Asymmetry parameter and surface excitation parameter for Ni derived by angle-resolved and energy-resolved HAXPES analysis at SPring-8

Hideki Yoshikawa[1)], **Hiromi Tanaka[1),5)]**, **Masahiro Kimura[2),6)]**, **Toshiya Ogiwara[3)]**, **Takashi Kimura[3)]**, **Sei Fukushima[3)]**, **Kazuhiro Kumagai[3)]**, **Shigeo Tanuma[3)]**, **Mineharu Suzuki[4)]**, **and Keisuke Kobayashi[1)]**

[1)] NIMS Beamline Station, National Institute for Materials Science, Japan
[2)] SPring-8 Service Co , Japan
[3)] National Institute for Materials Science , Japan
[4)] ULVAC-PHI, INC , Japan

Present address
[5)] Yonago National College of Technology
[6)] NIPPON MINING & METALS CO., LTD.

Outline

◆Motivation

Nondestructive depth profile analysis by angle-resolved (AR) XPS needs the precise knowledge of Emission Depth Distribution Function (EDDF).

◆Present target

Extract factors affecting EDDF of AR-XPS

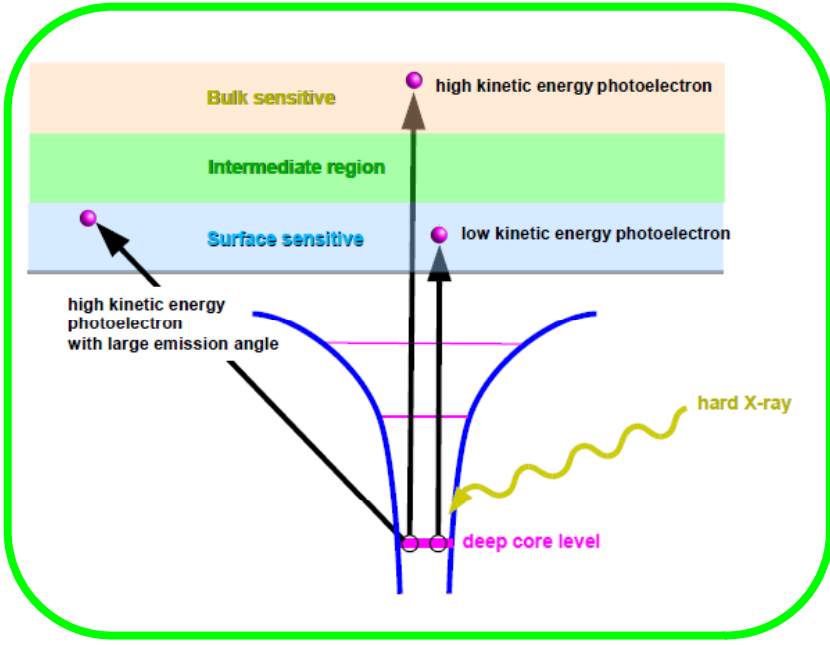
- asymmetry parameter
- refraction effect
- surface excitation
- plural elastic scattering

◆Methods

Experiment :

angle-resolved & energy-resolved XPS using energy tunable hard X-rays

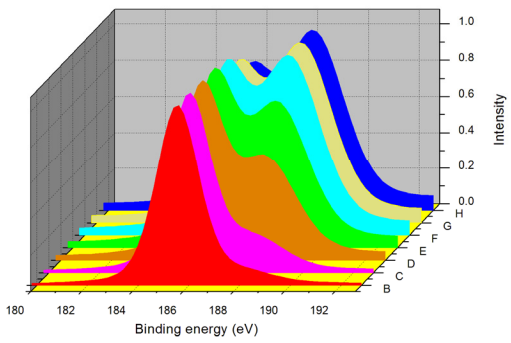
Simulation : Monte Carlo simulation



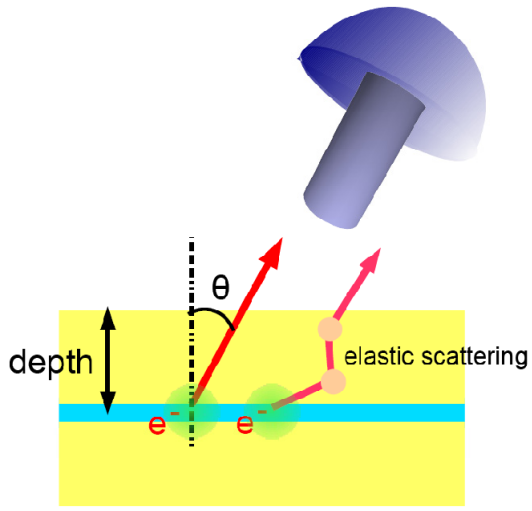
Motivation

Nondestructive depth profile analysis by angle-resolved high-energy XPS needs the precise knowledge of Emission Depth Distribution Function (EDDF).

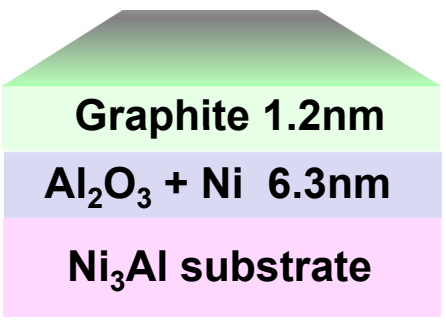
Experimental data of angle-resolved XPS



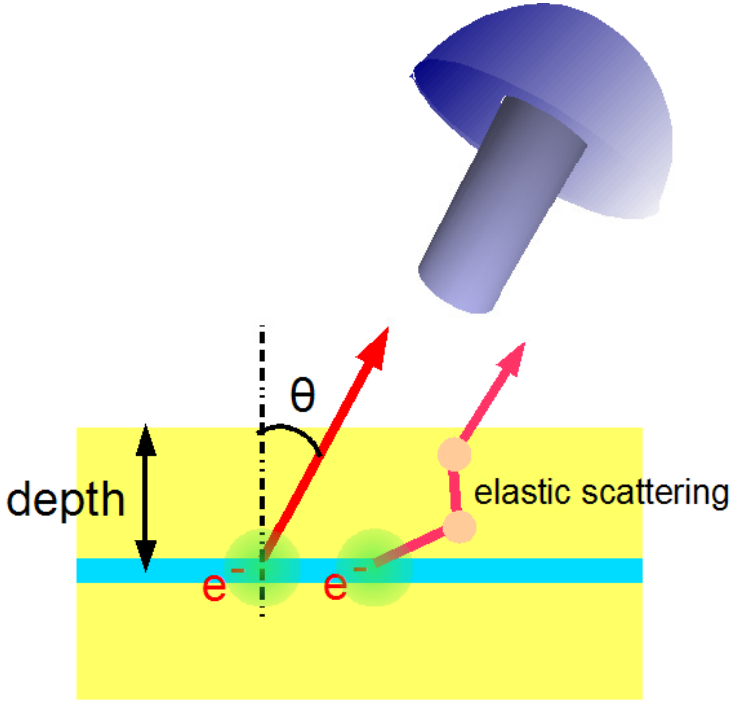
Evaluation of Emission Depth Distribution Function (EDDF)

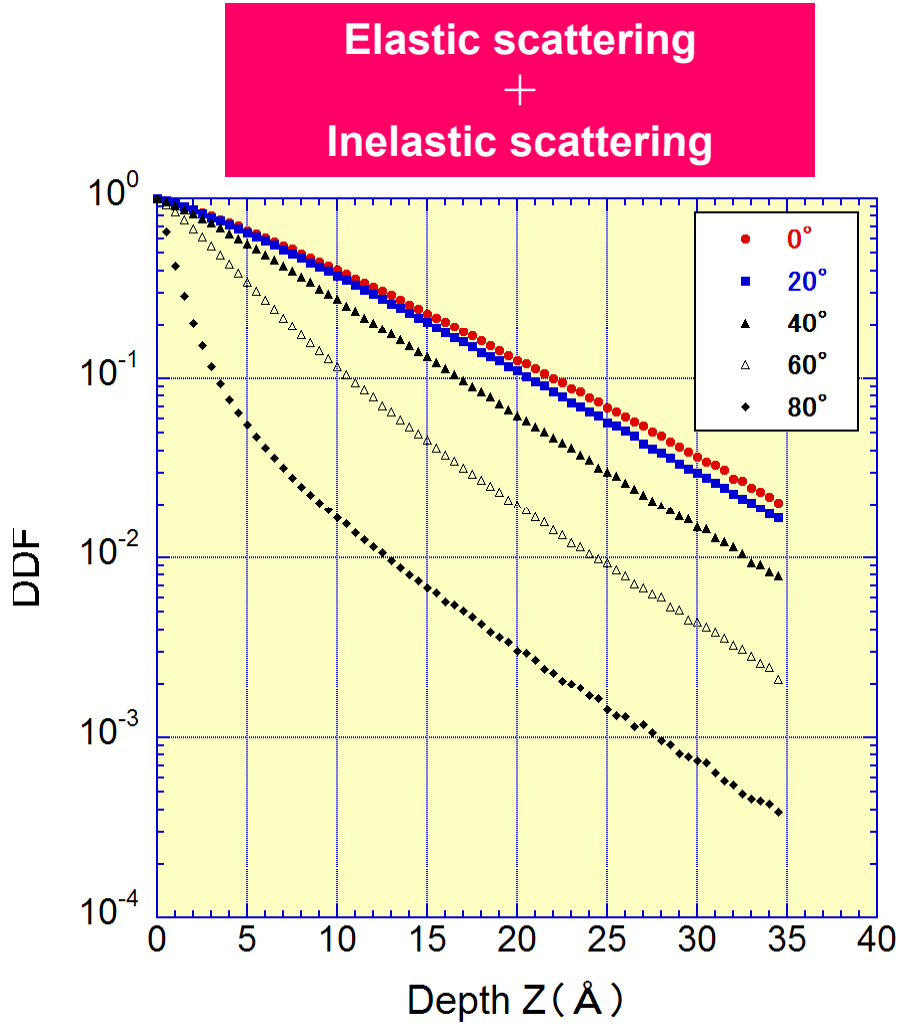


Estimation of internal structure of sample



Emission Depth Distribution Function (EDDF) calculated by Monte Carlo simulation Mo, 500eV





Initial angle distribution of photoelectrons is assumed to be symmetrical.

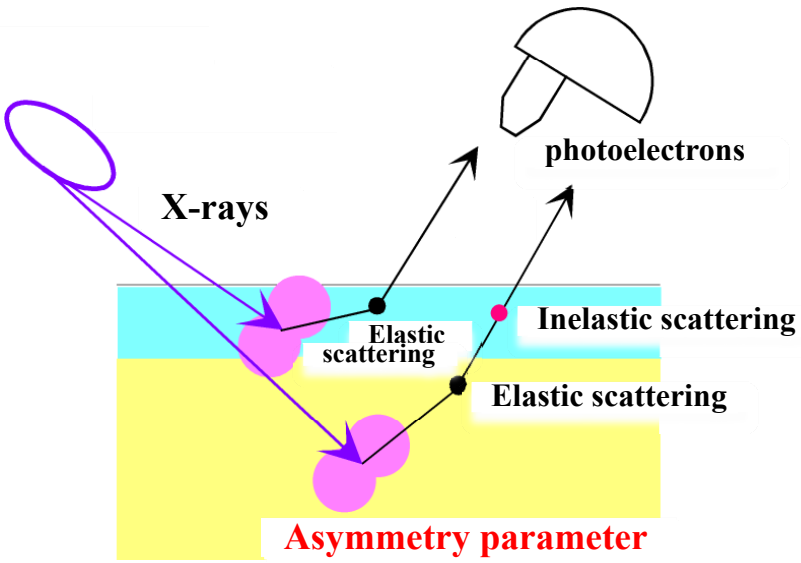
IMFP=13.97 Å

Approach

Factors affecting EDDF

- elastic scattering effect
- surface excitation and interface excitation
- asymmetry parameter
- diffraction effect

⋮

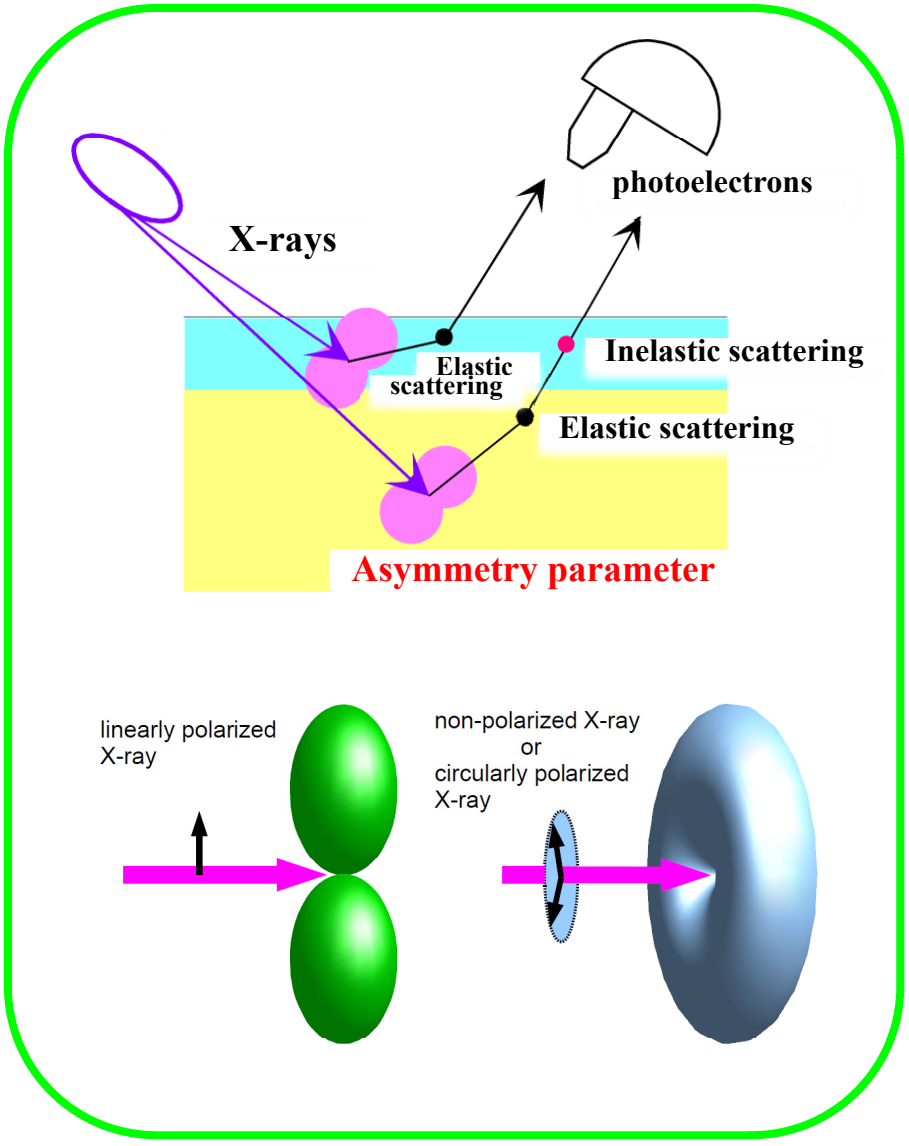


How to evaluate these complicated Factors

Energy-dependent and angle-dependent measurements are useful to evaluate these effects.

angle-resolved XPS with energy-tunable X-rays → Synchrotron Radiation (SR) X-rays

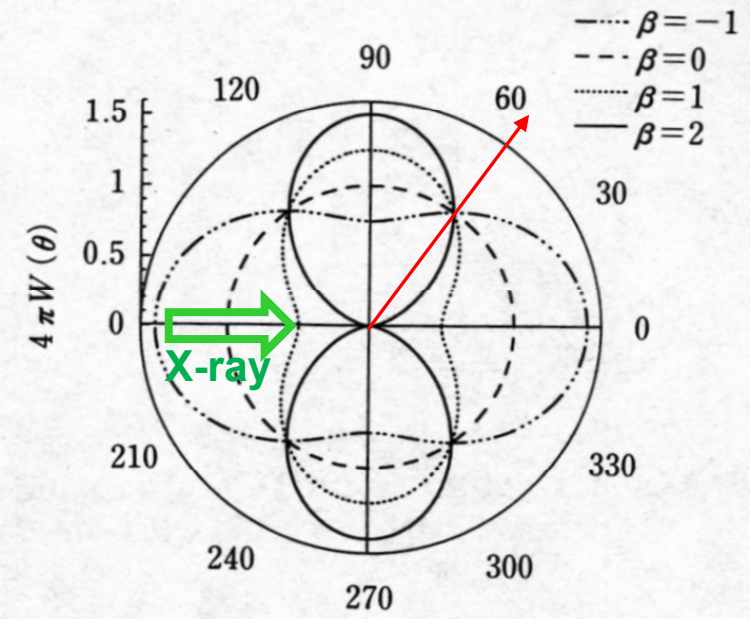
Asymmetry parameter



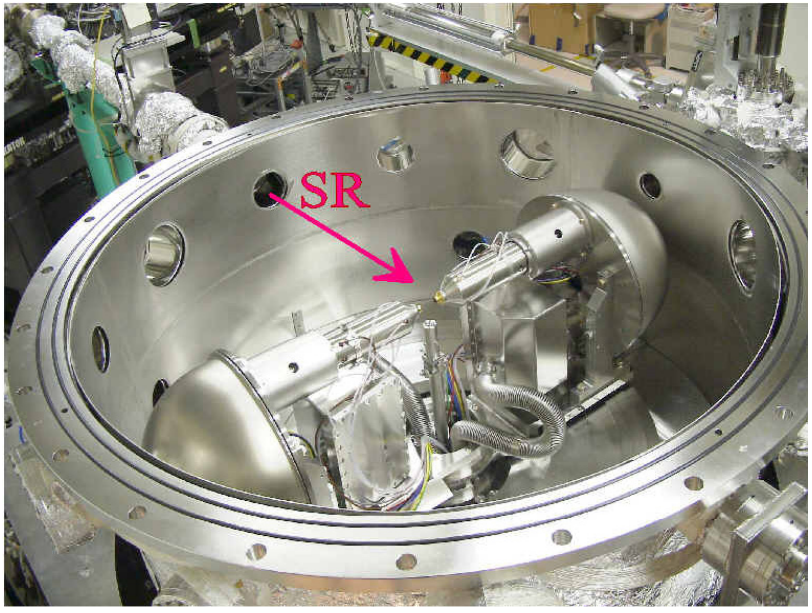
Asymmetry parameter depends on the incident X-ray energy and atomic orbital of target atom.

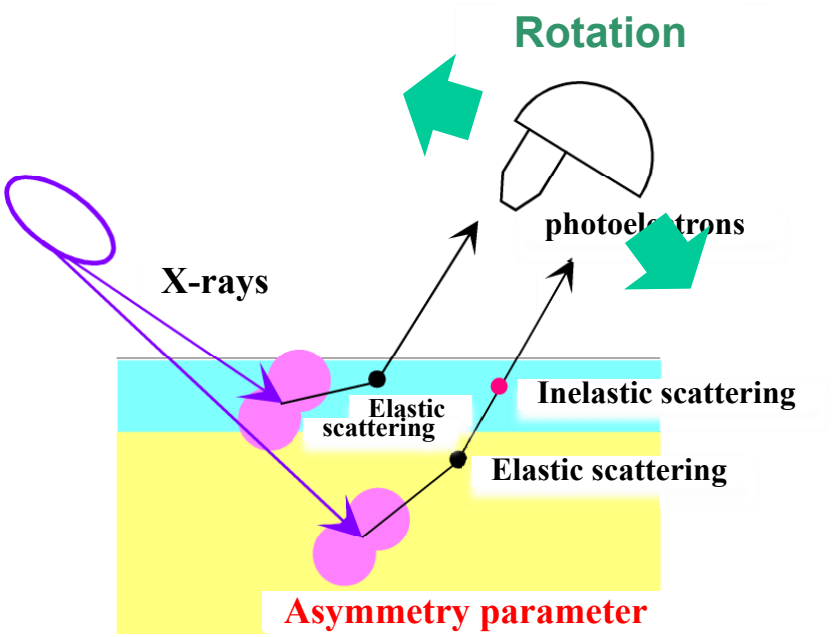
$$\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi}\left[1 - \frac{\beta}{4}(3\cos^2\theta - 1)\right]$$

54° 44' magic angle



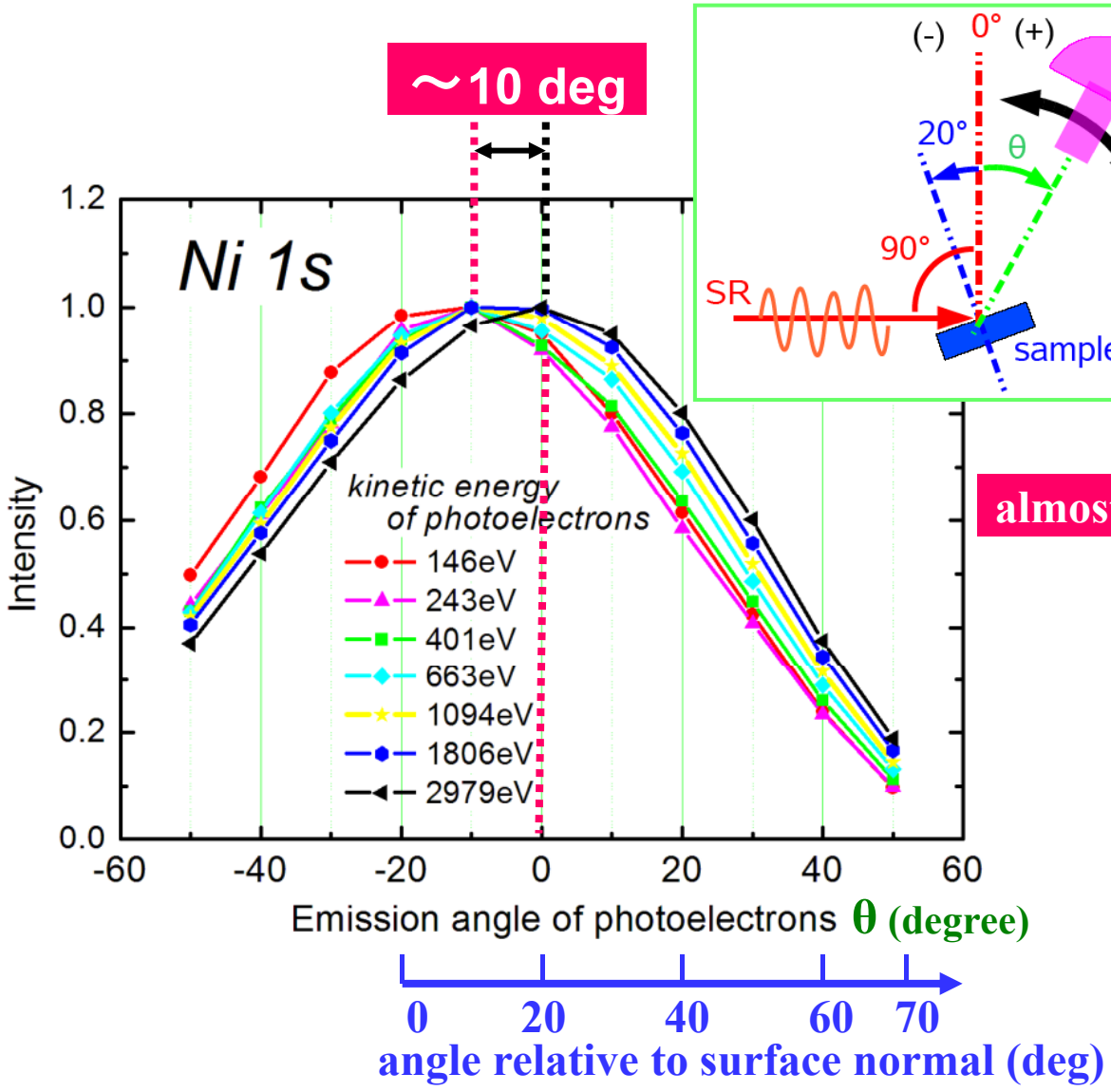
Angle resolved XPS at NIMS SPring-8 beamline

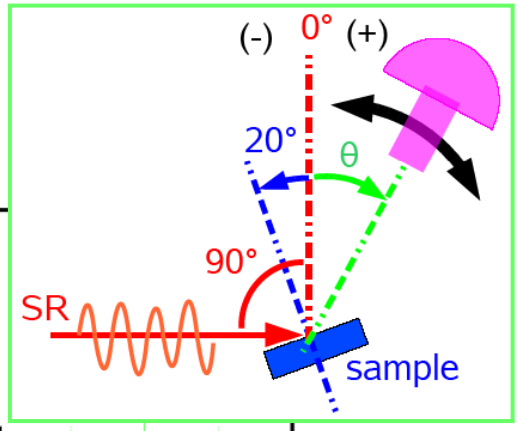


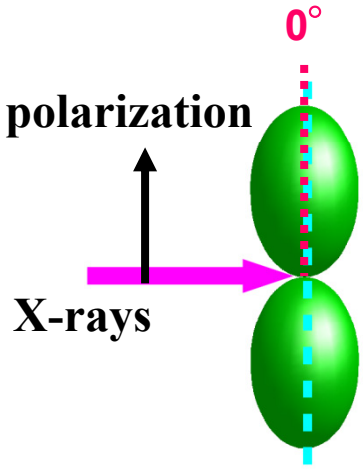


- maximum kinetic energy is 4800eV
- XPS analyzer rotates around the specimen center.

Experimental angle-resolved XPS data of Ni 1s photoelectrons



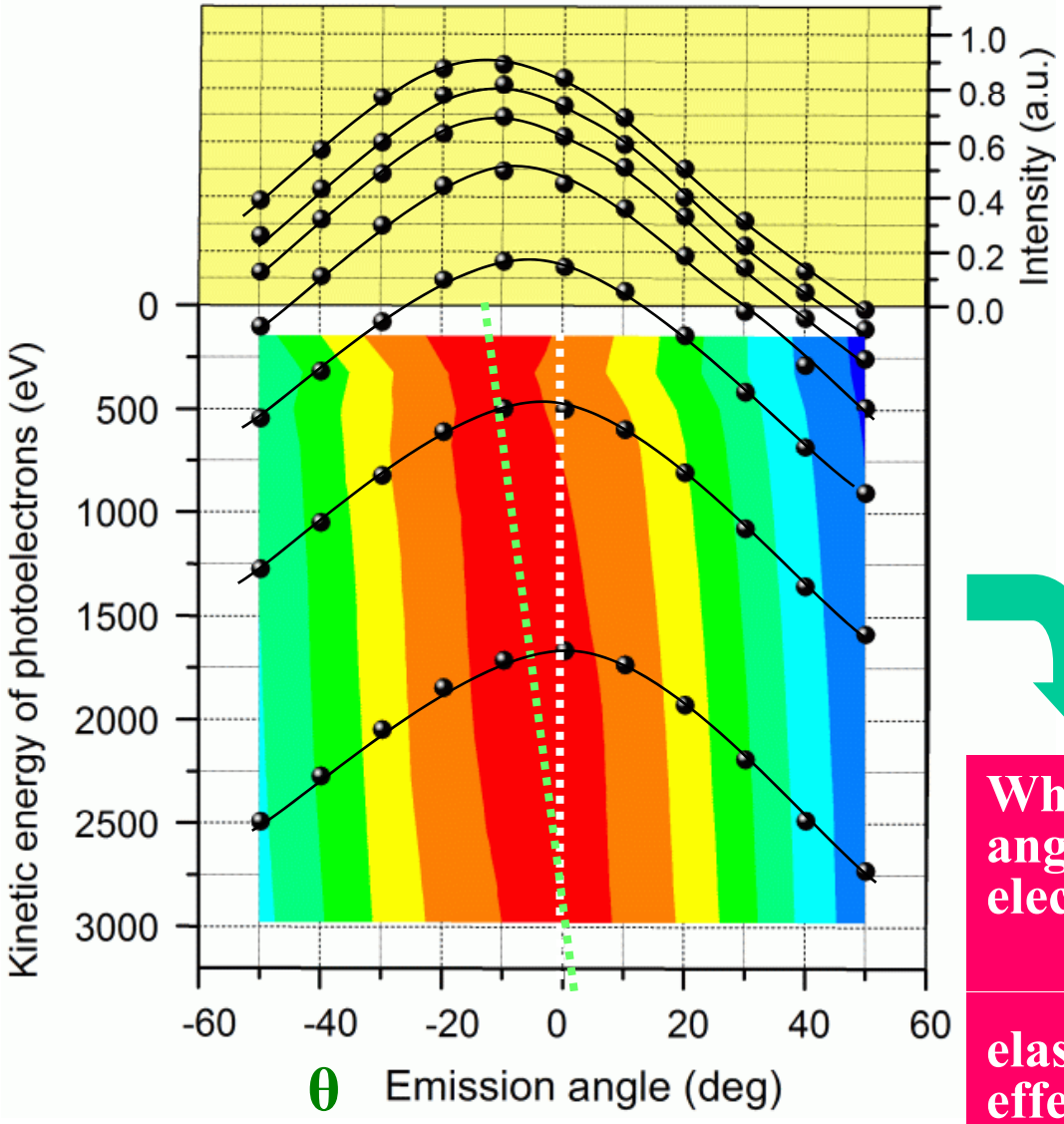


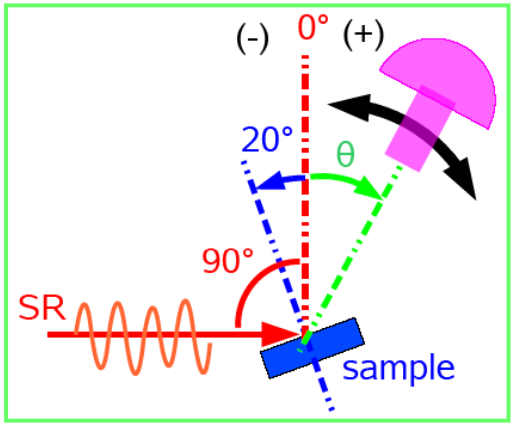


almost 100% linearly polarized X-ray

Ni 1s binding energy = 8333 eV	
X-ray energy	kinetic energy of photoelectrons
8479.4 eV	146.4 eV
8575.7 eV	242.7 eV
8734.4 eV	401.4 eV
8996.1 eV	663.1 eV
9427.6 eV	1094.6 eV
10139.0 eV	1806 eV
11312.0 eV	2979 eV

Contour map of experimental angle-resolved XPS data of Ni 1s photoelectrons





What is the origin of monotonous angular shift dependent on electron energy ?

elastic scattering effect or other effects ?

Multipole term of asymmetry parameter

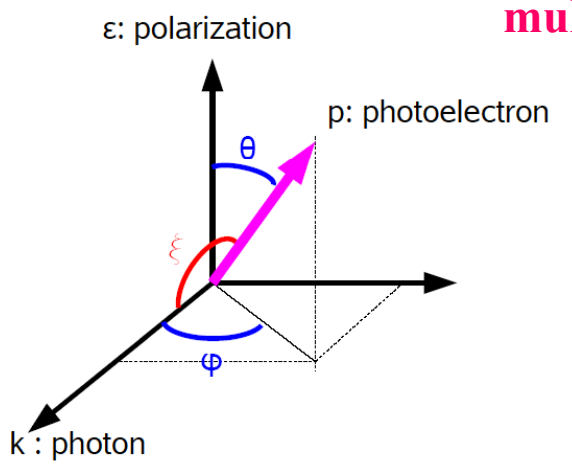
Asymmetry parameter

Case 1 : excited by linearly polarized light

$$\frac{d\sigma_i}{d\Omega x} = \frac{\sigma_i}{4\pi}\left[1 + \frac{\beta}{2}(3\cos^2\theta - 1) + \underbrace{\left(\gamma\cos^2\theta + \delta\right)\sin\theta\cos\varphi}_{\text{multipole}}\right]$$

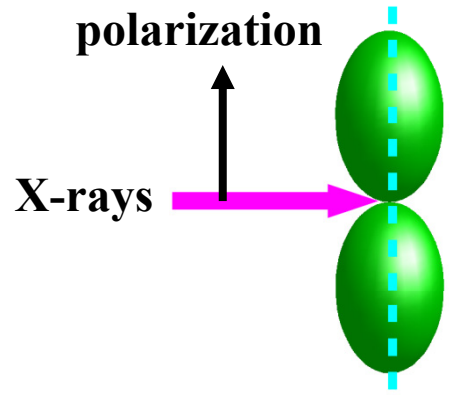
Case 2 : excited by unpolarized or circularly polarized light

$$\frac{d\sigma_i}{d\Omega x} = \frac{\sigma_i}{4\pi}\left[1 - \frac{\beta}{4}(3\cos^2\xi - 1) + \underbrace{\left(\frac{\gamma}{2}\sin^2\xi + \delta\right)\cos\xi}_{\text{multipole}}\right]$$

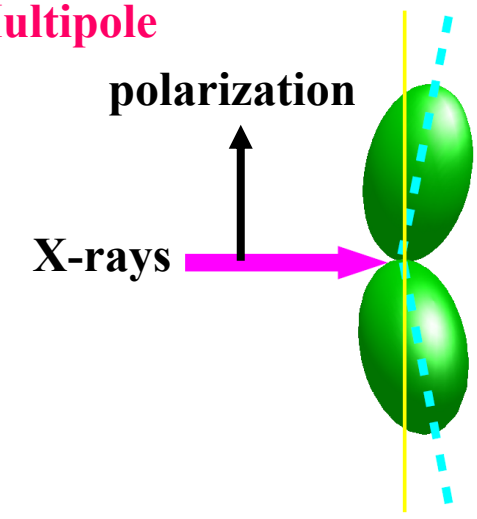


Dipole and Multipole shape

Dipole



Multipole



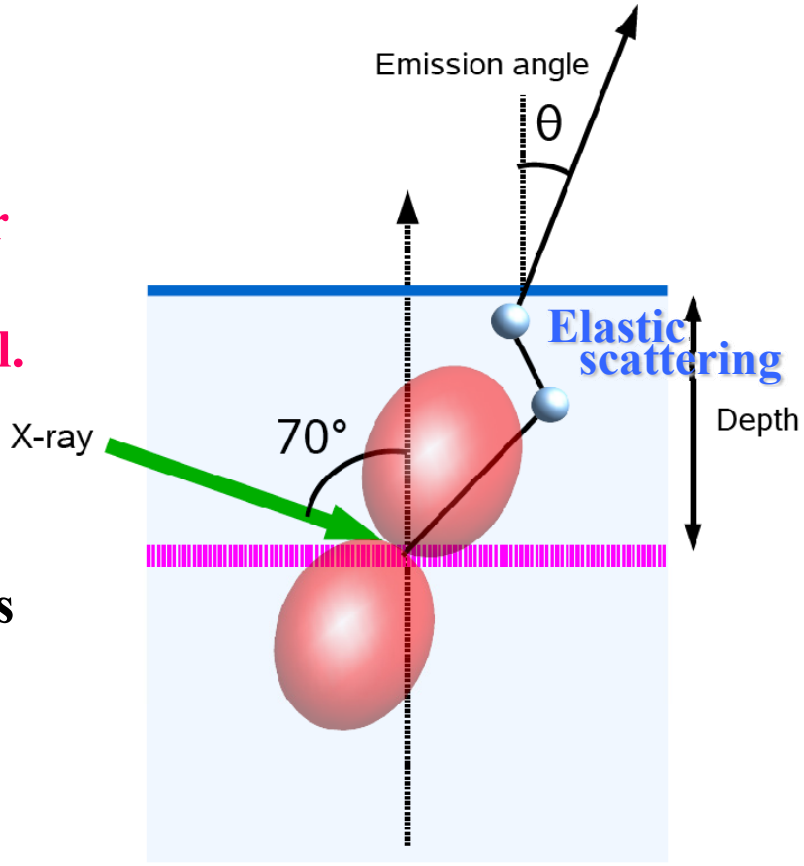
Model of Monte Carlo simulation

- **Atomic potential to calculate elastic scattering differential cross-section**
  Dirac-Hartree-Fock Potential

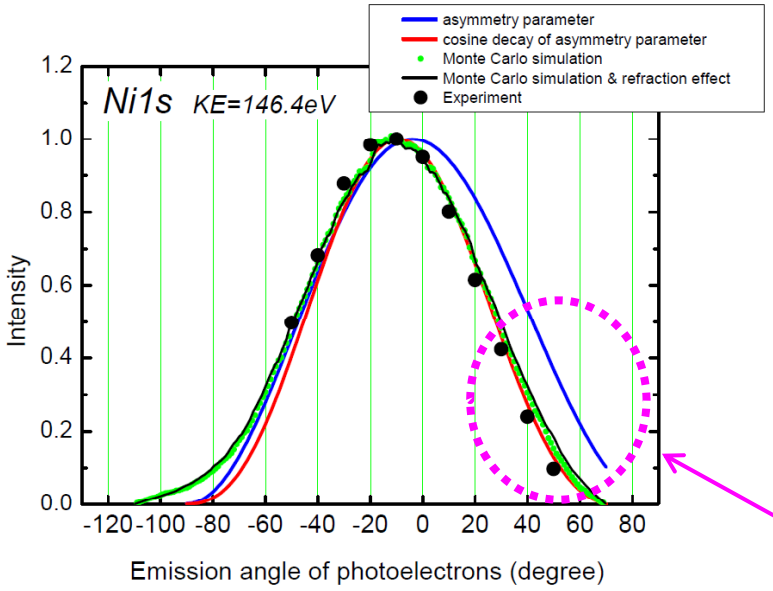
- **IMFP**
  TPP-2M

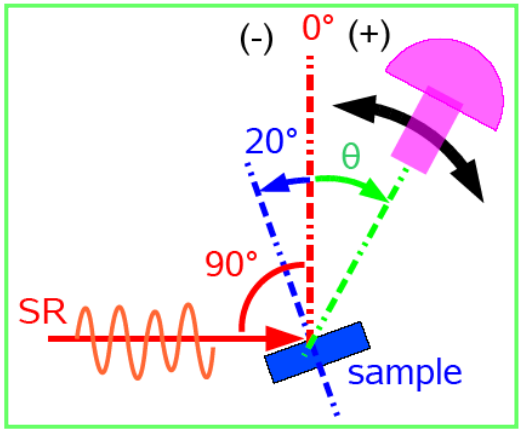
- **Theoretical value of asymmetry parameter with multipole term**
  Trzhaskovskaya et al. [Atomic Data Nucl. Data. Tables 77 (2001) 97]

- **Other**
  include refraction effect of photoelectrons which go through sample surface

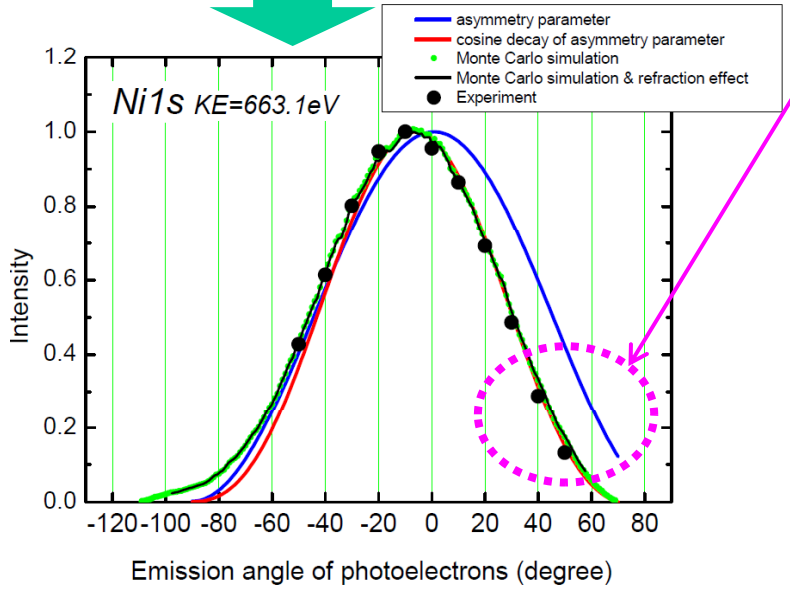


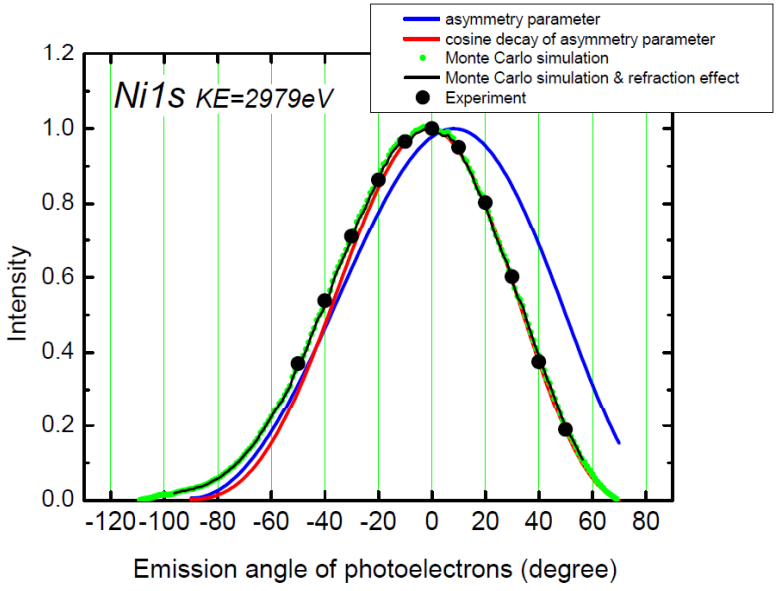
Monte Carlo analysis of Angle-resolved XPS data of Ni 1s photoelectrons
Kinetic energy range 146～2979 eV





disagreement → caused by surface excitation ?





Surface excitation effect

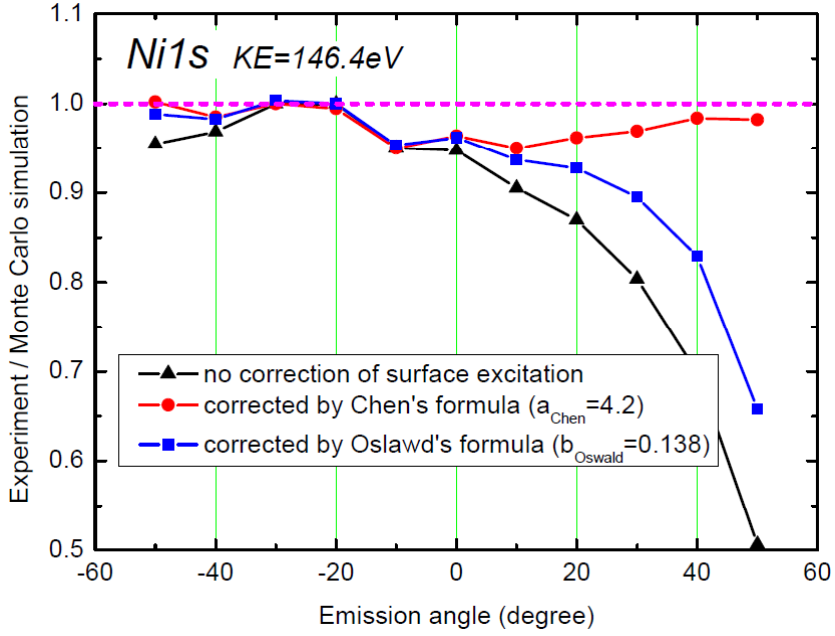
Surface excitation parameter (SEP)

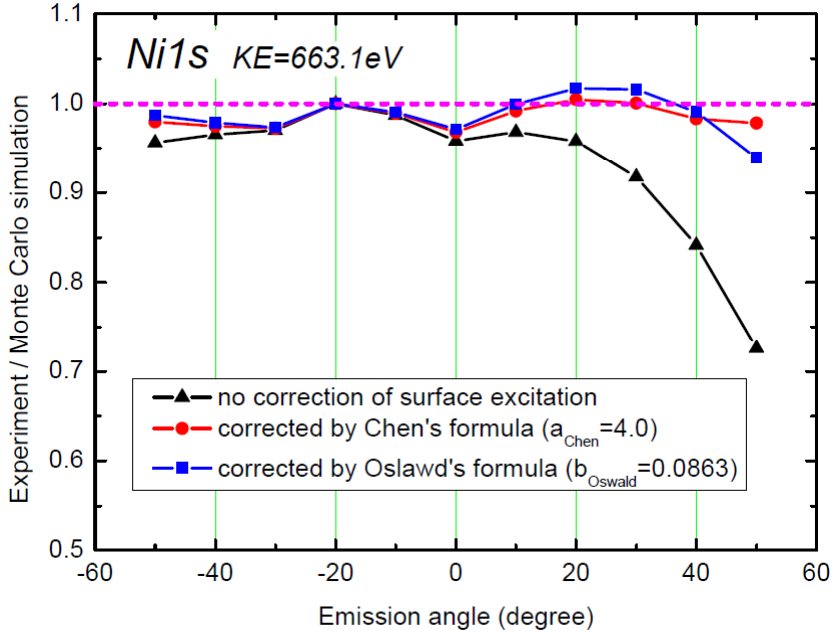
Chen's formula

$$P_s(E,\theta) = \frac{a_{Ch}}{\sqrt{E}\cdot\cos\theta}$$

Oswald's formula

$$P_s(E,\theta) = \frac{1}{b_{Os}\sqrt{E}\cdot\cos\theta + 1}$$





◆Angular dependence of surface excitation for Ni was well described by not Oswald's formula but Chen's formula.

Energy dependence of Chen's coefficients for Ni of Surface excitation parameter

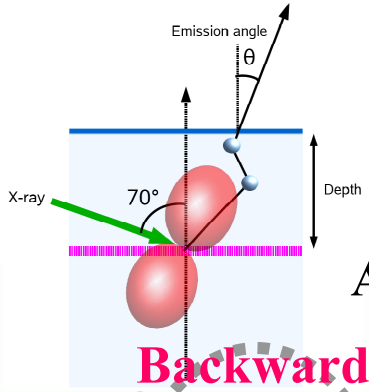
Coefficients a_{ch} of Chen's formula are obtained by analysis of the angular distributions of photoelectrons.

Energy (eV)	Chen's parameter a_{ch}
146.4	4.2
242.7	4.3
401.4	4.2
663.1	4.0
1094.6	3.8
1806	3.6
2979	1.5

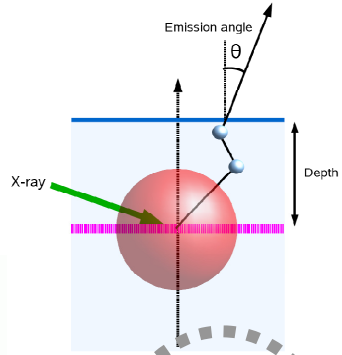
◆Present coefficient a_{ch} of Chen's formula at low energy region for Ni agree with Nagatomi's result a_{ch}=4.3, which was obtained by analysis of the REELS intensity.

[Nagatomi and Goto, Applied Physics Lett. 87 (2005) 224107]

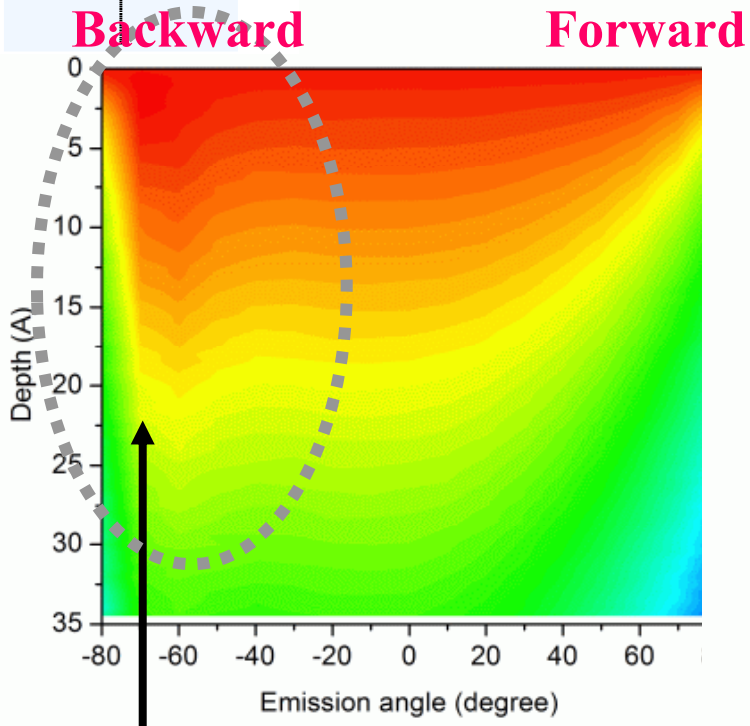
Contour map of EDDF of Ni 1s 1094.6eV photoelectrons which distribute asymmetrically or symmetrically

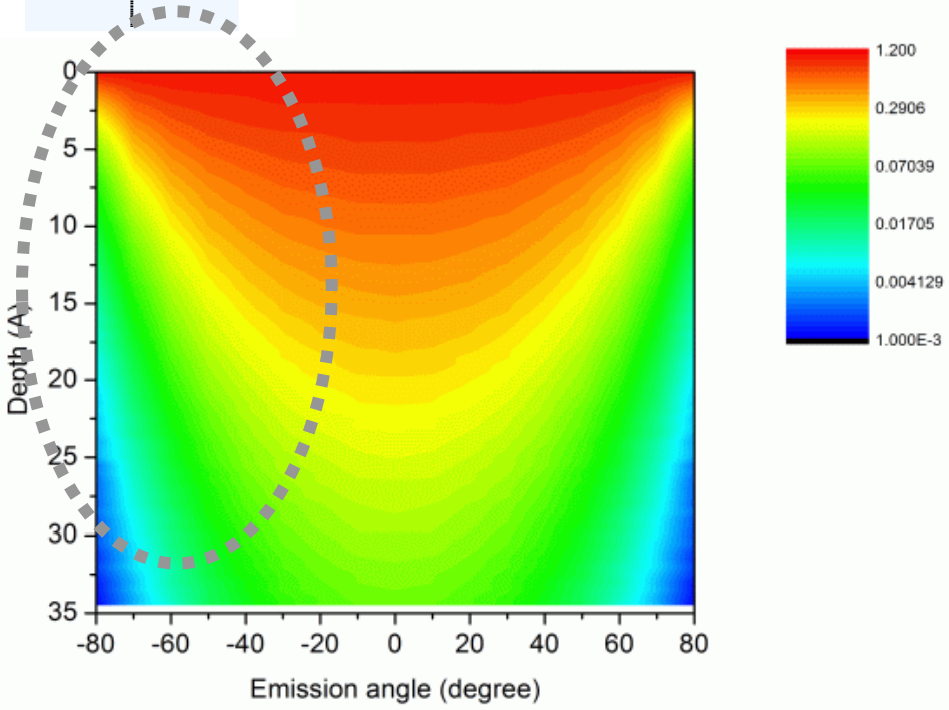


Asymmetrical



Symmetrical





valley of the shape of asymmetry parameter

◆EDDF depends on the shape of asymmetry parameter.
Angular range of ±30 degree with respect to the dip of asymmetry parameter is deformed by plural elastic scatterings.

Conclusion

Factors affecting angle-resolved XPS

1) Asymmetry parameter

Multipole transition is not negligible.

2) Refraction effect

not negligible in the low energy region less than several hundred eV

3) Surface excitation

Angular distribution by surface excitation is described by Chen's formula well.

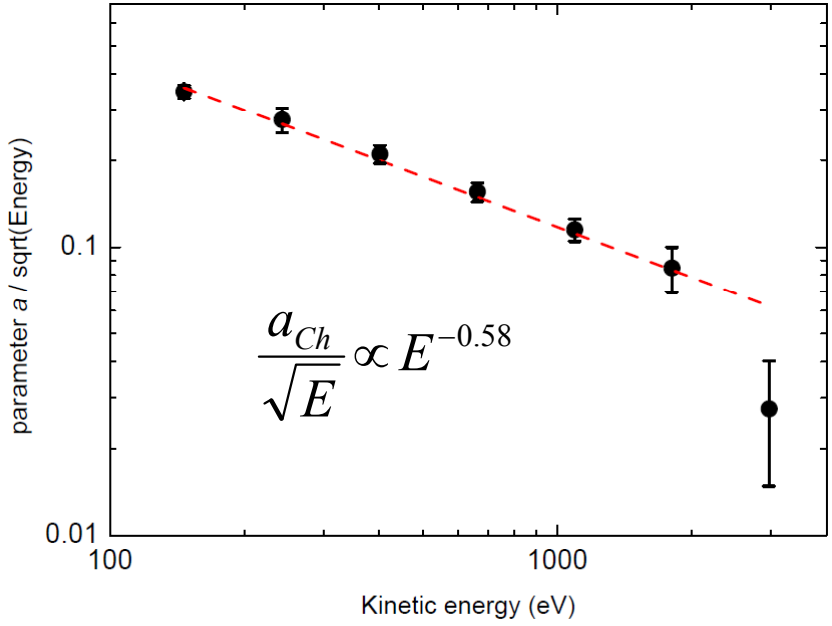
4) Elastic scattering

Deformation of angular distribution by elastic scattering is not significant at the main ejection angle of photoelectrons.

But the deformation is significant at the angular range of ±30 degree with respect to the dip of asymmetry parameter.

Thank you for your attention.

Energy dependence of Chen's coefficient of surface excitation parameter



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