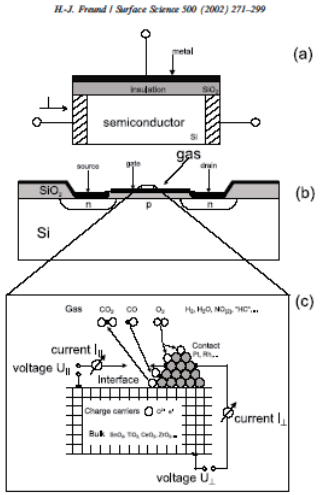
偏光全反射蛍光XAFSによる表面高分散金属種の研究とERLへの期待

朝倉清高

北海道大学触媒化学研究センター

Metal on oxide support

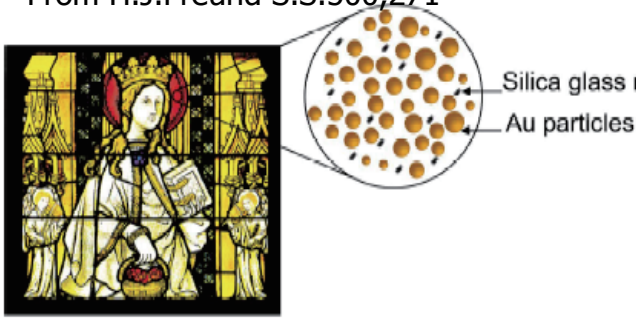
- Metal-oxide interfaces are involved in technologically important area
  - Composites, protective coatings, and thin film technology,
  - Electronic and magnetic devices(MOS, Q-dot, Magnetic recording).
  - Soil pollution, nuclear combustible and waste packaging,
  - Heterogeneous catalysis, gas sensors and the glass industry.
  - The electrical, mechanical,chemical or thermal properties of many technologically important devices depend on the **structure and morphology of metal-oxide interfaces.**



MOS From H.J.Freund S.S.500,271

Stained glass

From H.J.Freund S.S.500,271



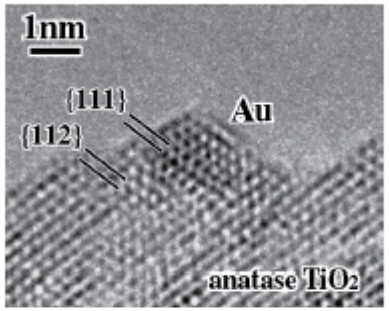
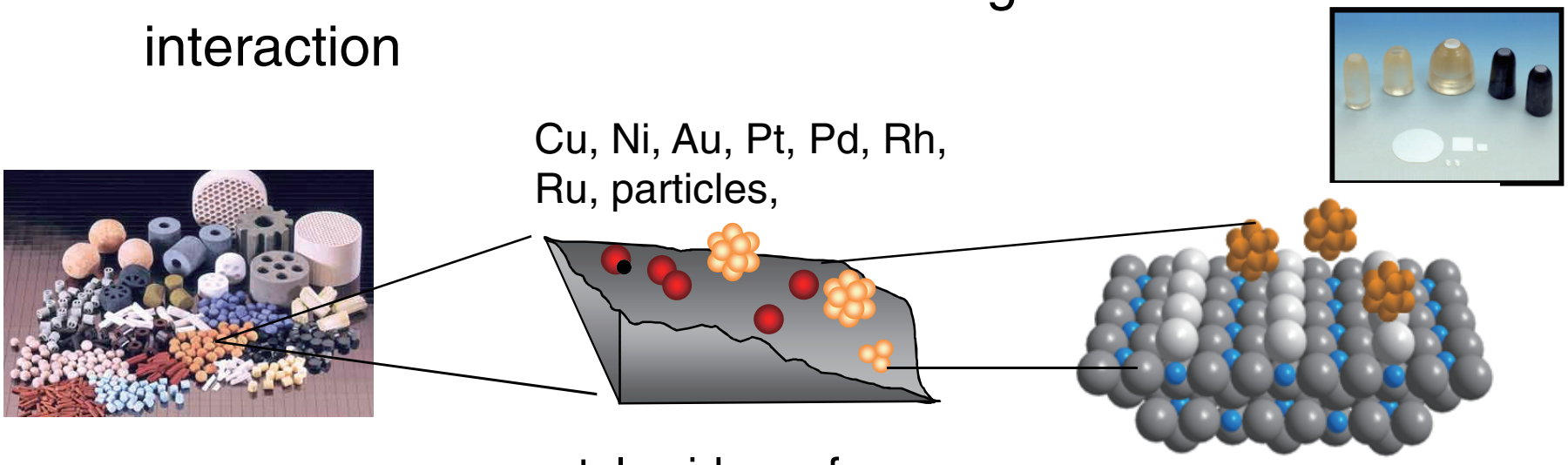


Fig. 1. TEM image for Au/anatase TiO_2 catalysts prepared by deposition-precipitation and by calcination at 673 K.

Au on TiO_2 Haruta, 26(2005) 578

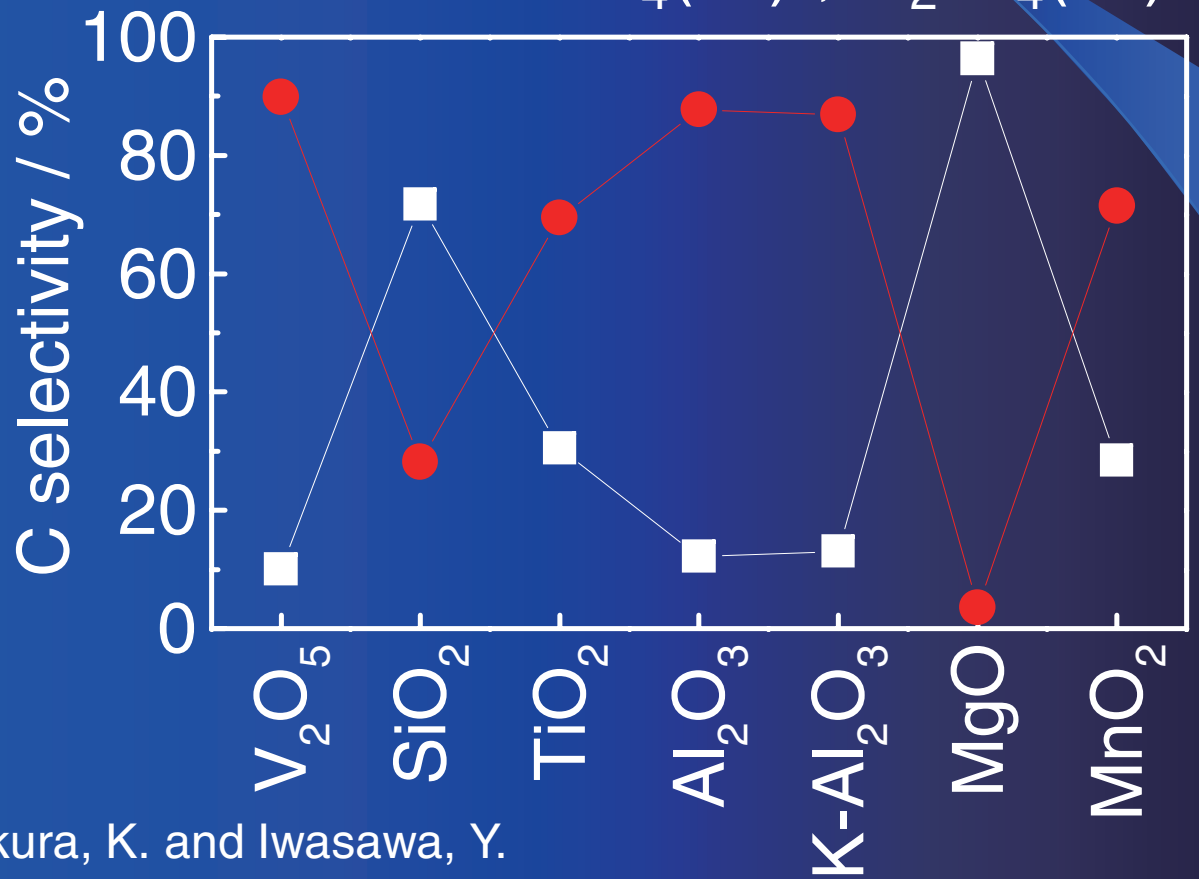
Metal oxides are used as supports.

- Catalysts, sensors, fuel cells, batteries etc.
  - highly dispersed metal clusters (less than a few nm) are stabilized by a metal-oxide chemical interaction
- A well-defined single crystal oxide
  - an ideal model substrate to investigate the metal-oxide interaction



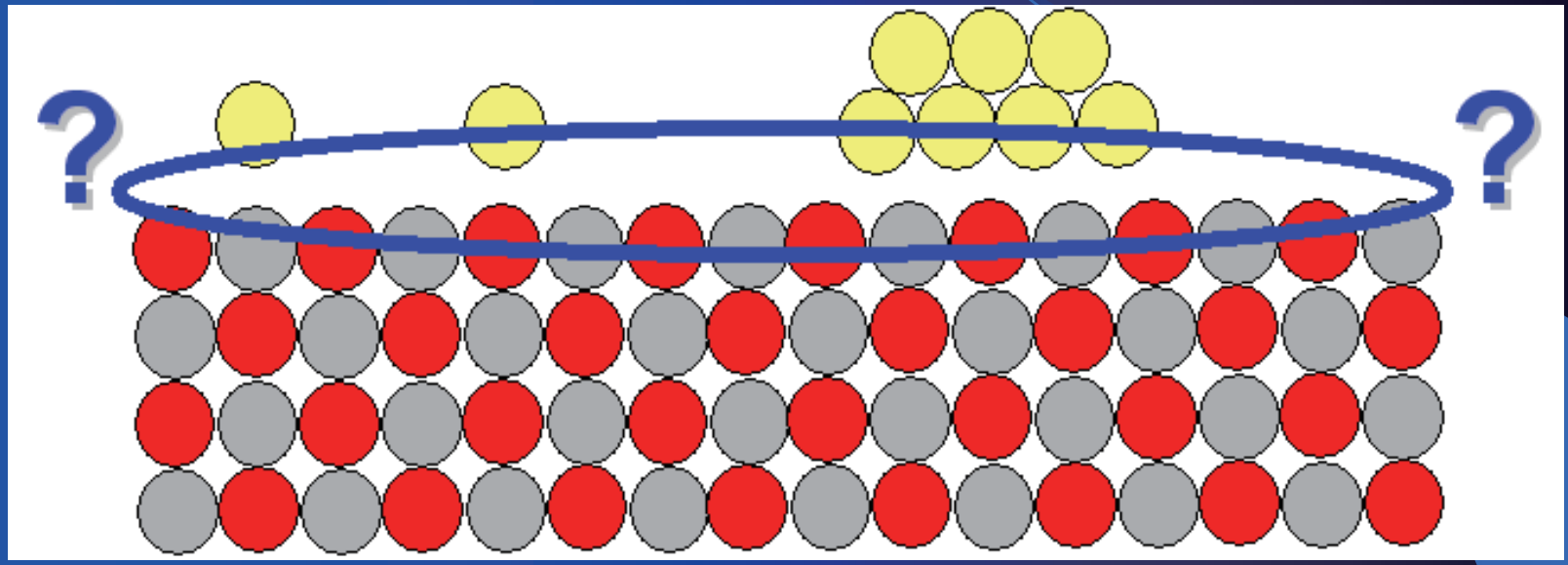
金属担持触媒

担持Ru触媒によるCO水素化に対する選択性の担体依存性；CH_4(●)，C_2-C_4(■)



Ref. Asakura, K. and Iwasawa, Y.
Journal of the Chemical Society-Faraday Transactions **1990**, *86*, 2657-2662.

高分散した金属種の界面結合構造



- 相互作用の主役はだれか？
(どの原子が強く相互作用するのか？)

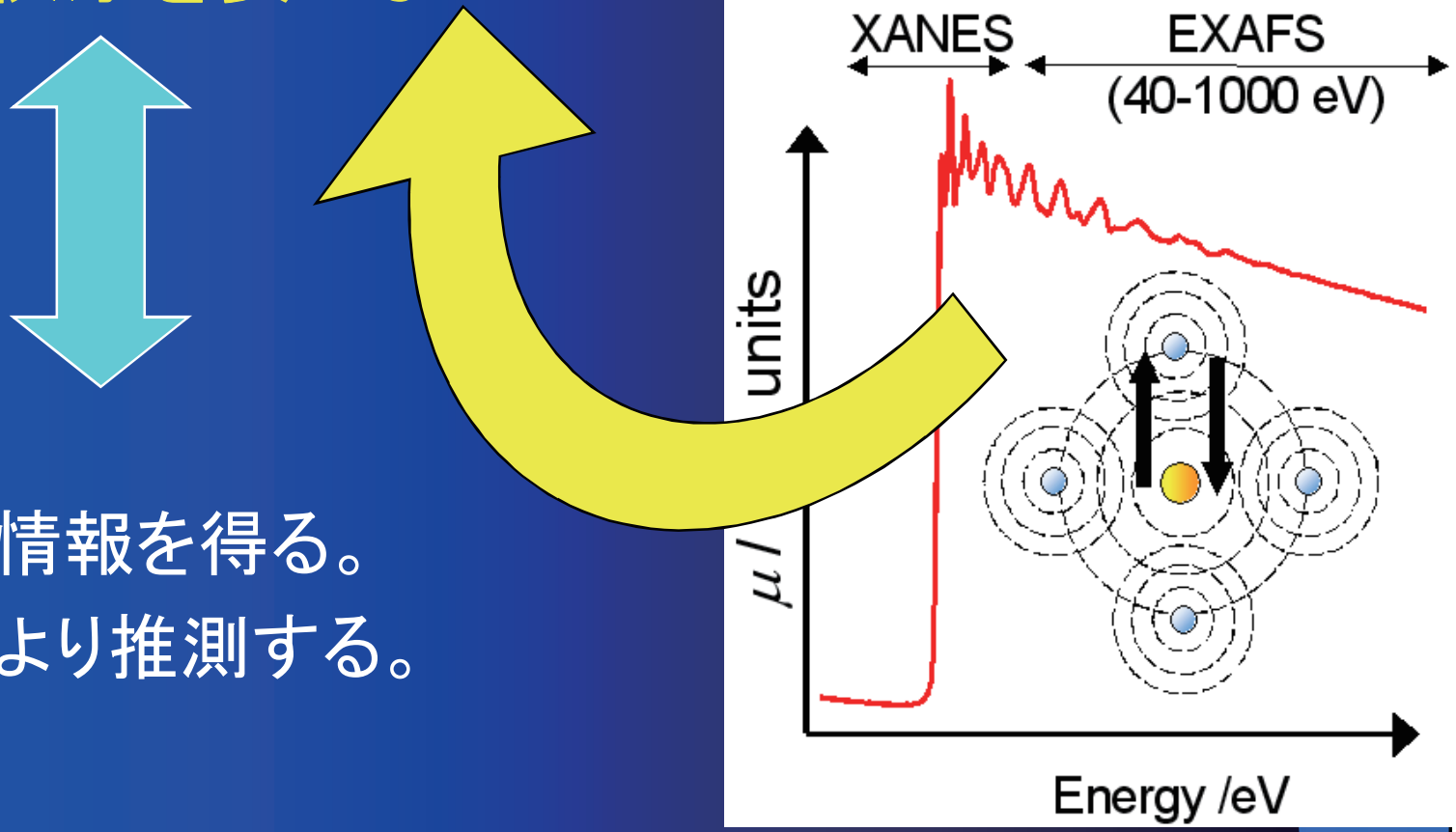
- 何が金属種の構造や分布を決定しているのか？

XAFS

X-ray Absorption Fine Structure

吸収原子近傍の局所構造情報を与える手法

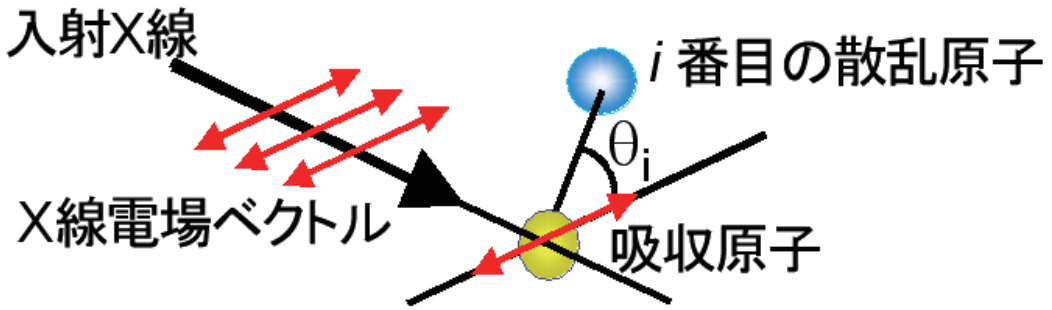
長距離秩序を要しない



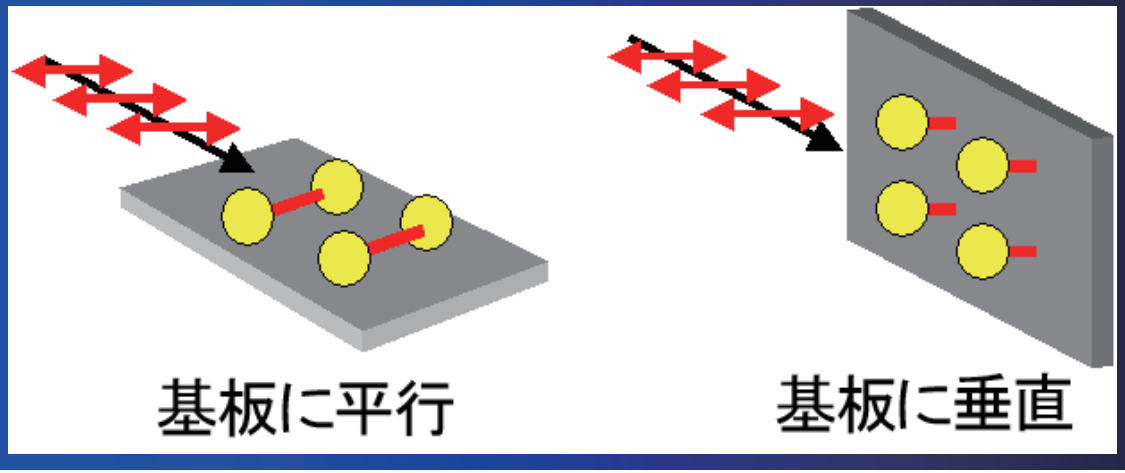
- 1次元情報を得る。
- 1次元より推測する。

偏光依存性

$\chi_i(k) \propto 3\cos^2\theta_i$ (K 吸収端)



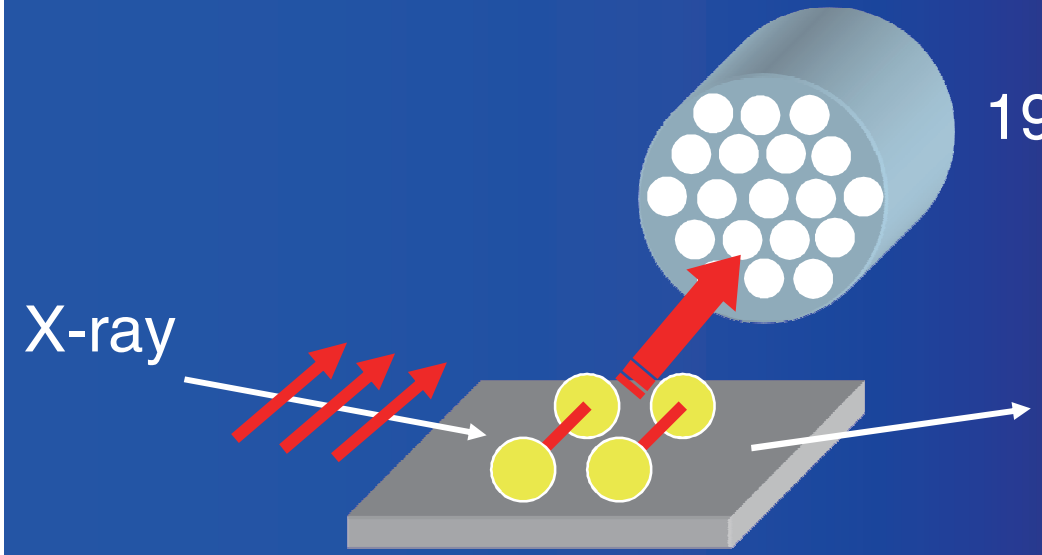
X線の電場ベクトルに対し基板の向きを
変化させることでEXAFSから**三次元情報**を得る

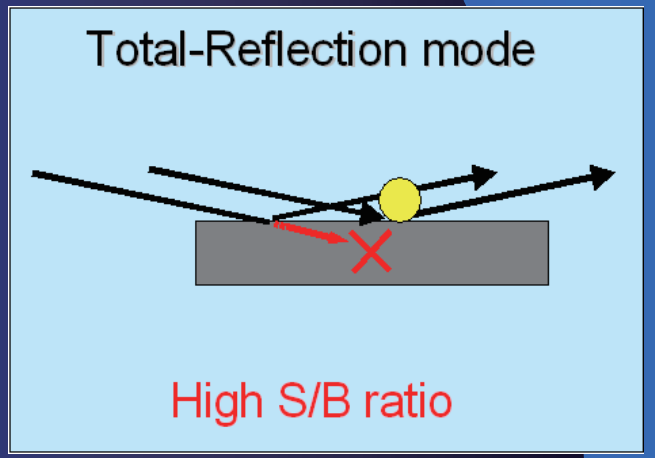


PTRF-EXAFS

Polarization Dependent **T**otal-**R**eflection **F**luorescence
Extended **X**-ray **A**bsorption **F**ine **S**tructure

単結晶表面上に高分散した金属種の**界面を含む**
三次元構造を低濃度 (x 10^{13} atoms/cm^2)から
決定することの出来る唯一の実験的手法



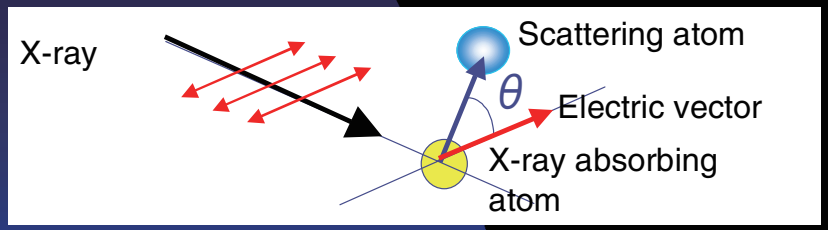


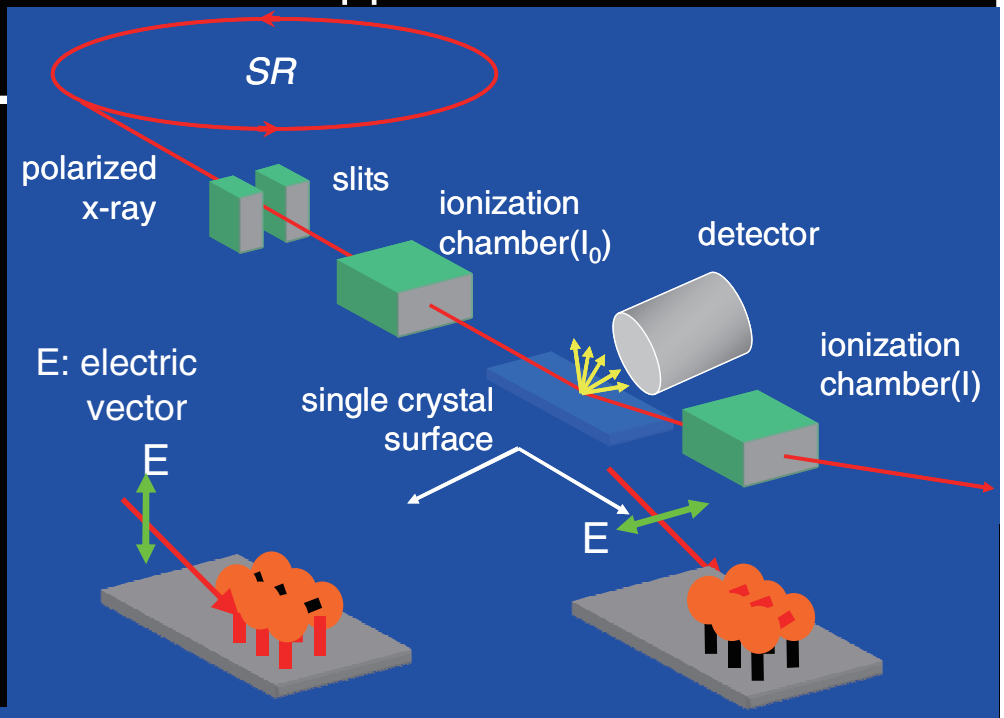
Ref. Chun, W. J.; Asakura, K.; Iwasawa, Y. *J. Phys. Chem. B* 1998, *102*, 9006-9014.

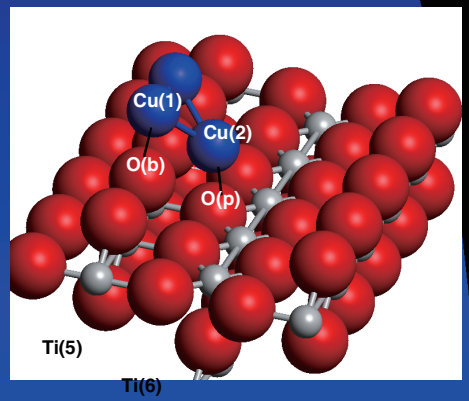
Polarization dependent total reflection fluorescence XAFS

- Polarization dependent XAFS(X-ray absorption fine structure) provides us 3D bond information between the cluster and support as well as inside the cluster

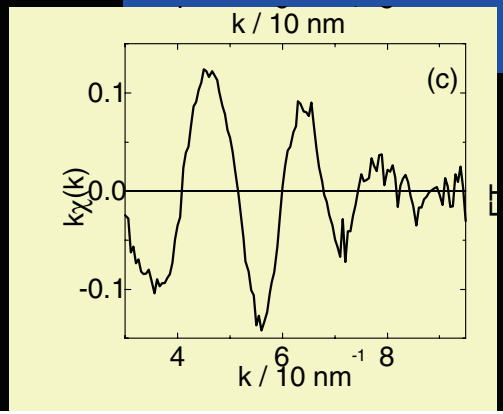
$$\text{Amplitude of XAFS} \propto 3\cos^2\theta$$

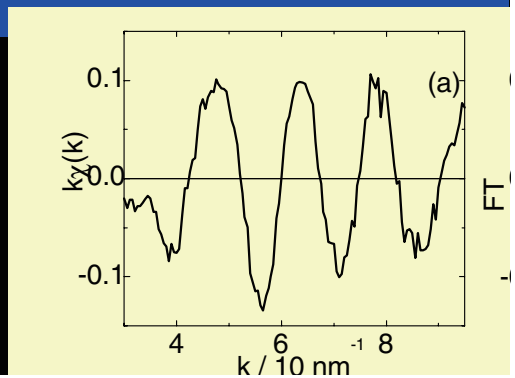






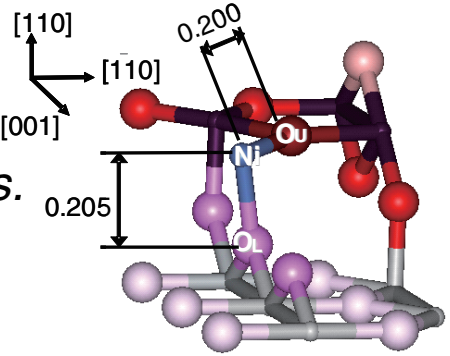
Tanizawa, JPC 2001



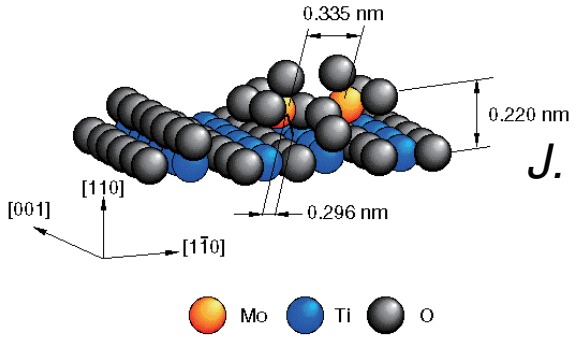


PTRF-XAFS

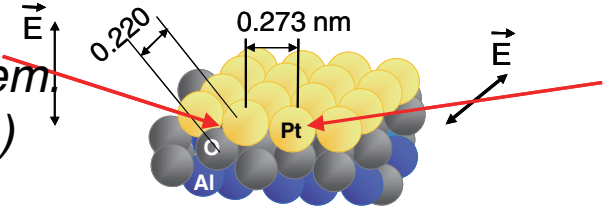
- **P**olarization-dependent **T**otal **R**eflection **F**luorescence **X**-ray **A**bsorption **F**ine **S**tructure
  - 3D structure information at sub-Å resolution in the presence of air and liquid.
  - Atomic species, bond distance, coordination, oxidation states, location, growth direction etc.



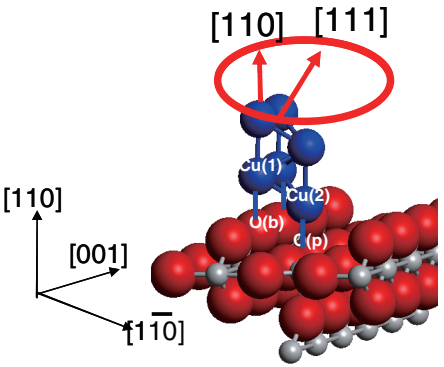
Chem. Phys. Lett.,421 (2006)p. 27



J. Phys Chem. B ***102***(1998) *p. 9006*

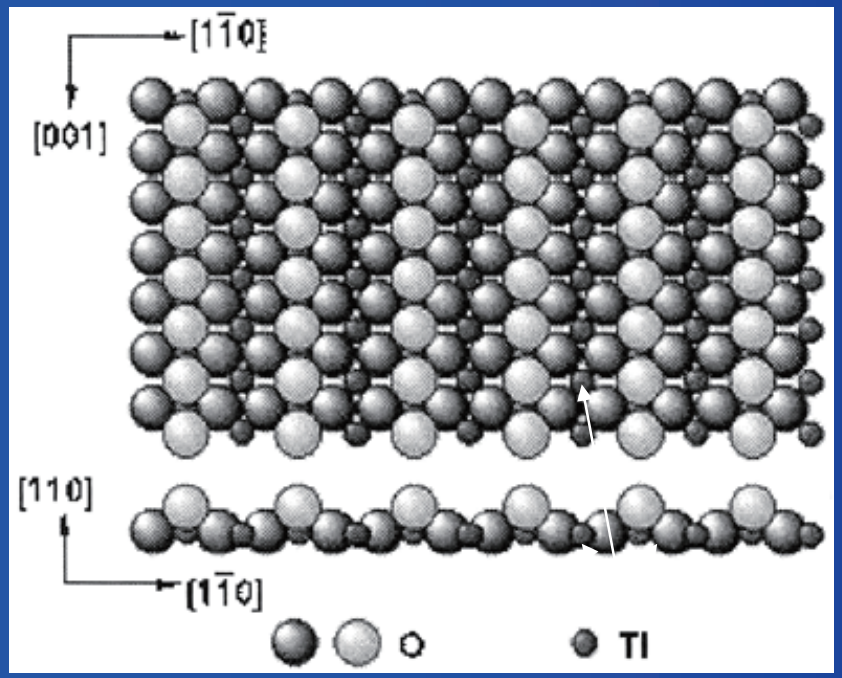


J. Phys Chem. B ***101***(1997) *p.* 5549

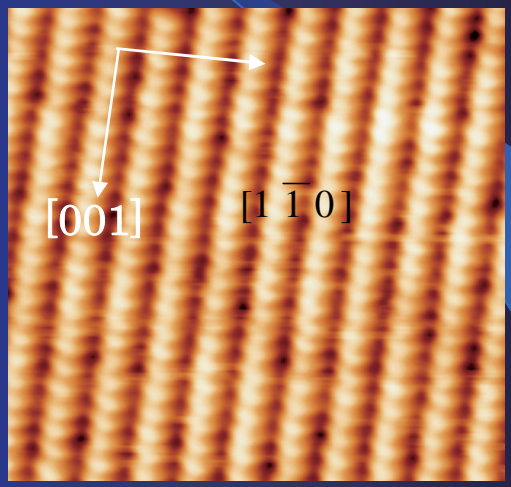


J. Phys Chem. B ***107*** (2003) *p.12917*

TiO_2(110) : A rutile 110 surface



TiO_2(110)-(1 ×1) structure STM image

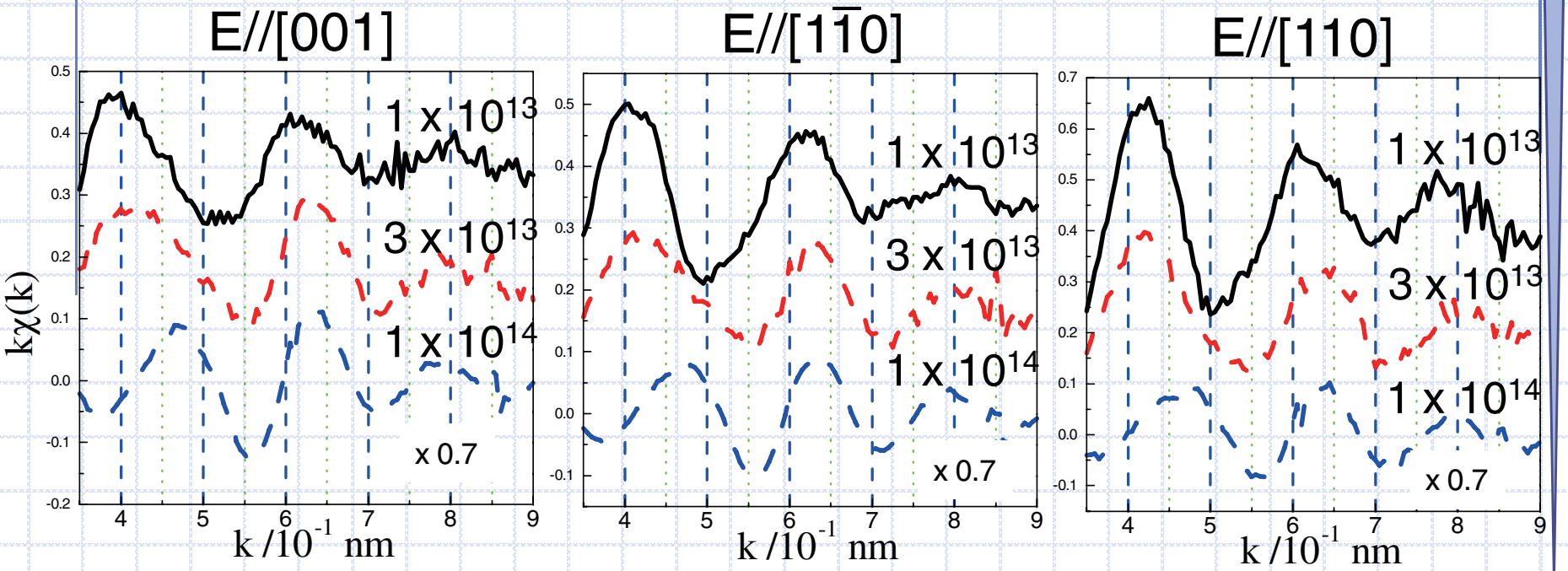


10 nm × 10 nm

Sample Bias Voltage :+ 1.5 V
Tunneling current : 0.2 nA

A surface well characterized by STM, XRD, ISS

PTRF-EXAFS oscillations



1 x 10^{13} atoms/cm^2 ; <u>no Ni-Ni</u> bonds were observed

Ni atoms dispersed monoatomically.

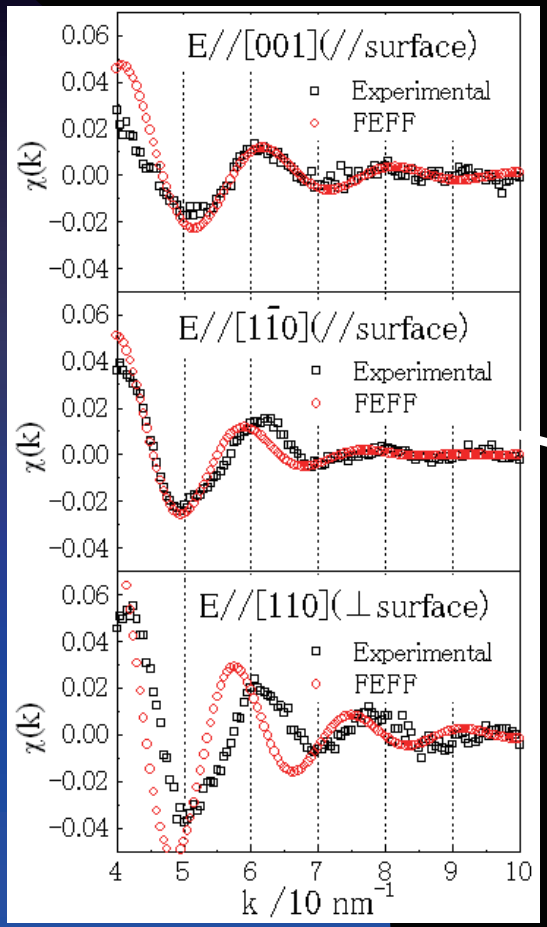
In all directions, Ni-O bonds were observed.

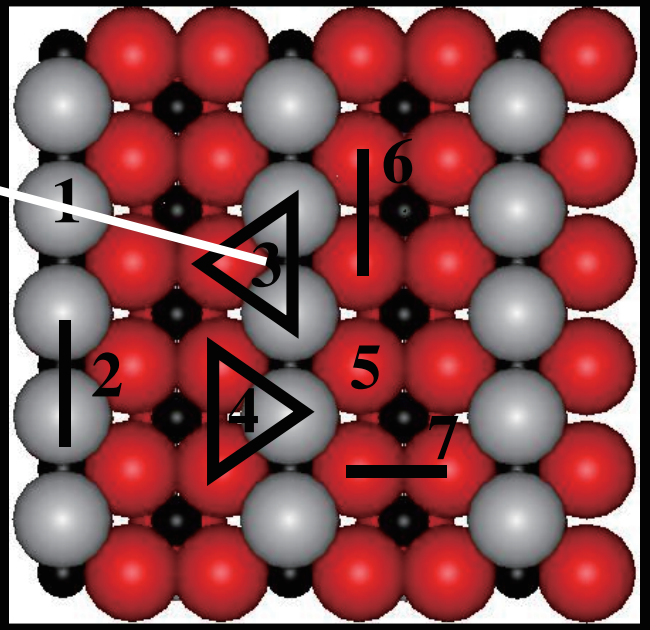
⇩

Ni atoms preferably interact with O^{2-}

Adsorption sites on TiO_2(110)

We could not reproduce the spectra with <u>any model on terrace</u>.

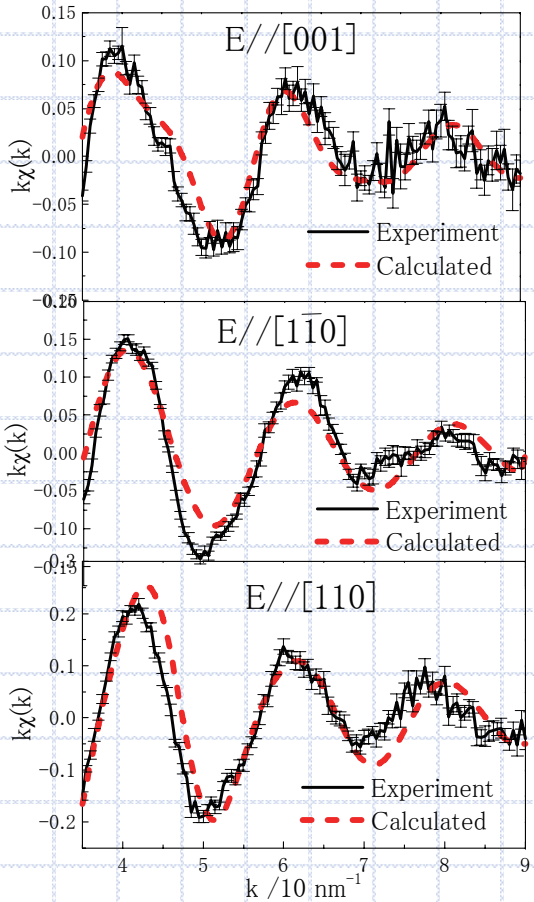


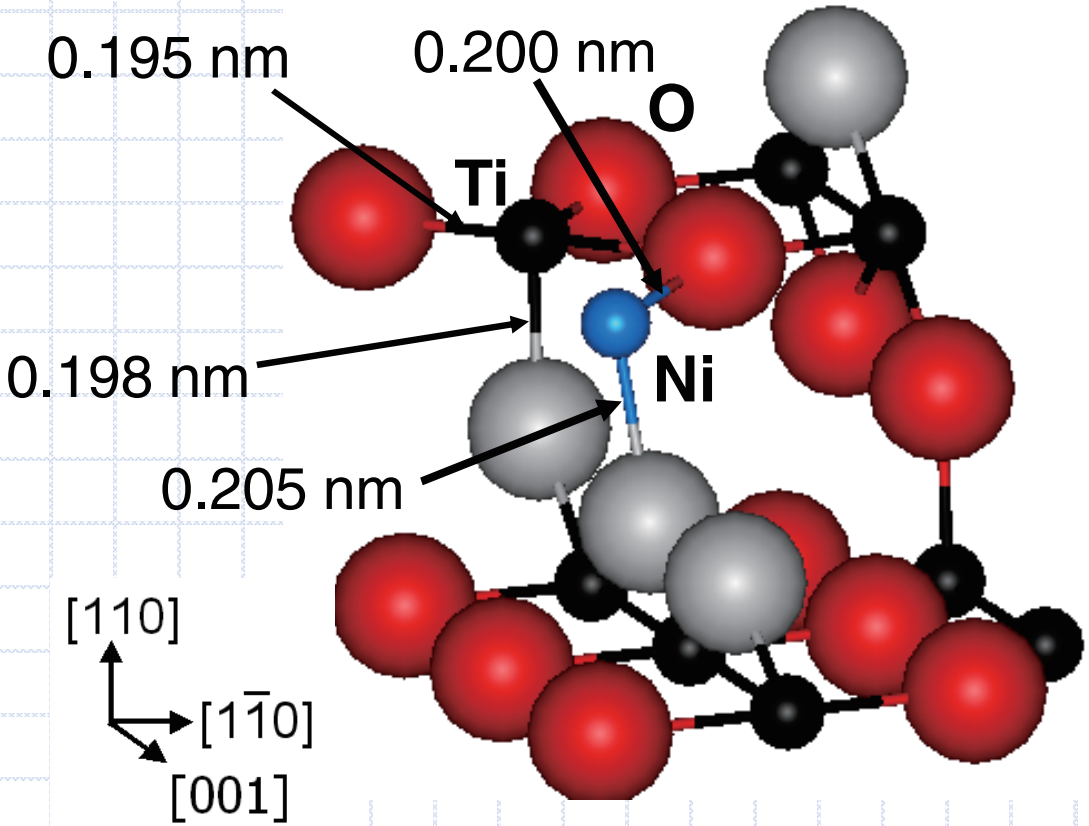


The amount of the adsorption site be 1 x 10^{13} atoms / cm^2

The step-site-model-structure

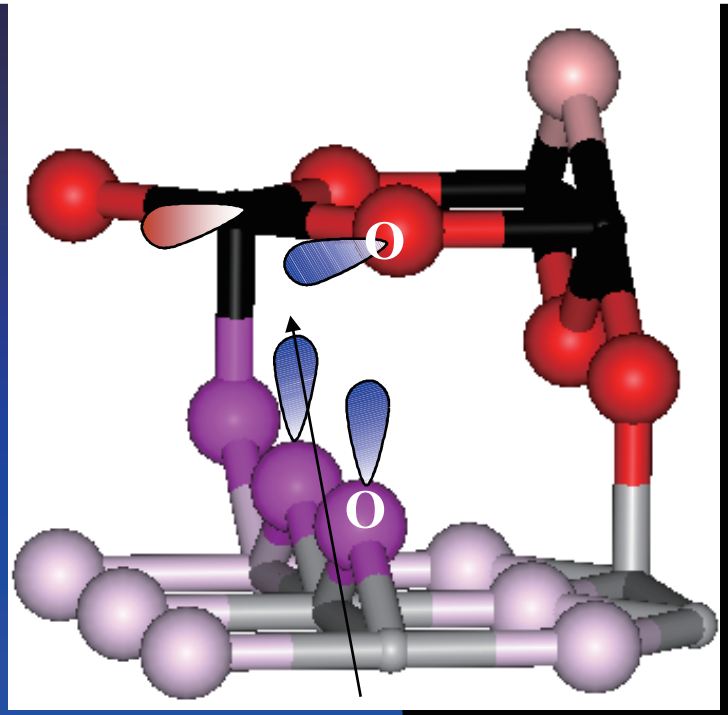
We succeeded to reproduce experimental spectra

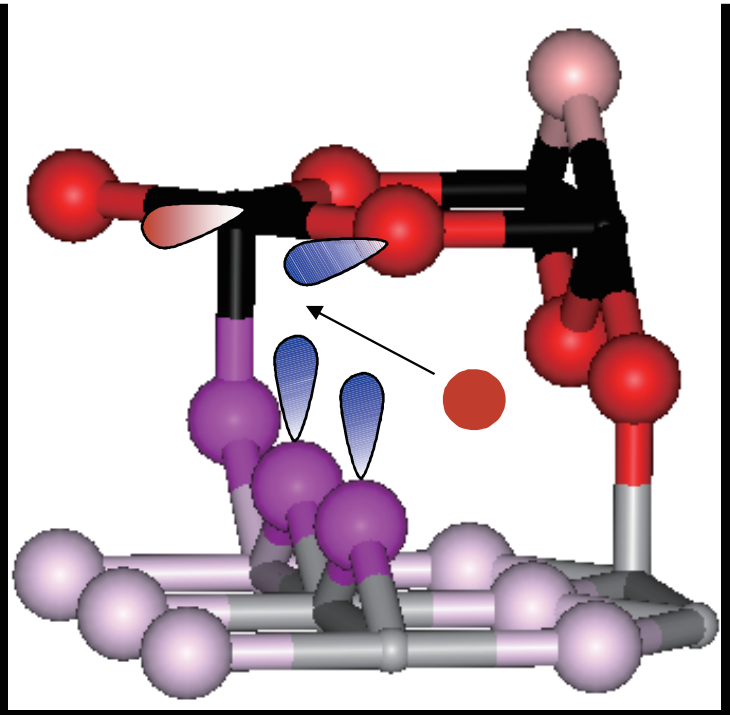




Oxygen dangling bonds

- Dangling bond of oxygen atoms affords the adsorption site for Ni.
- More than two bonds are necessary to fix the Ni.

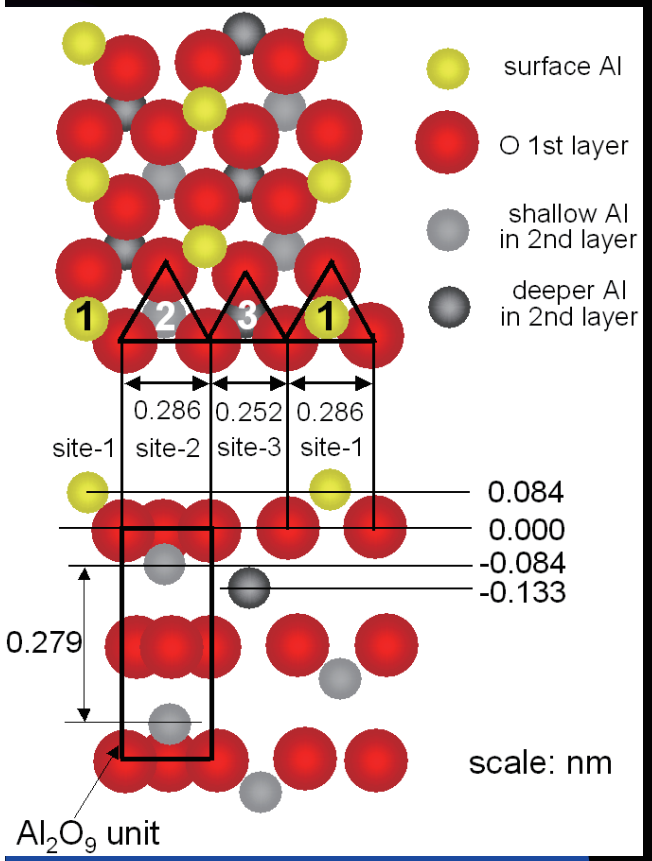


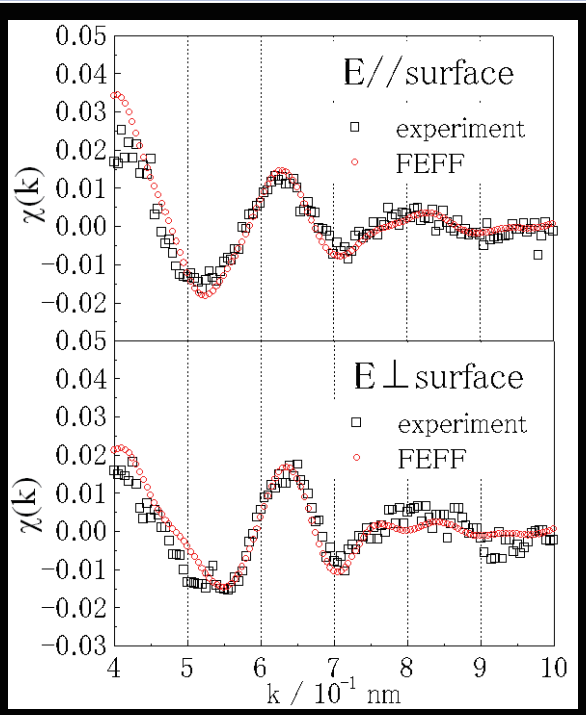


Virtual Ti site

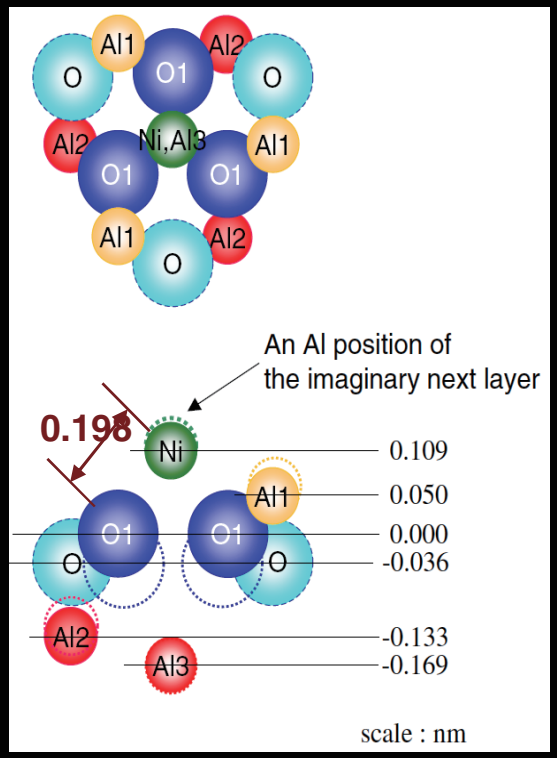
Ni on α-Al_2O_3(0001)

Ijima, K.; Koike, Y.; Chun, W.-J.; Asakura, K. et al. ; *Chem,Phys.Lett.* 2004, *384*, 1





XAFS oscillations.

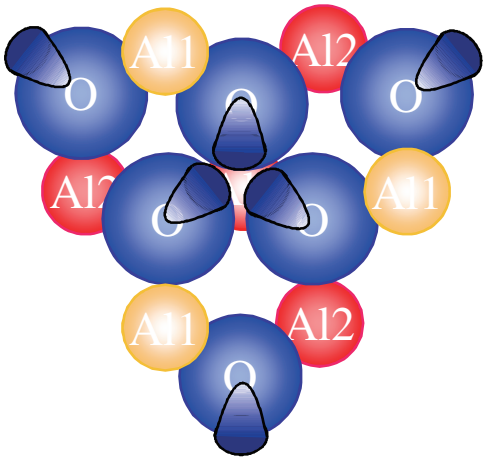


Adsorption structure

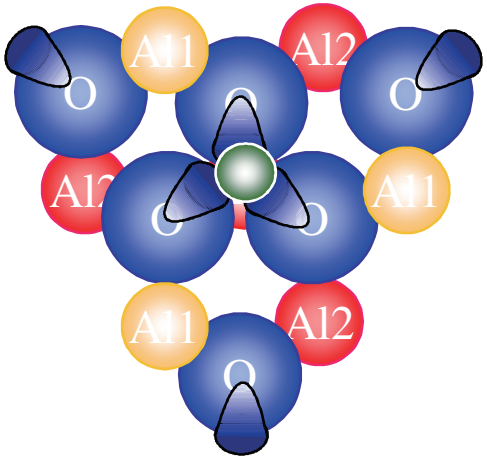
Al2O3 (0001) surface

Ni is adsorbed on a virtual Al position over the surface.

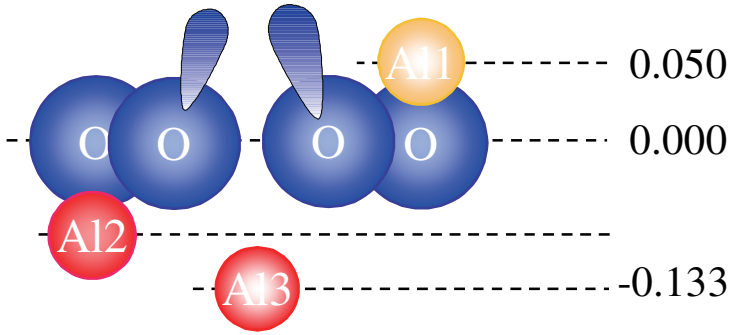
Oxygen dangling bonds and adsorption sites.



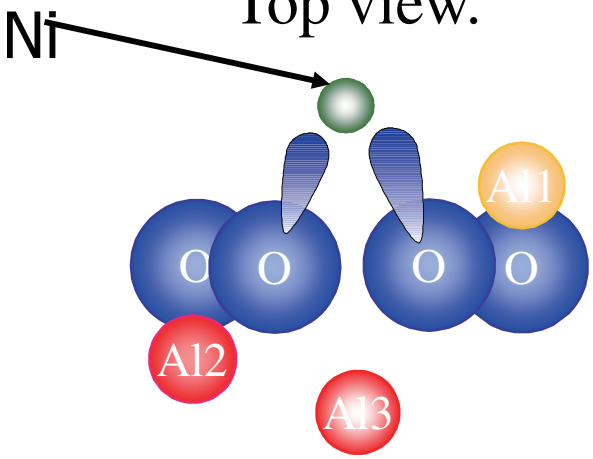
Top view.



Top view.



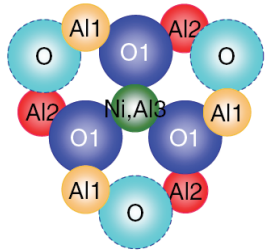
Side view.

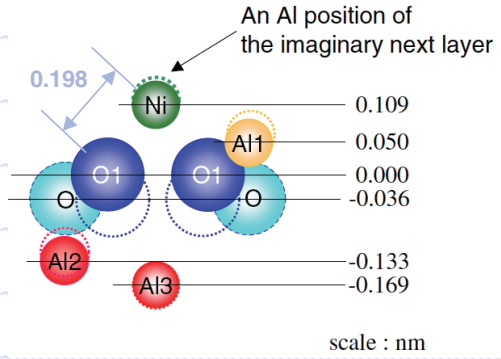


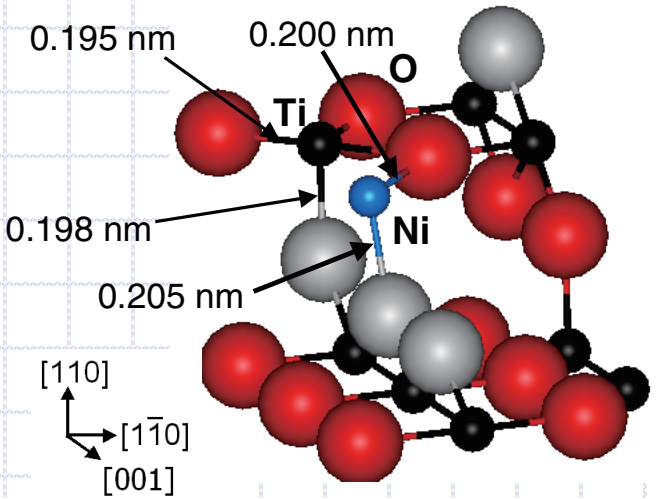
Side view.

Conclusions for late transition metal

- Atomically dispersed state occurs at low coverage.
- The interacting site is Oxygen atoms.
- The distance indicates the bond is rather strong chemical bond.
- The site is the virtual cation site.
- The oxygen dangling bond may play important role.
- The late transition metal can also interact with anions.



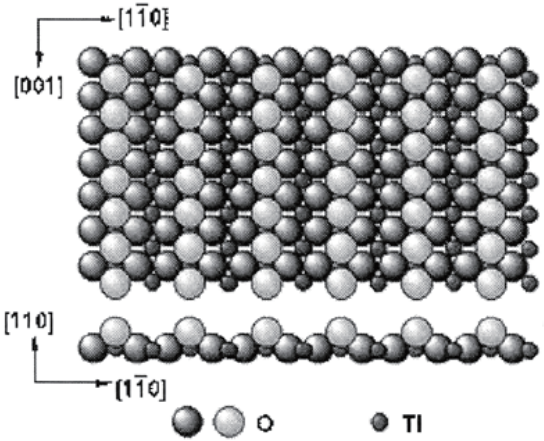


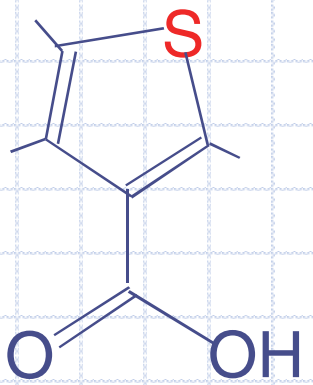


Cu on the TCA-covered surface

*base pressure : ~10^{-9} Pa

- Premodified surface with thiophene carboxylic acid (TCA)
  - It is on exposed Ti site



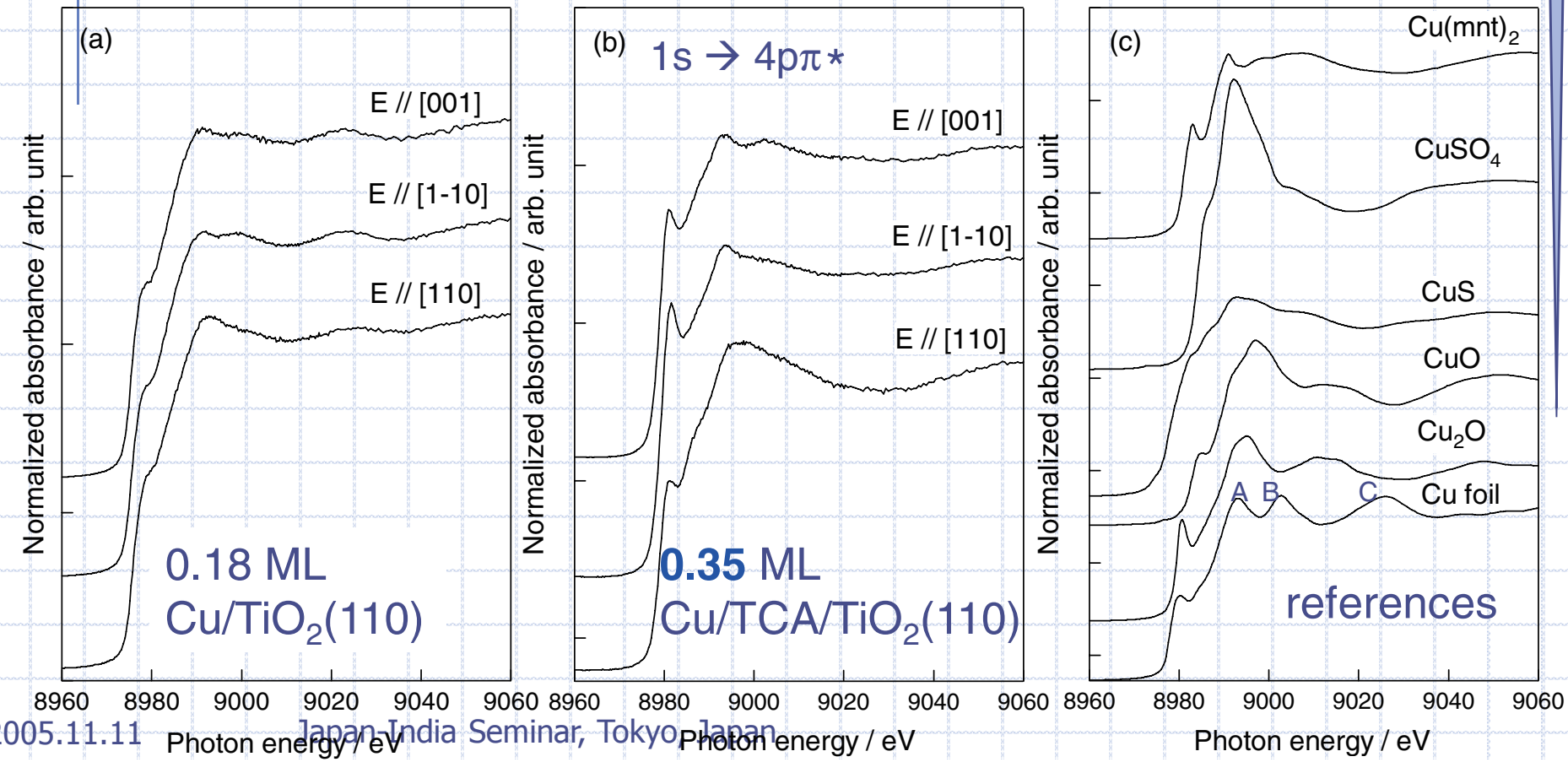


- Cu deposition
  - evaporation of Cu wire
  - 1 ML (monolayer) = 5.2 x 10^{14} /cm^2 determined by XPS

- Surface structure determined by PTRF-XAFS
  - Cu K-edge, Si(111), RT @ KEK-PF BL9A, Tuskuba, Japan

XANES spectra

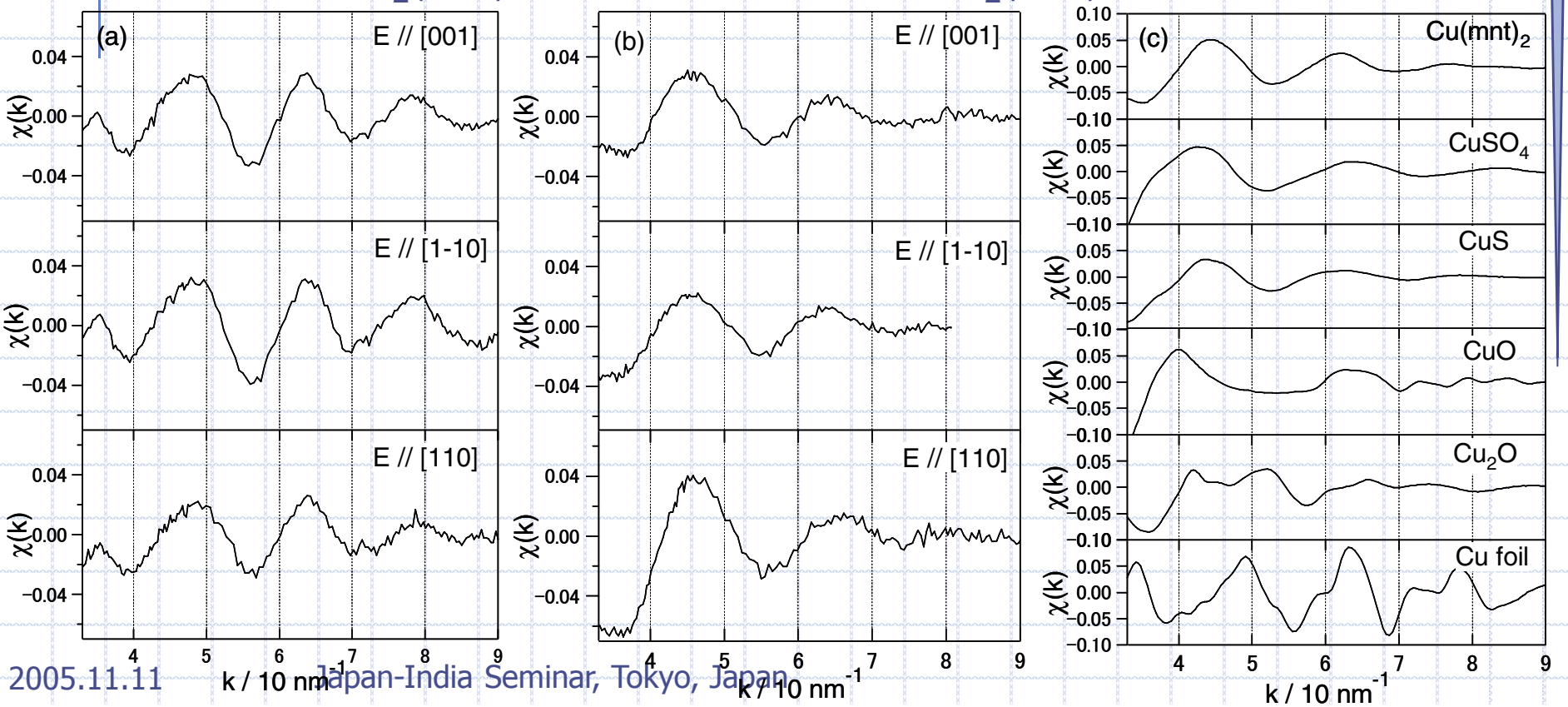
- Cu species on premodified surface is not metallic
  - Characteristic the mid-edge features appeared in all orientations (1s → 4pπ* transition)
  - The oxidation state of Cu species is monovalent



EXAFS spectra

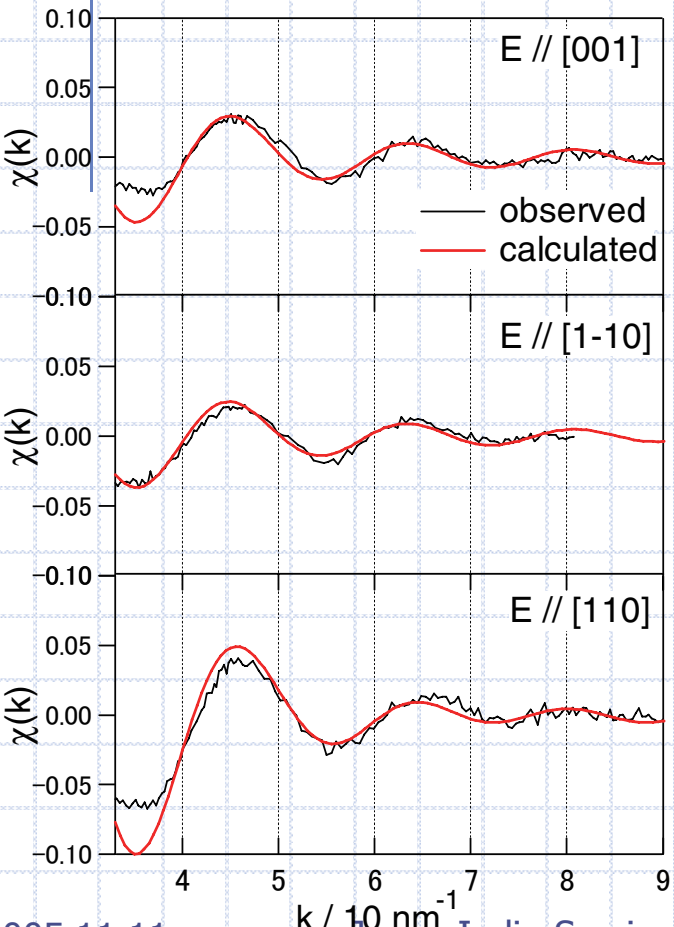
- Cu/TCA/TiO_2(110): No Cu-Cu, Cu-Ti bond but Cu-S was found in all orientation (0.214~216 nm)
  - 0.02 nm shorter than the Cu-S bond lengths found in CuS and $Cu(mnt)_2$
    - plays an important role in preventing the diffusion of Cu species

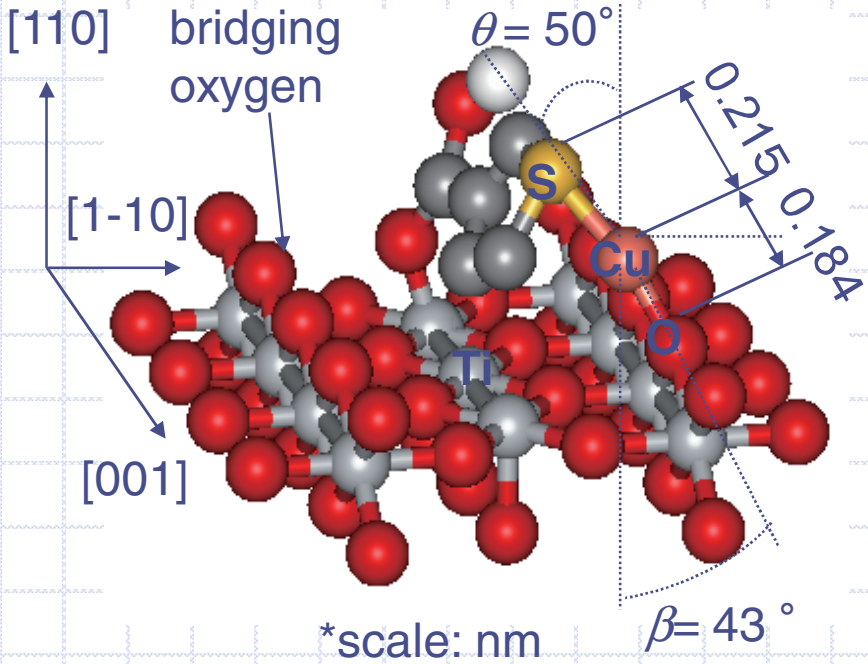
0.18 ML Cu/TiO_2(110) **0.35** ML Cu/TCA/TiO_2(110) references



Proposed model of Cu/TCA/TiO_2(110)

- Two covalent bonds, Cu-S and Cu-$O_{surface}$, were found
  → Two chemical interactions play a role in stabilizing Cu species and preventing their diffusion





The bond angle S-Cu-O was estimated as 165°
→ Many Cu(I) compounds (monovalent) : linear structure accompanied by two ligands.

TPRF-XAFS

- It can provide a small amount of metal species on top of the oxide surfaces.
  - 1×10^{13} cm^{-2}
- 3 dimensional Information can be obtained.

But

- It requires a large flat surface for glazing angle incidence.
- For example, 10 mm long flat surface Is required when beam height is 0.1 mm with less than 10 mrad
  - 0.1 / 0.01=10 mm substrate is necessary.

ERL への期待

サンプルサイズの最小化

- 0.01 nm･rad　丸ビーム?
- 100 μm程度
- 偏光特性の切り替え

◆幅広くサンプルを選べる。

- 小さい単結晶サンプルの利用
- MoO3（数ミリ）, VO2（1mm程度）など、