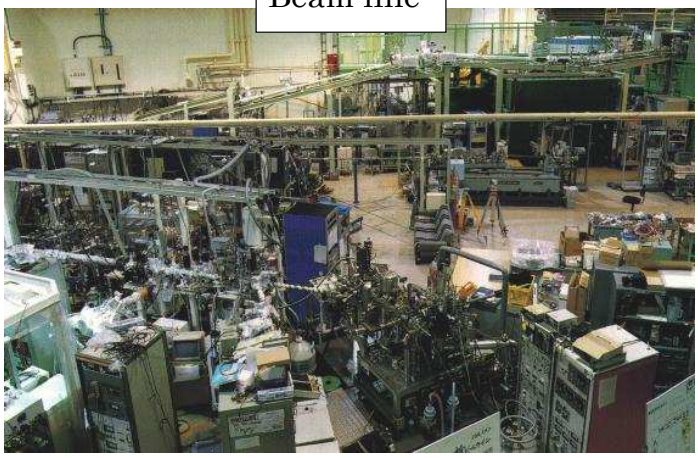




Photon Factory

PF(Photon Factory Since 1982)

PF Experimental Station(BL2-4)

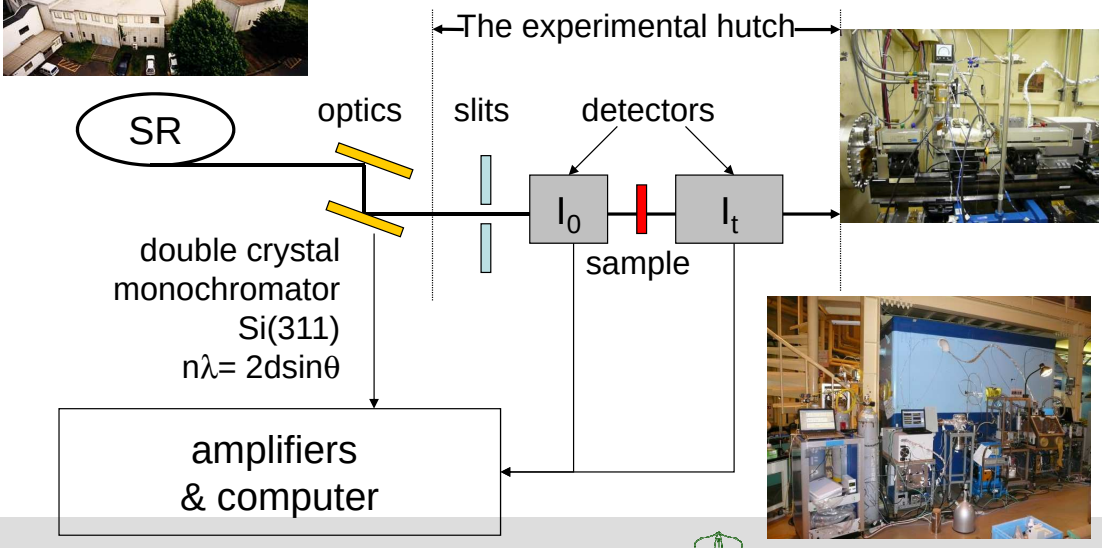


SPring8(Super Photo Ring)

Since 1997

Experimental setup

Beamline BL9C, KEK-PF



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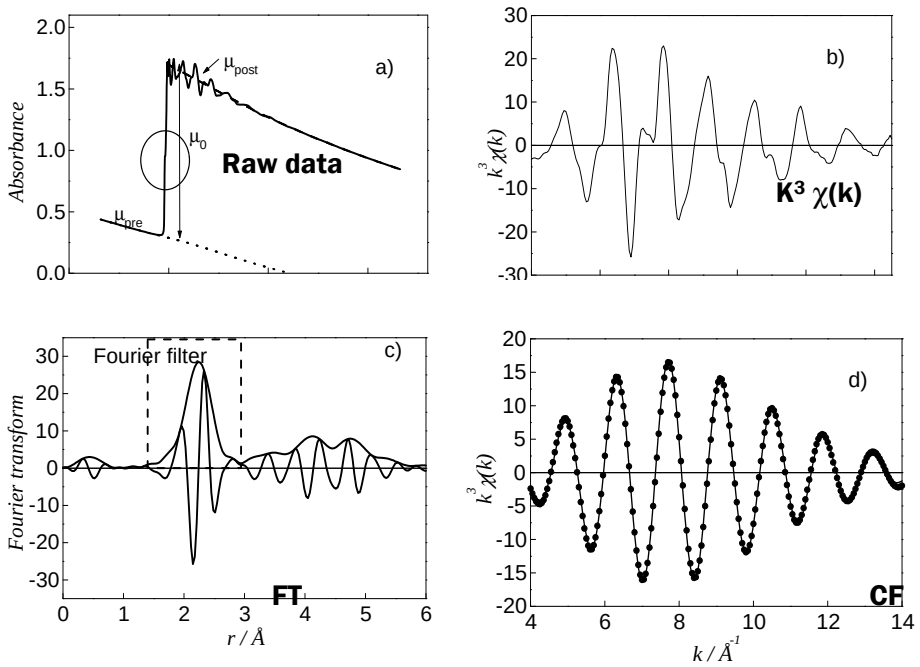
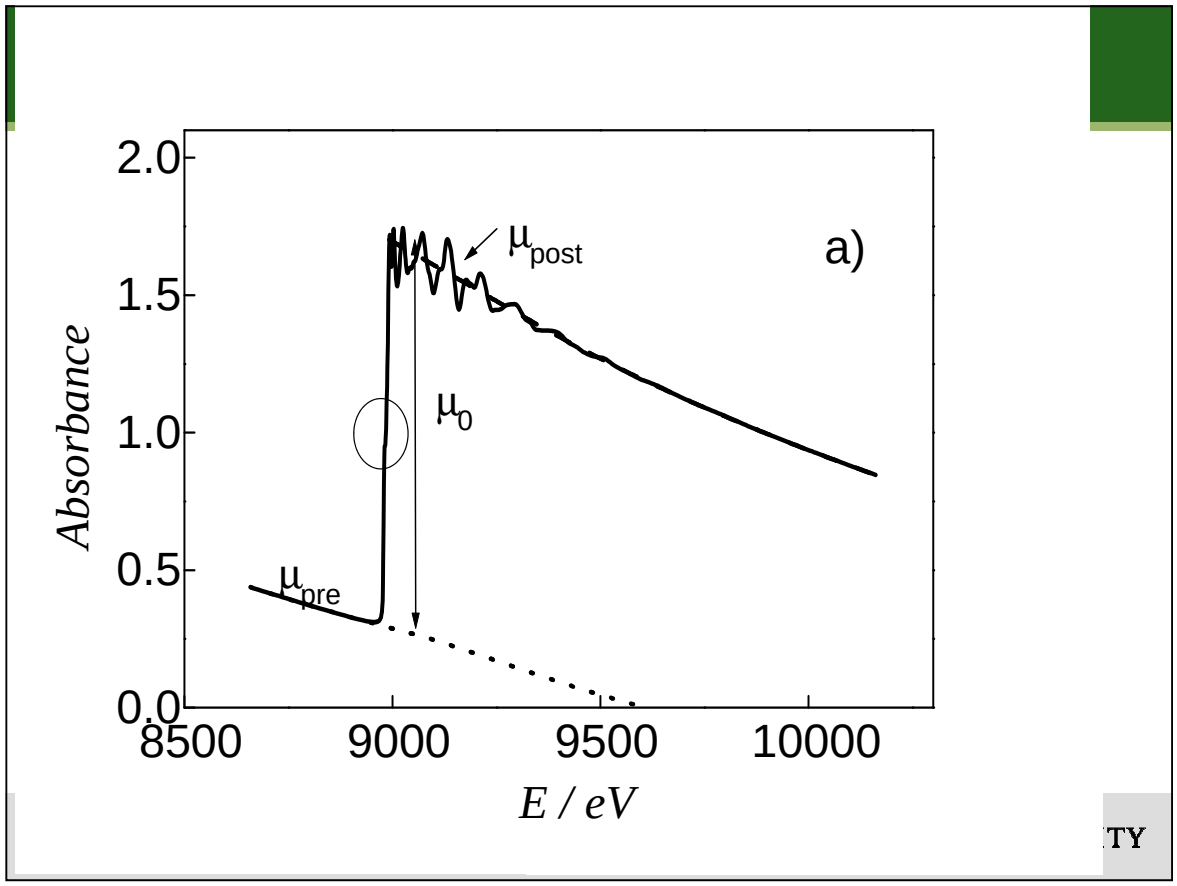
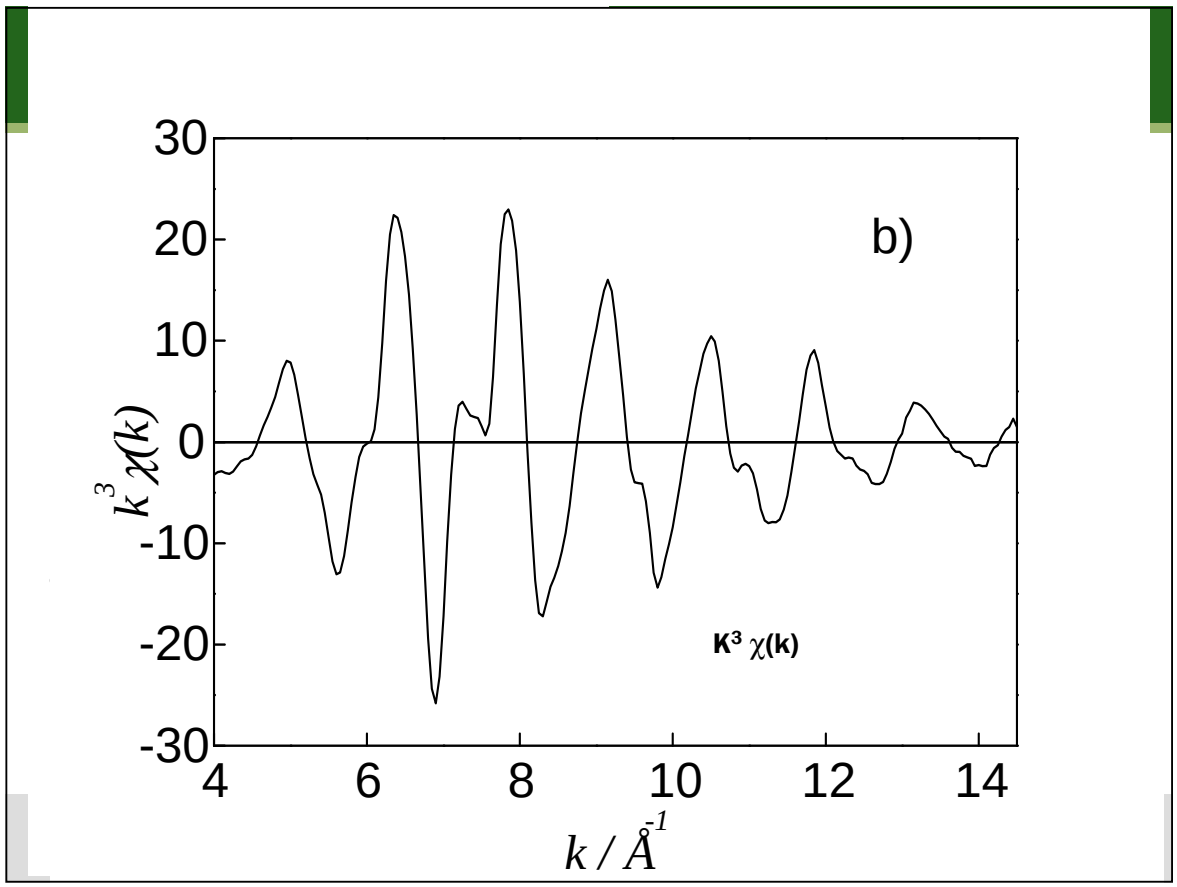
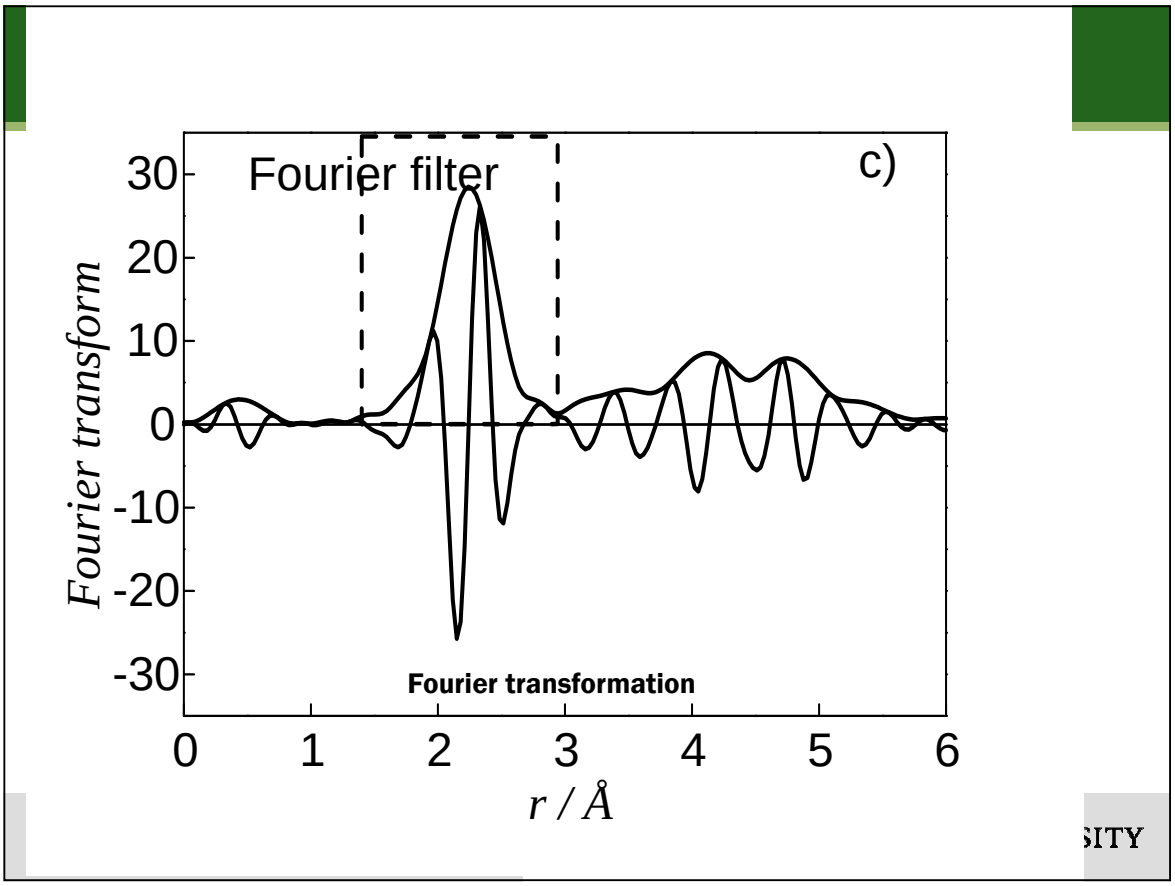
Sketch of EXAFS analysis



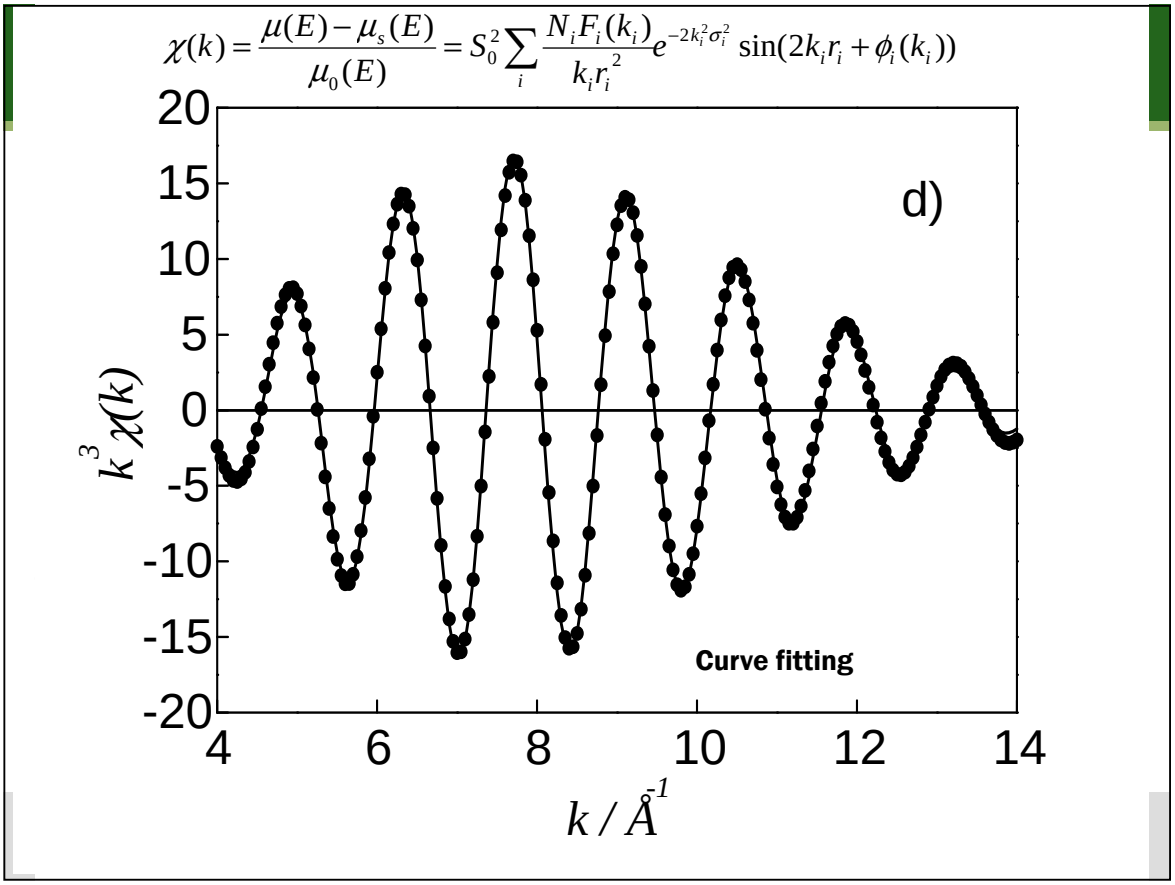

2.0
1.5
1.0
0.5
0.0
Absorbance
8500
9000
9500
10000
E / eV
μpost
μ0
μpre
a)


30
20
10
0
-10
-20
-30
4
6
8
10
12
14
k / Å-1
k3 χ(k)
b)
K3 χ(k)



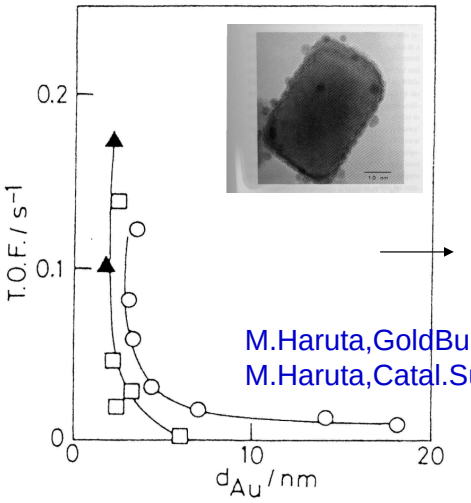
SITY

$$\chi(k) = \frac{\mu(E) - \mu_s(E)}{\mu_0(E)} = S_0^2 \sum_i \frac{N_i F_i(k_i)}{k_i r_i^2} e^{-2k_i^2\sigma_i^2} \sin(2k_i r_i + \phi_i(k_i))$$

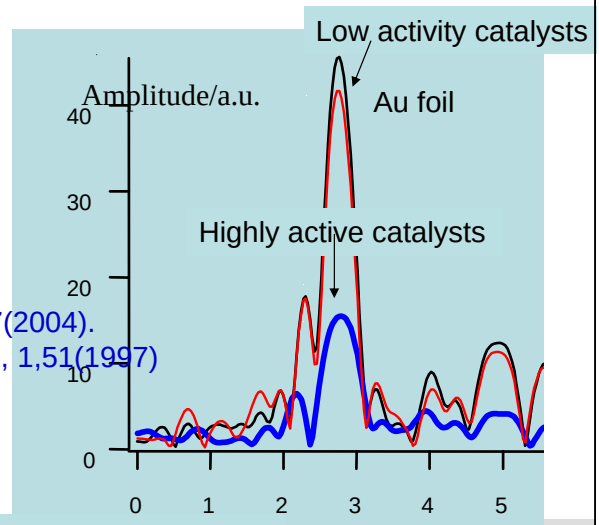


Supported nano Gold catalsyts

High activity for CO oxidation at room temperature when it is in nanosize



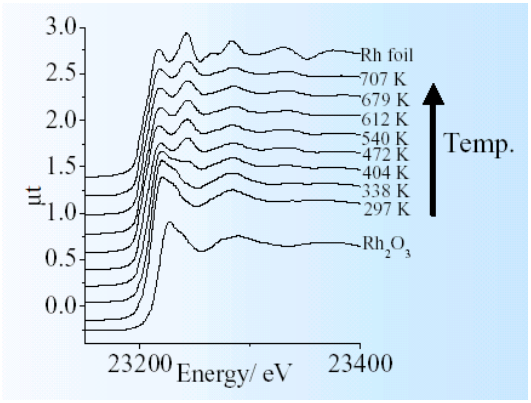
M.Haruta,GoldBull.37,27(2004).
M.Haruta,Catal.Surv.Jpn, 1,51(1997)

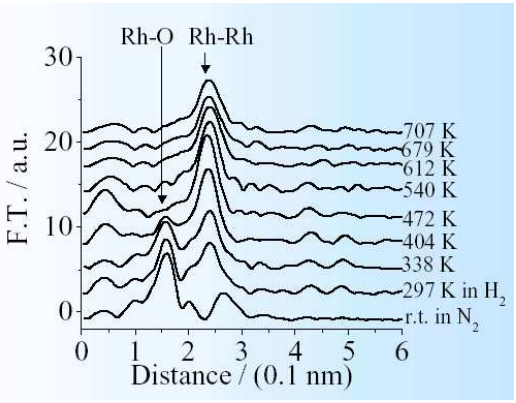


EXAFS does not require long range order!!
Amorphous, liquid, Enzyme, powder

Reduction process of Rh

In-situ XAFS spectra observed during H_2 reduction





Flow rate :20 % H_2/Ar 100ml/min
Temperature rate: 7K/min

XANES : Oxidized Rh species → Rh metal
EXAFS : Rh-O → Rh-Rh

K. Bando et al. in-situ high pressure & high temperature XAFS

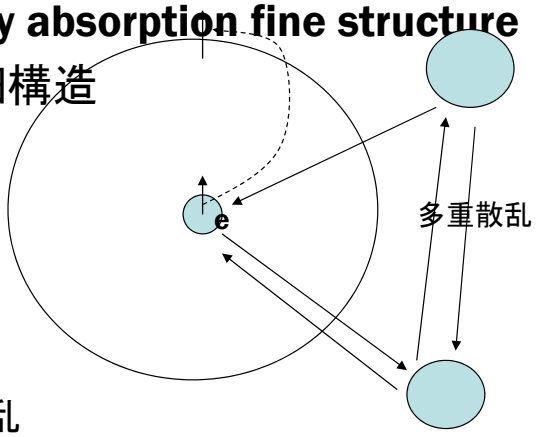
XANES(NEXAFS)とは、

XANES=X-ray Absorption Near Edge Structure

NEXAFS=Near edge x-ray absorption fine structure

吸収端近傍に現れる微細構造

- 非占有軌道への励起
  - **GAUSSIAN WIEN2K**



- 周りの原子との多重散乱
  - **FEFF,FPMS,FDMNES**

XANESでわかること

一般論

- 中心原子の価数　Fe^{2+} Fe^{3+}
- 中心原子の形

L吸収端を使った場合。

- d軌道の空軌道数

XANES(NEXAFS)

配向、価数

XANESを理解する上で知っておくこと。

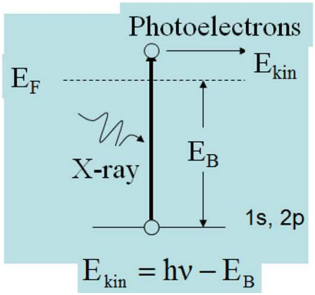
吸収端の名前　K, L, M, N・・・・・・・吸収端

原子の電子配置、1s,2s,2p, 3s, 3p, 3d・・・・・・・・

1sを励起したばあいには、K吸収端

2s,2pを励起した場合には、L吸収端

$2p_{3/2}$ L_3、 $2P_{1/2}$ L_2、 2s L_1



双極子遷移ということ

- ｜<i|r|f>｜^{2}　<iは始状態,fは終状態,rは電場の向き
- 角運動量の変化がプラス1であるということ。
- （対称性を考えればよい。たとえば、電場の向きは原点に対して反対称、1sは対称、だからfは反対称のPでないといけない。）

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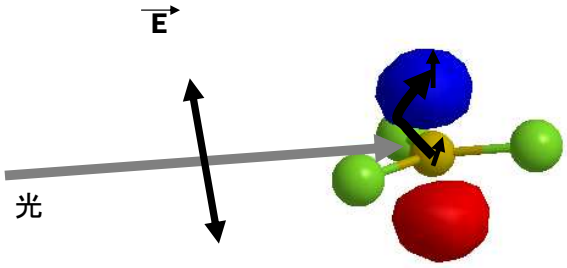
電場ベクトルの方向に



光ー電場と磁場の横波

放射光は水平偏光している。

K吸収端では、終状態の軌道の広がりと電場の向きが一致すると遷移が起こる。

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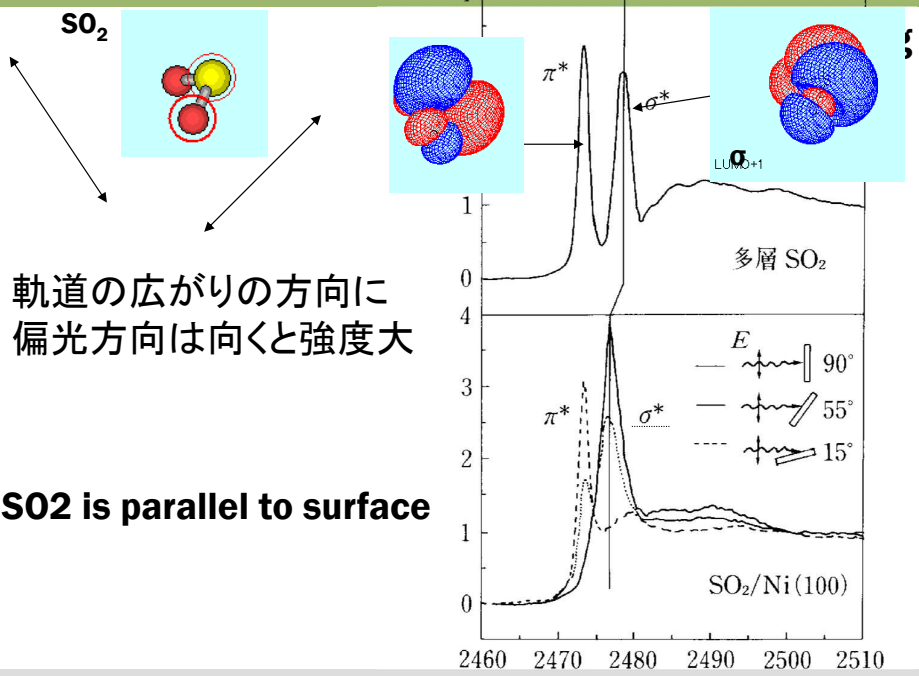
S K-edge NEXAFS of SO_2 adsorbed on Ni(100)

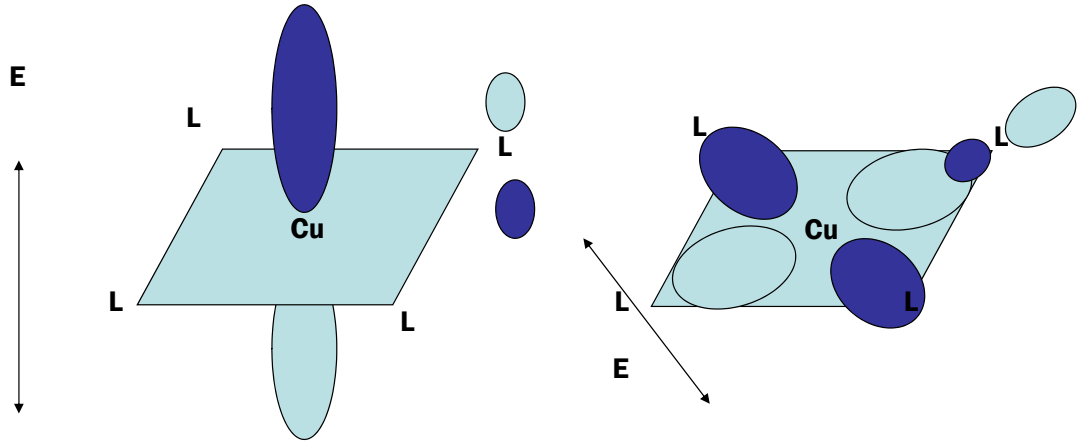
[1]T. Ohta, T. Yokoyama, S. Terada, A. Imanishi, Y. Kitajima, Research on Chemical Intermediates 26 (2000



軌道の広がりの方向に
偏光方向は向くと強度大

S02 is parallel to surface

平面対称性の場合には、



反結合π軌道
（エネルギーが低い）

反結合σ軌道
（エネルギーが高い）

CuとXANES

[1] N. Kosugi, T. Yokoyama, K. Asakura, H. Kuroda, Chem. Phys. **91** (1984) 249.

Cu のedgeに現れるピークは何か？ 1s-4sか

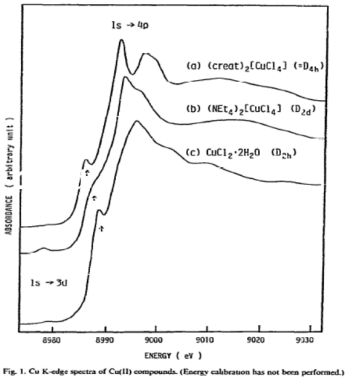
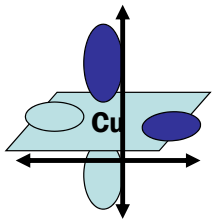


Fig. 1. Cu K-edge spectra of Cu(II) compounds. (Energy calibration has not been performed.)



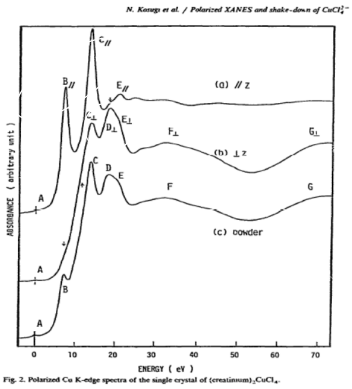
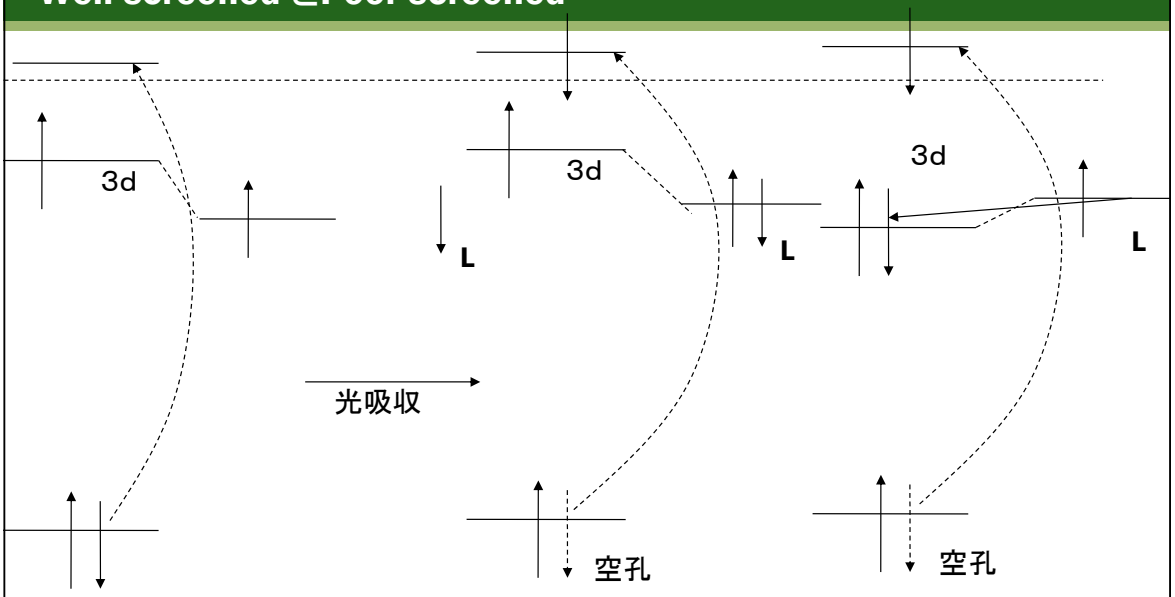


Fig. 2. Polarized Cu K-edge spectra of the single crystal of (creatinium)$_2$CuCl$_4$.

Intensity $\propto \cos^2\theta$ 偏光**XANES**

対称性により、**2**つに分裂
スクリーニングによりまた二つに

Well-screened とPoor-screened



$f >= 1s^1 3d^9 \varepsilon p > + 1s^1 3d^{10} \overline{L} \varepsilon p >$

$i >= 1s^2 3d^9$

緩和していない。
(**Poor-screened**)
不安定

電子の緩和
(Well-screened)
安定

CuとXANES

[1] N. Kosugi, T. Yokoyama, K. Asakura, H. Kuroda, Chem. Phys. **91** (1984) 249.

Cu のedgeに現れるピークは何か？ 1s-4sか

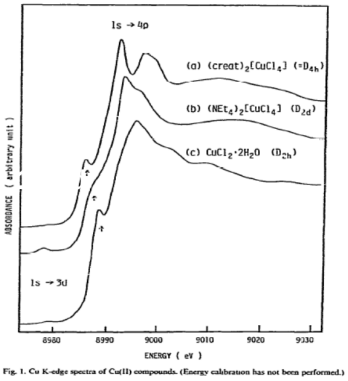
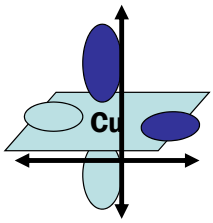


Fig. 1. Cu K-edge spectra of Cu(II) compounds. (Energy calibration has not been performed.)



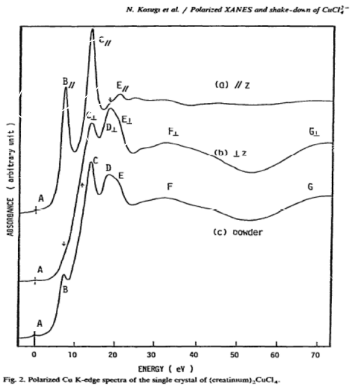


Fig. 2. Polarized Cu K-edge spectra of the single crystal of (creatinium)$_2$CuCl$_4$.

Intensity

偏光**XANES**

対称性により、**2**つに分裂
スクリーニングによりまた二つに

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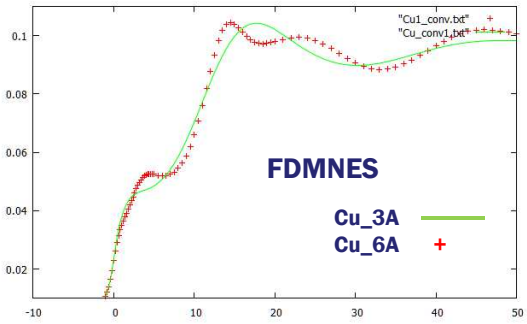
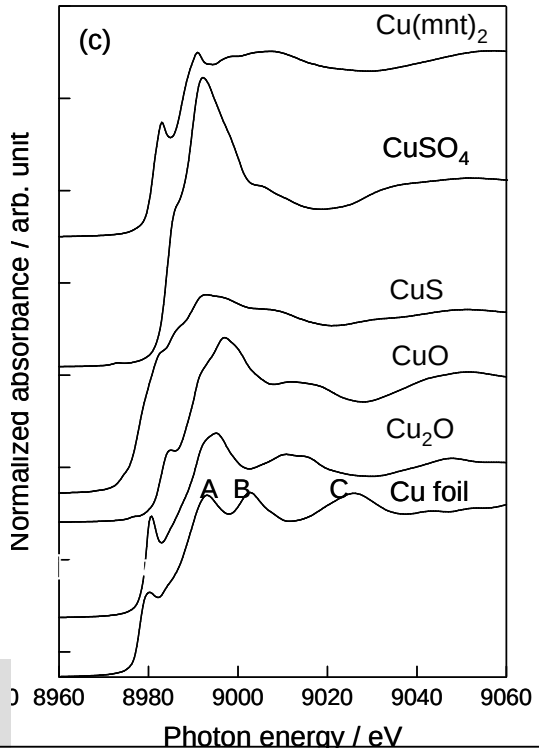
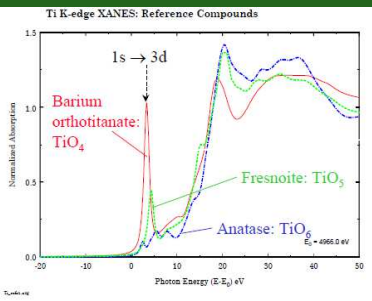
Cu XANES





Preedge 吸収の大きさ(1s-nd)



- Symmetry around absorbing atom strongly affects pre-edge transition: ability to differentiate 4, 5, 6-fold coordination.

1s->3d

対称性（中心対称性）の問題

- 軌道角運動量と選択則 **1s->np** （双極子近似）
- **1s-nd**は四重極子
  - 中心対称性がなくなるとpとdは混じり合う。

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TiO2のXANES

[1] Y. Joly, D. Cabaret, H. Renevier, C.R. Natoli, Phys.Rev.Lett. **82** (1999) 2398.

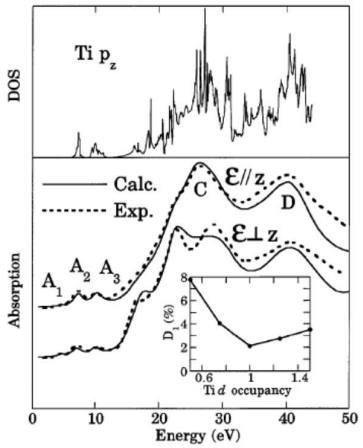


FIG. 1. Lower panel: Comparison between the experimental (dotted line) and calculated (solid line) Ti K-edge XANES spectra of single crystal TiO_2-rutile for two orientations of the electric field and wave vectors; bottom: (ε, k) = ([1$\bar{1}$0],[110]) ($\varepsilon \perp$ k) top: (ε, k) = ([001],[110]) ($\varepsilon \parallel$ k). Inset: Variation of the R factor with the Ti 3d occupancy. Upper panel: p_z-projected density of states on Ti atom calculated by the FLAPW method.

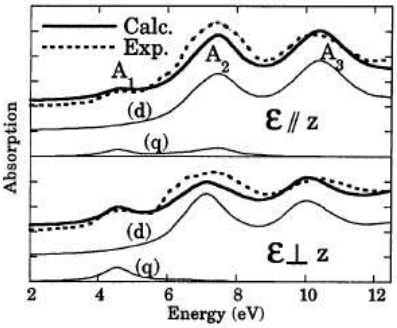
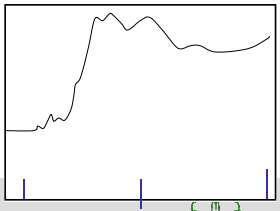


FIG. 2. View of the pre-edge region. Quadrupolar (q) and dipolar (d) components and their sum for $\varepsilon \parallel$ (top) and $\perp$ (bottom) to z. The dotted line is the experimental curve.



Rutile Powder

Non-maffin tin full potential APW

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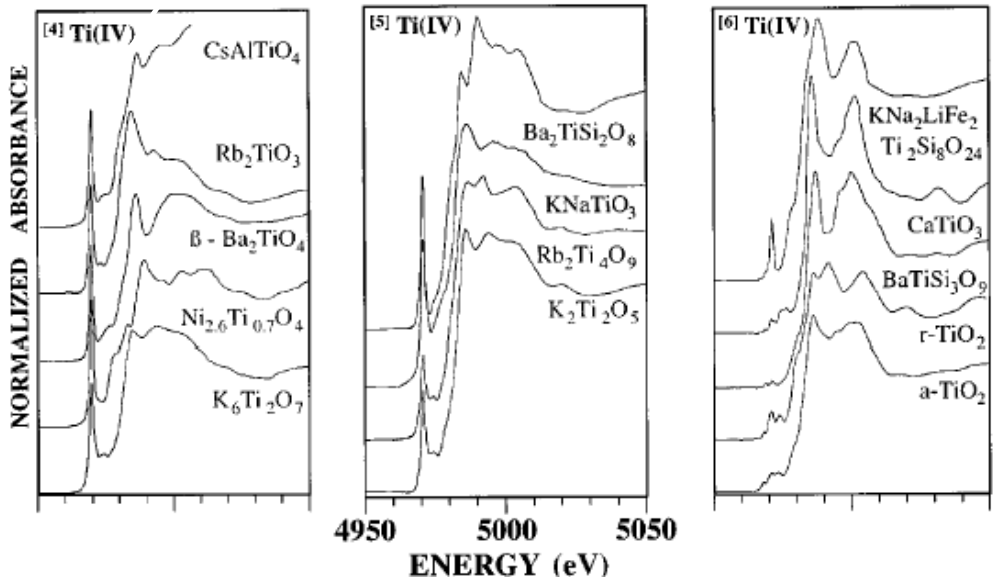
Ti化合物のXANES



François Farges Gordon E. Brown, , Jr. J. J. Rehr ,Phys. Rev. B 56, 1809–1819 (1997)

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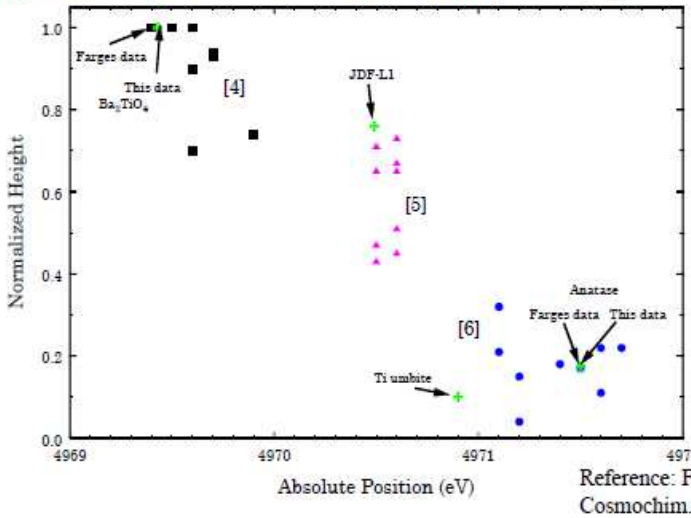
配位数　対称性

Ability to distinguish Ti coordination from pre-edge peak information.



Reference: Farges et al., Geochim. Cosmochim. 60 (1996) 3023

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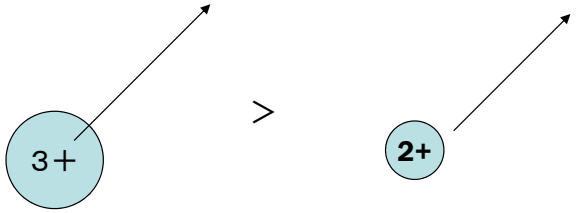
吸収端の位置

吸収端とは、電子を無限遠まで持っていくのに必要なエネルギーと定義すると、中心の原子の電荷が大きい方がよりエネルギーが必要になる。(**XPS**の化学シフトと同じ考え)



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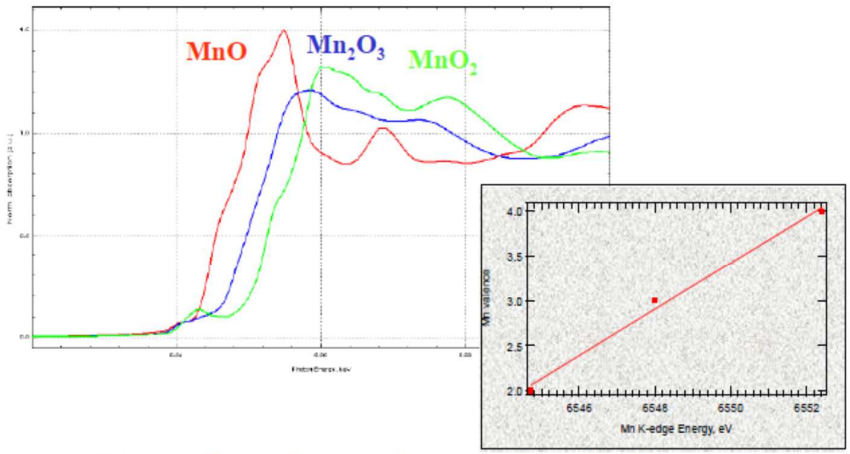
吸収端の位置



- Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.

http://cars9.uchicago.edu/xafs/NSLS_EDCA/Sept2002/
高エネルギー側には高価数物質

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V化合物

J. Wong, F.W. Lytle, R.P. Messmer, D.H. Maylotte, Physical Review B **30** (1984) 5596.

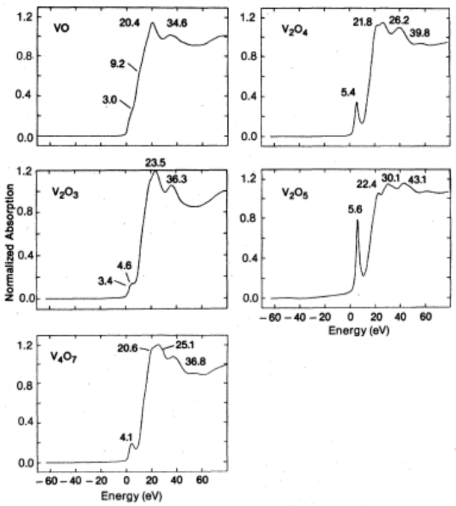

FIG. 3. Normalized *K*-edge XANES spectra of vanadium oxides, the zero of energy taken at 5465 eV.

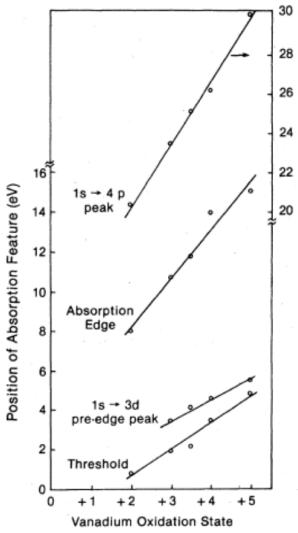

FIG. 5. Oxidation state vs energy positions of various absorption features in the V *K*-edge XANES spectra of various vanadium oxides.

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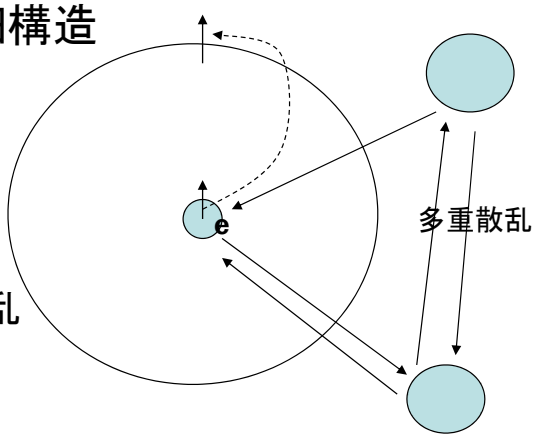
XANESとは、

XANES=(X-ray Absorption Near Edge Structure)

吸収端近傍に現れる微細構造

- 非占有軌道への励起



- 周りの原子との多重散乱
  - **FEFF,FPMS,FDMNES**

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結合距離との関係

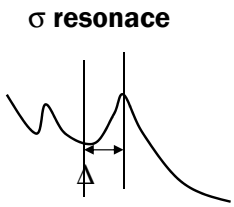
J.L. Shreeve, M.T. Tysoe, D.K. Saldin, Physical Review B **51** (1995) 13015.

多重散乱理論

$\Delta = A/\rho^2$

ρは原子間距離

Δはσ resonanceとイオン化レベルとの間隔



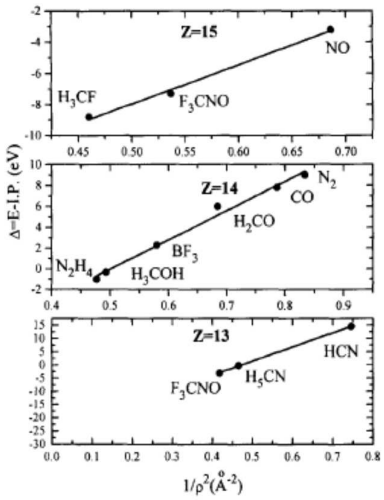


Fig. 5. Plot of the σ resonance energy Δ relative to the ionization potential I.P. versus the inverse square of the bond length ρ between the pair of atoms from which the resonance arises. Each atomic pair is characterized by a particular value of Z, the sum of the atomic numbers of the absorber and scatterer. The data are taken from Ref. [2].

結合距離の問題

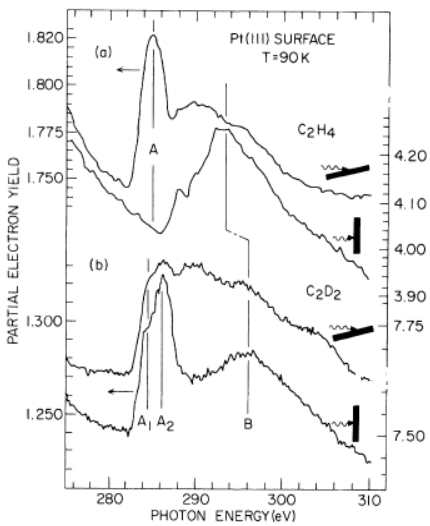
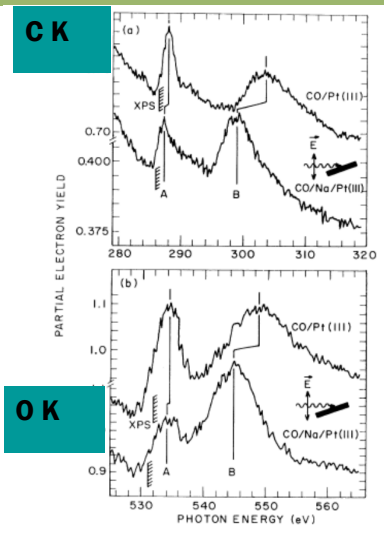


FIG. 3. (a) NEXAFS spectra of ethylene (C_2H_4) on Pt(111) at saturation coverage at 90 K for grazing and normal x-ray incidence. (b) Spectra of acetylene (C_2D_2) on Pt(111) under same conditions as (a).

J. Stohr, F. Sette, A.L. Johnson, Phys.Rev.Lett. **53** (1984) 1684.

C K

O K



CO/Pt

CO/Na/Pt

CO/Pt

CO/Na/Pt

FIG. 2. (a) C *K* edge NEXAFS spectra recorded at 20° grazing x-ray incidence for the same two samples as in Fig. 1. Peak *A* is a π resonance and peak *B* a σ shape resonance. XPS denotes the C 1*s* binding energy relative to the Fermi level. (b) O *K* edge NEXAFS spectra for the same samples and same conditions as in (a).

F. Sette, J. Stör, A.P. Hitchcock, J. Chem. Phys. **81** (1984) 490

NiのXANES多重散乱による解析

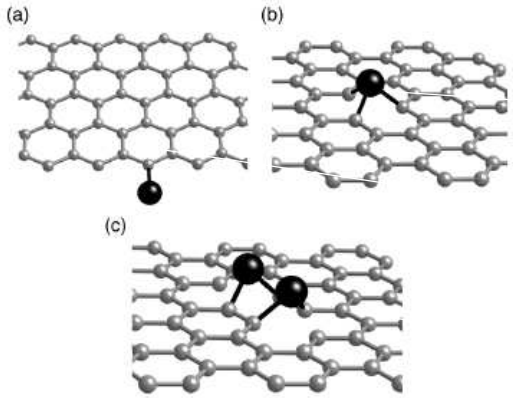
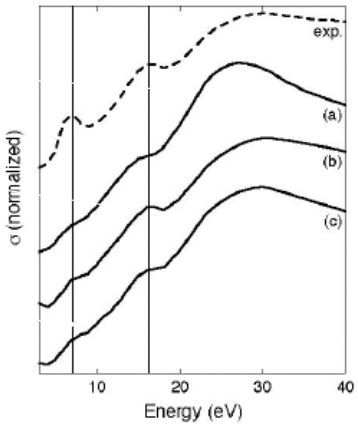


FIGURE 1. An edge model (a) and two substitution models (b) and (c), where black (gray) balls are Ni (C) atoms. In the model (a), a Ni atom bind to a carbon atom at the nearest edge site. In the model (b), a Ni atom replaces a carbon atom of a graphene sheet (monomer model), and in the model (c) two Ni atoms replace two carbon atoms (dimer model).



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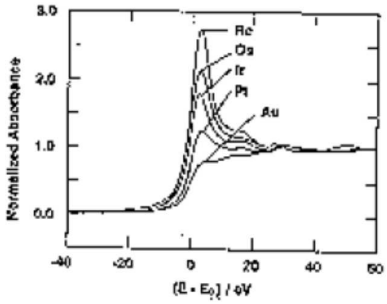
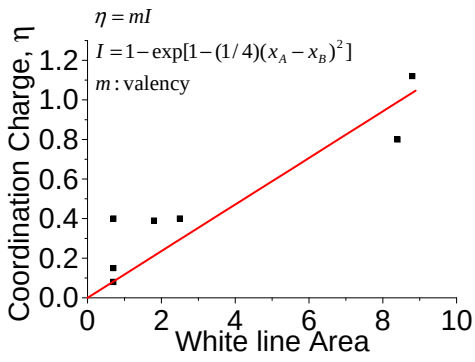
L殻吸収端XANES（White line)



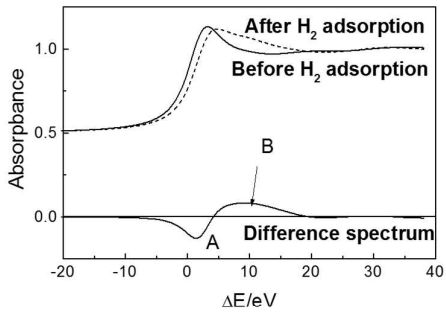
L_3 edge XANES
for 5*d* metals

[1] J.H. Sinfelt, G.D. Meitzner, Acc.Chem.Res., **26** (1993) 1.

White line2p－5d遷移、大きさは5dの空軌道の数に依存する。



水素吸着に伴うPt L_3 edge 吸収端の変化と吸着水素の定量



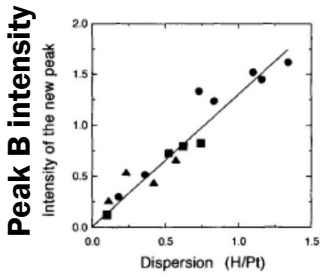


Fig. 3. Plots of the intensity of the new peak at the Pt L_3-edge against H/Pt for SiO_2 (●), Al_2O_3 (■), and MgO (▲).

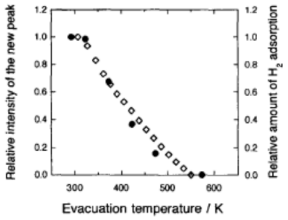


Fig. 4. Plots of the relative intensity of the new peak (●) and the relative amount of adsorbed hydrogen (◇) as a function of evacuation temperature for the Pt/SiO_2 catalyst with H/Pt = 1.2.

Peak B と吸着量は比例関係ー＞ in-situで水素量を測定できる。

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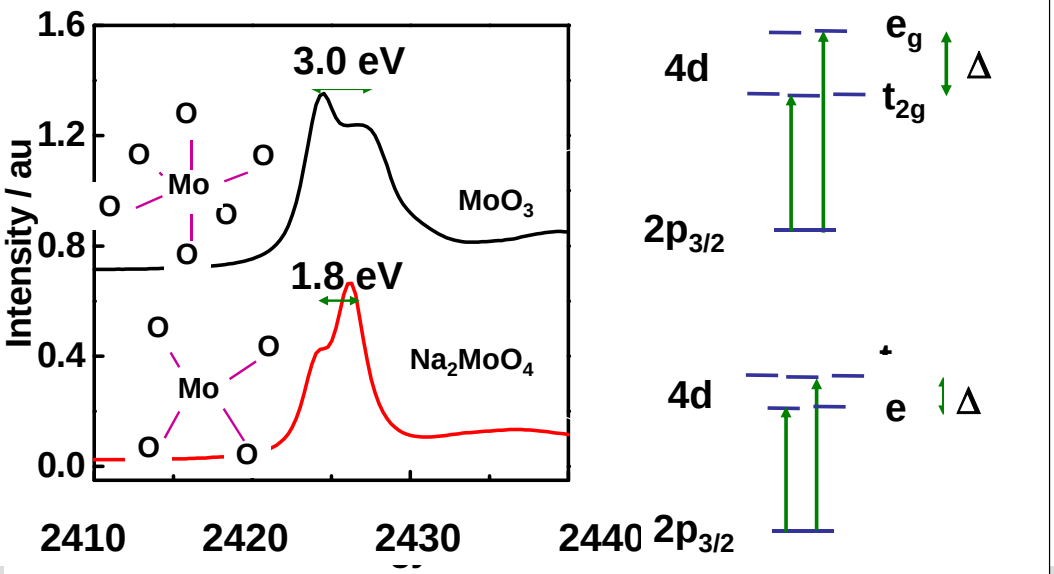
L_3-edge XANES for MoO_3 and Na_2MoO_4

→Sensitive to Symmetry

R. Radhakrishnan, C. Reed, S.T. Oyama, M. Seman, J.N. Kondo, K. Domen, Y. Ohminami, K. Asakura, J.Phys.Chem.B **105** (2001) 8519.



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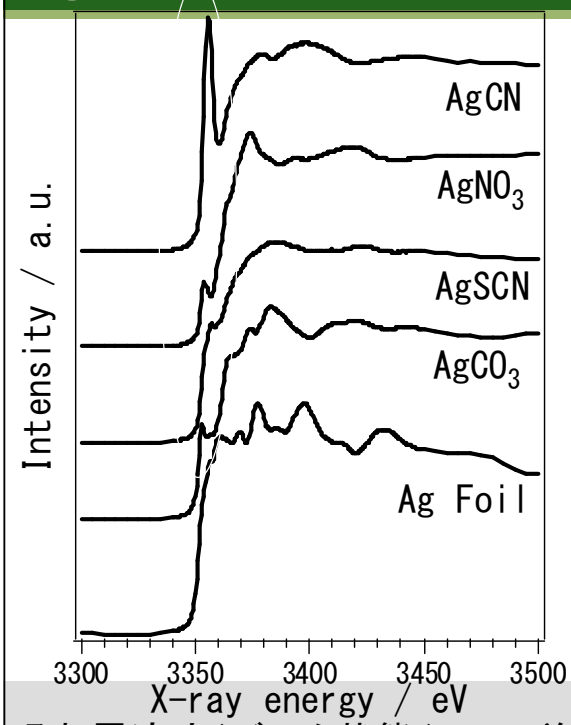
Ag化合物のLIIIXANESスペクトル

T.Miyamoto et al., In press



Ag化合物ではedge－peakが存在

Ag foilにはedge-peakが存在しない

→d^{10}であるため2p-4dはないはず、

Coordination charge

吸収電流法（バルク状態（50nm前後）反映）

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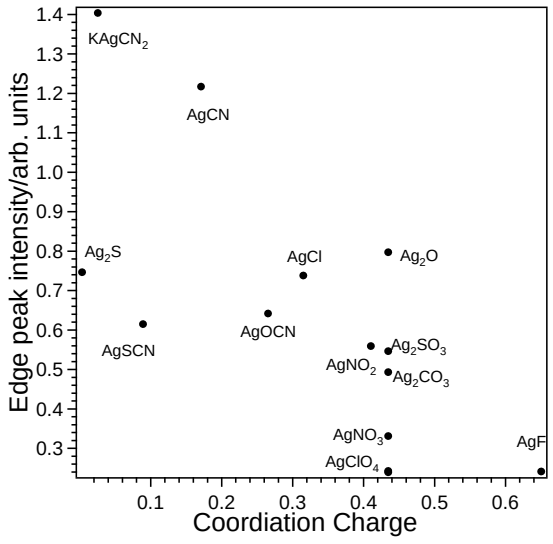
Edge peak intensity and coordination charge for Ag L_3



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Ag Compounds structure.

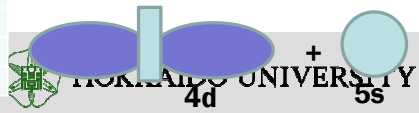
Table 1. The structural parameters of silver compounds.

Compound	Formal Valence	Bond type	No. of bonds	Bond distance	reference
Ag metal	0	Ag-Ag	12	2.89	
Ag2O	1	Ag-O	3	2.16	[4]
Ag2CO3	1	Ag-O	4	2.24, 2.24, 2.44, 2.74	[9]
Ag2SO3	1	Ag-O	4	2.23, 2.30, 2.47, 2.50	[12]
		Ag-O	4	2.40, 2.45, 2.45, 2.73	
AgNO3	1	Ag-O	7	2.48, 2.48, 2.50, 2.56, 2.58, 2.75, 2.77	[6]
Ag2SO4	1	Ag-O	6	2.41, 2.41, 2.43, 2.43, 2.69	[5]
AgClO4	1	Ag-O	8	2.53, 2.53, 2.53, 2.53, 2.73, 2.73, 2.73, 2.73	[1]
AgNO2	1	Ag-O	6	2.44, 2.44, 2.72, 2.72, 2.72, 2.72	[10]
	1	Ag-N	1	2.3	
K(Ag(CN)2)	1	Ag-C	2	2.13	[3]
AgCN	1	Ag-C	1	2.06	[7]
		Ag-N	1	2.06	
AgSCN	1	Ag-S	1	2.43	[2]
		Ag-N	1	2.22	
AgOCN	1	Ag-N	1	2.11	[8]
Ag2S	1	Ag-S	2	2.42, 2.45	[11]

No octahedral nor tetrahedral structure

s-d hybridation is possible.

For example s and d of X-Ag-X belongs to A1g symmetry.

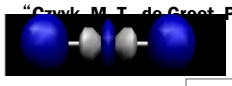


Covalency and hybridization

Covalent and ionic character

High covalency --> large directionality->large s-d hybridazation

"Czyżyk, M. T., de Groot, Physical Review B 39, 9831 (1989)."



X-Ag-X linear structure

$$\Psi_1 = (c_{11}\phi_{5s} + \mathbf{c_{12}}\,\phi_{4dz^2} + c_{13}\phi_{Lg})$$

$$\Psi_2 = (c_{21}\phi_{5s} + c_{22}\,\phi_{4dz^2} + c_{23}\phi_{Lg})$$

$$\Psi_3 = (\mathbf{c_{31}}\phi_{5s} + c_{32}\,\phi_{4dz^2} + c_{33}\phi_{Lg}).$$

Covalent charac

Covalency determines the edge peak intensity

$$AgX + NaF \Leftrightarrow AgF + NaX$$

$$\Delta H_{formation}(AgX) = \Delta H_{atom}(X_n) + \Delta H_{atom}(Ag(s)) + E.A.(X) + I.E.(Ag) - H_{lattice}(AgX)$$

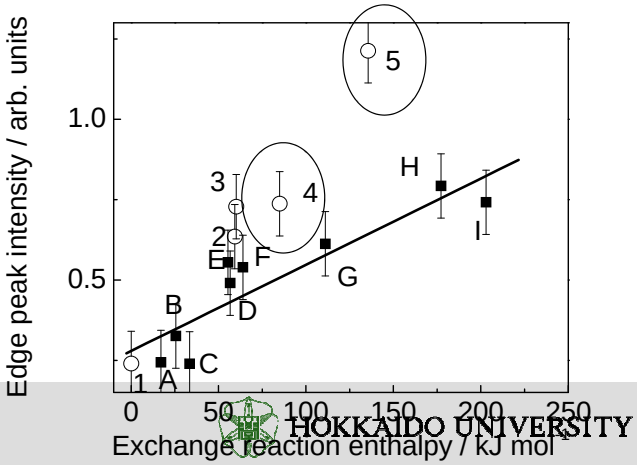
$$H_{ex} = \Delta H_{formation}(AgF) + \Delta H_{formation}(NaX) - \Delta H_{formation}(AgX) - \Delta H_{formation}(NaF)$$

$$\approx H_c(AgX)$$

(A) AgClO4;(B) AgNO3; (C) Ag2SO4; (D)Ag2CO3; (E)AgNO2; (F) Ag2SO3; (G) AgSCN; (H)Ag2O; (I)Ag2S; (1) AgF;

(2) AgCNO; (3) Ag(CH3COO);

(4) AgCl; (5) AgCN.

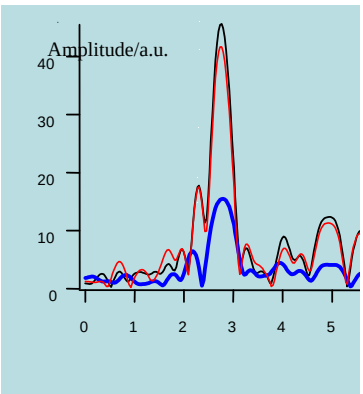


XAFS Summary

EXAFS and XANES

EXAFS Local Structure Single scattering.

- **Fourier transform**
- **Coordination number**
- **Distance**
- **Operando XAFS**



XANES

- **Electronic state**
- **Local structure**